



Road-deposited sediments mediating the transfer of anthropogenic organic matter to stormwater runoff

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Abstract It has been regarded that road-deposited sediment (RDS) is one of the important sinks of anthropogenic pollutants as well as the major source of pollutants in stormwater runoff. However, the role of RDS, as a mediator of pollutants to the stormwater runoff, has not yet been investigated so far. Therefore, in this study, the leaching of dissolved pollutants, especially dissolved organic matter (DOM) from RDS, in synthetic precipitation was investigated. A significant amount of metals, nutrients, dissolved compounds, and DOM was leached. The leaching of DOM during 10 sequential leachings was 1811.3 and 2301.7 mg C/kg for larger (63 μm –2 mm) and smaller (< 63 μm) RDS, respectively. The results of UV/Vis spectroscopy, fluorescence spectroscopy, and size exclusion chromatography showed that the leached DOM was of anthropogenic/abiotic origins with lower molecular weight and humification degree. It is

ubiquitous in stormwater runoff and industrial discharges and differs from natural organic matter. The results strongly suggest that RDS is an important mediator transferring anthropogenic pollutants to stormwater runoff. In addition, the removal of RDS, such as sweeping, would significantly reduce the pollutants input to the runoff.


Keywords Anthropogenic organic matter · Leaching · Pollutants transfer mediator · Road-deposited sediment · Stormwater runoff

Introduction

It has been suggested that road-deposited sediment (RDS) plays an important role in urban sediments cascade system both as a sink and as a transport medium of various pollutants (Charlesworth and Lees 1999). The first role of RDS as a sink seems clear because RDS is seriously polluted with a variety of pollutants. The organic matter (OM), TOC, VS, T-N, TKN, and T-P were measured to be in the ranges of 1–20%, 6–28%, 11–54%, 1050–9340 mg/kg, 2080–13,200 mg/kg, and 645.1–5150 mg/kg, respectively (Bian and Zhu 2009; Seattle Public Utilities and Herrera Environmental Consultants 2009; Miguntanna et al. 2013; Kim et al. 2019). In addition, heavy metals are also associated with RDS. The reported

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concentrations of Cu, Ni, Pb, Zn, and Cd were 28.7–3093.7, 23–708, 37.3–699, 0.9–4024, and 0.44–2665 mg/kg, respectively (Wei and Yang 2010; Hu et al. 2011; Bian and Zhu 2009; Bourliva et al. 2017; Kim et al. 2019).

The pollutants associated with RDS are originated from intrinsic sources such as exhaust emissions, road materials abrasion, vehicle wear, and atmospheric deposition (Froger et al. 2018; Wang et al. 2019). However, extrinsic sources, i.e., neighboring industries, contribute much to the organic carbon and heavy metals in RDS (Aatmeeyata and Sharma 2010; Li et al. 2015). For example, it was shown that the heavy metal content was significantly higher for the RDS in an industrial area than in a residential area (Yuen et al. 2012) and that industrial processes provide a high anthropogenic signal on the distribution of the pollutants deposited on roads (Lau and Stenstrom 2005; Hengren et al. 2006). Since RDS can pose a substantial threat to the environment due to the associated anthropogenic pollutants, it is classified as one of “designated wastes”, which means the harmful industrial wastes (Wastes Control Act, Act No. 15103, Nov. 28, 2017, Republic of Korea).

On the contrary, the second role of RDS, i.e., as a transport medium, has not been evidenced enough. It was shown that RDS itself was transported from the road surfaces to the adjacent water system by stormwater runoff during rainfall events and that the runoff would be a major transport mechanism for sediments (Davis and Birch 2010; Chen et al. 2017). In this regard, RDS would be an important source of the OM, considering that the DOC of runoffs was substantially higher than that of precipitation. It was shown that the average (\pm standard deviation) DOC of the precipitation in 81 sites throughout the world, reported in 83 publications, was 2.64 ± 1.9 mg/L (Iavorivska et al. 2016), while the DOC of runoffs was in a range of 15.9–181.9 mg/L (Kayhanian et al. 2012; McElmurry et al. 2014; Zhao et al. 2015; Winston and Hunt 2017; Yuan et al. 2019). In addition, a variety of pollutants found in RDS has also been detected in road stormwater runoff, at higher concentrations than in precipitation (Table S1).

However, there is little information available on the contribution of RDS to the dissolved pollutants in runoff. Deletic and Orr (2005) wet-sieved the RDS from Aberdeen, Scotland, filtered the effluent with 0.75- μ m filters, and measured the soluble organics, nutrients, and heavy metals. Miguntanna et al. (2013)

determined the nutrients in RDS collected in Gold Coast, Australia, using the effluent and particles that passed through a 1- μ m glass fiber filter. These results represent only the instantaneous wash-off of pollutants from RDS that are dissolved and associated with very fine particles. Thus, it is thought that those results cannot provide enough information about the long-term release and the characteristics of the dissolved pollutants derived from RDS.

Therefore, despite the previous works, it needs much more elaboration to understand the pollutant transport from RDS to runoff. In this regard, the leaching of dissolved pollutants from RDS was investigated and the leached dissolved organic matter (DOM) was characterized in this study, to better understand the role of RDS in the urban sediment cascade.

Materials and methods

RDS

RDS was collected along the Kyungbu expressway, Korea (Fig. 1), nearby industrial complexes of machinery, electronics, plastics, metal processing, chemistry, medical, and precise machining (Korea Industrial Complex Corporation 2016). The average traffic in the experimental area was 192,955 vehicles/day in 2018, which is greater than the average for all expressways in Korea (47,745 vehicles/day) (Korea Ministry of Land, Infrastructure and Transport 2019). The sampling section was 3 m along the curb and 1 m wide away from the curb. The RDS was taken by vacuuming the whole 3×1 m area 3 times. A 1.3-kW vacuum cleaner (Shop-Vac, USA), consists of metal-free and hard plastic parts, was used (Seattle Public Utilities and Herrera Consultants 2009; Hu et al. 2011; Crosby et al. 2014). Brushes and dust pans have also been used for collecting RDS (Bian and Zhu 2009; Bourliva et al. 2017). However, vacuuming was used in this study for a quick sampling because it was risky to take the RDS in an active highway with dense traffic and because it was worried that the RDS in dust pans would be blown away by the turbulence and winds. A total of five (5) RDS samples were collected in sunny days from April to July, when the temperature was 7.8–25.4 °C, the relative humidity was 45.1–71.8%, and the antecedent dry days were 5–7 days.

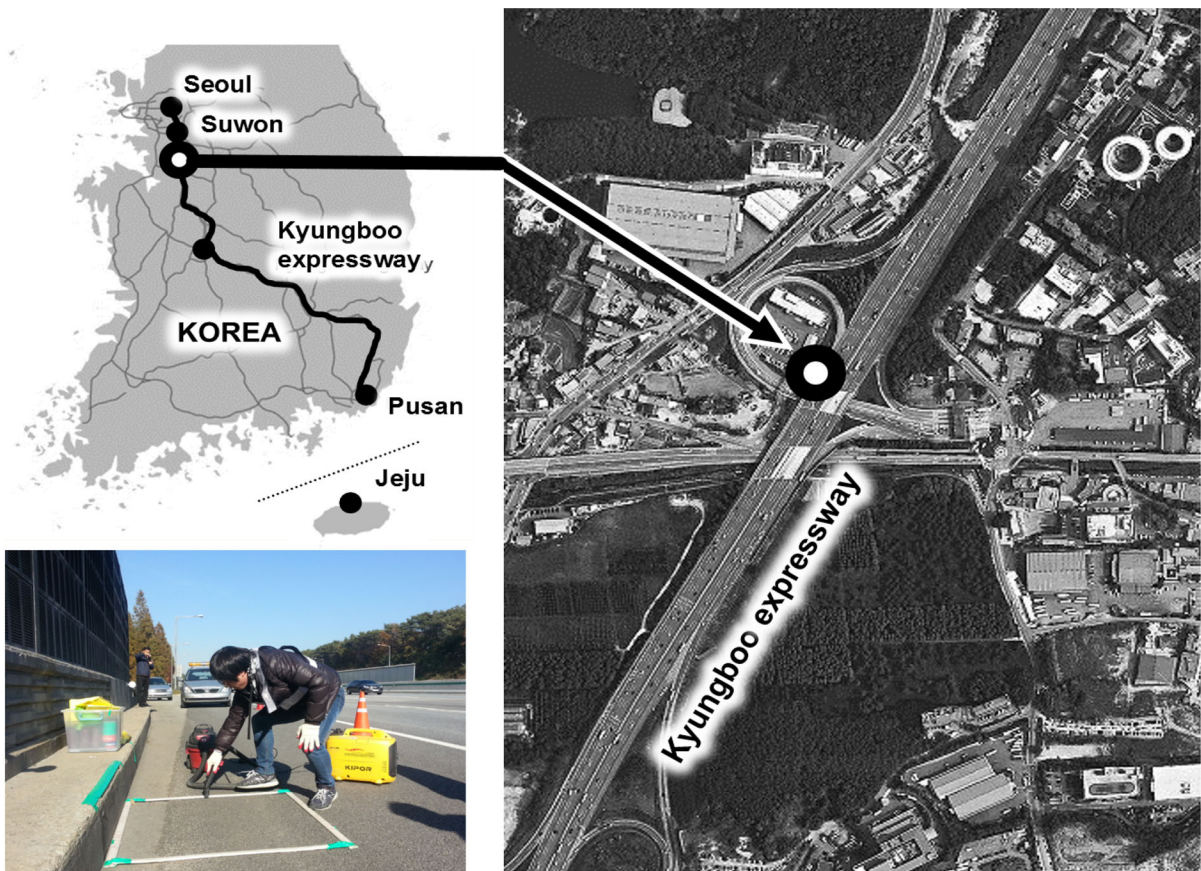


Fig. 1 The site where the RDS was collected

All samples were transferred carefully to clean, airtight plastic bags (Crosby et al. 2014). Grass clippings, leaves, broken pieces (metals, plastics, and glasses), cigarette butts, gravel, and bricks were removed manually, then, the samples were dried at 60 °C until the moisture content was less than 0.1%, and separated into particles of > 2 mm (coarse), 63 μm–2 mm (larger RDS), and < 63 μm (smaller RDS). The > 2 mm particles were not used in this study because it is known that they are of limited importance, from both hydraulic and geochemical perspectives, in transporting adsorbed pollutants in urban systems (Stone and Marsalek 1996). The RDS was fractionated into 63 μm–2 mm and < 63 μm particles considering previous research (Charlesworth and Lees 1999; Bian and Zhu 2009; Seattle Public Utilities and Herrera Environmental Consultants 2009). It was also considered that smaller RDS is readily washed off by rainfall (Zhao et al. 2016) to contribute dominantly to the solids in urban runoff

(> 90%, Wang et al. 2017). In addition, the OM content of RDS was considered. Badin et al. (2008) separated the particles in stormwater runoff into the size fractions of 10, 10–160, 160–1000, and > 1000 μm, and showed that the OM content of < 160 μm particles was significantly different from that of > 160 μm particles. Recently, it was proposed that the proper size fractionation for RDS would be < 10 μm, 10–63 μm, 63–250 μm, and 250–2000 μm (Lanzerstorfer 2020). Therefore, 63 μm was selected as the fractionation criterion representing the differences in OM and mobility.

The fraction of larger and smaller RDS particles was 93.8% and 6.2%, respectively. However, the fraction of smaller particles could be a little underestimated because they could be lost by minor turbulence during the transfer from the vacuum cleaner to the bags. A more detailed transfer process must be proposed in the future.

Sequential batch leaching experiment

For each size fraction (larger and smaller), the same amount was taken from the 5 samples of RDS and separately mixed homogeneously. Part of each mixture was analyzed for concentrations of BOD, TOC, COD, and metals, and another part was used for leaching experiments.

Sequential batch leaching experiments were performed by repeating the synthetic precipitation leaching procedure (U.S. EPA SW 846 Method 1312) because most RDS is not washed away by runoff, but instead remains on the road surface (Wijesiri et al. 2015; Zhao et al. 2016) and is thus exposed to rainwater many times intermittently. For example, Zhao et al. (2016) showed that the wash-off of < 63 μm RDS and 63–1000 μm RDS was less than 30% and 15%, respectively, during an artificial rainfall with an intensity of 15.18 mm/h, which can represent the 60-min maximum value in Korea (Korea Meteorological Administration 2017).

The leachant, i.e., synthetic precipitation, was prepared with distilled, deionized water (DDIW), and the pH was adjusted to 5.0 with a 60/40 weight percent mixture of H_2SO_4 and HNO_3 (U.S. EPA SW 846 Method 1312). The pH was comparable to the annual average pH the precipitation of the years 2010–2018 in the sampling area during the sampling period, i.e., 4.7–5.2 (Korea National Institute of Environmental Research, 2018). A certain amount of RDS was put into the leachant (solid/liquid ratio 1/10). The mixture was shaken for 1 h at room temperature (20–22 $^\circ\text{C}$ and relative humidity 65–75%, 150 rpm) and then centrifuged at 4500 rpm. Next, the supernatant was filtered through a 0.45- μm polyvinylidene fluoride (PVDF) filter, and the filtrate was analyzed. Fresh leachant was introduced to the centrifuged RDS for the next leaching. This procedure was repeated 10 times.

Analysis

The TOC and T-N of the RDS were analyzed using an elemental analyzer (Flash EA 1112, CE Elantech, Inc., USA) after carbonate removal with HCl (Seattle Public Utilities and Herrera Environmental Consultants 2009). BOD of the RDS was measured using the procedure proposed by Tetra Tech (1986) (Kim et al. 2019), while T-P was measured using alkaline

extraction and the concentration of metals in the RDS were analyzed after microwave acid digestion (Kim et al. 2019; Seattle Public Utilities and Herrera Consultants 2009). Blanks and duplicate determinations were performed for the pollutants to ensure the QA/QC (Zhang et al. 2013). The standard reference material was purchased from Sigma-Aldrich (BCR-280R). The recovery was in a range of 94.5–103.8% of the certified values of the standard reference material.

The COD, BOD, NO_3^- -N, NH_4^{++} -N, PO_4^{3-} -P, and metals of the filtered leachants were analyzed according to Standard Methods (APHA, AWWA, WEF 1998). DOC was measured using a TOC analyzer (TOC-V CPH, Shimadzu). UV/Vis spectra were obtained using a UV/Vis spectrophotometer (UVmini-1240, Shimadzu, Japan) at wavelength of 800–200 nm. Excitation–emission (Ex/Em) matrices (EEMs) were obtained at Ex/Em wavelengths of 220–400/250–600 nm using a spectrofluorophotometer (RF5301PC, Shimadzu, Japan) for the leachants after the first and eighth leachings. The molecular weight (MW) distribution (MWD) was analyzed using a high-performance liquid chromatography system (Ultimate 3000, Thermo Fisher, USA) with a size exclusion chromatography (SEC) column (Protein PakTM 125, Waters, USA). The MWD was analyzed only for the DOM leached from the filtrates at the first and eighth leaching. The MWD of chromophores was analyzed using UV/Vis absorption at 254 nm. The flow rate of the mobile phase was 0.8 mL/min, and the mobile phase was a 0.1 M NaCl solution buffered at pH 6.8 with 2 mM $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and 2 mM Na_2HPO_4 . Sodium polystyrene sulfonate standards with nominal molecular weights of 18, 8, 4.6, and 1.8 kDa (Polysciences, Inc., USA) and acetone (58 Da, HPLC grade, Aldrich, USA) were the standards used. The weight average molecular weight (MW_w), the number average molecular weight (MW_n), and polydispersity (p) were determined by Eqs. (1), (2), and (3), respectively:

$$MW_w = \frac{\sum_{i=1}^N (h_i MW_i)}{\sum_{i=1}^N (h_i)} \quad (1)$$

$$MW_n = \frac{\sum_{i=1}^N (h_i)}{\sum_{i=1}^N (h_i / MW_i)} \quad (2)$$

$$p = MW_w / MW_n, \quad (3)$$

where h_i and MW_i represent the signal height and molecular weight, respectively (Hur et al. 2006). The MWD of fluorophores was analyzed separately at Ex/Em wavelengths of 335/450 and 245/430 nm. The wavelengths were selected by peak-picking the EEMs obtained (Goldman et al. 2012).

Results and discussion

pH and electric conductivity of leachant and the leaching of metals and nutrients

The pH of the leachant increased from 5.0 to 7.5 and 9.0 after the first leaching of larger and smaller RDS, respectively, and showed slight changes thereafter as the leaching was repeated (Fig. 2a). The pH of the leachants was comparable to or higher than the stormwater runoff in urban area and highways. Since the larger RDS was dominant, the pH of the leachant of the total RDS, i.e., the mixture of 93.8% of larger RDS and 6.2% of smaller RDS, would be within the range of observed pH of stormwater runoff in literature. It was in a range of 6.4–8.42 (Ernst et al. 2016; Göbel et al. 2007; Kayhanian et al. 2012; Wang et al. 2017), while the precipitation was generally acidic as mentioned above (Korea National Institute of Environmental Research 2018; Wang et al. 2017). This suggests that the RDS, especially smaller RDS, might supply stormwater runoff with alkalinity and thereby affect the fate of the metals it contains (Nason et al. 2012).

The electric conductivity (EC) was notably high at the first leaching and decreased as the leaching was repeated (Fig. 2b). After the first leaching, the EC of the leachants larger RDS was 327 $\mu\text{S}/\text{cm}$, and that of smaller RDS was 938 $\mu\text{S}/\text{cm}$ which was comparable to a solution of 10 mM NaCl in DDIW.

Thus, a significant amount of soluble species was leached from the RDS, most significantly at the first contact between the RDS and the leachant. Considering that the EC of rainwater in Korea is as low as 13.9 $\mu\text{S}/\text{cm}$ (Kim et al. 2005), RDS would greatly increase the abundance of dissolved ions in the runoff. It was reported that the EC of rainwater was 28–223 $\mu\text{S}/\text{cm}$ in Germany, but that of the runoff from highly trafficked areas was 108–2436 $\mu\text{S}/\text{cm}$ (Göbel et al. 2007). Also, the EC of the runoffs from expressways with a wide drainage area in Oregon, USA was in a range of 16.3–1065 $\mu\text{S}/\text{cm}$ (Nason et al. 2012).

The pH and EC were higher for smaller RDS than for larger RDS. Because the specific surface area is higher for smaller particles, it is thought that a significant fraction of the soluble species, i.e., alkalinity and electrolytes, was leached from the surface of the RDS.

The leaching of several metals and nutrients was preliminarily investigated. A considerable amount of metals was leached (Table S2, Fig. S1). Zn was the most leached metal followed by Cu and Fe. This indicates that the anthropogenic influence on RDS because Cu and Zn are the elements commonly found in the sediments of a significant anthropogenic

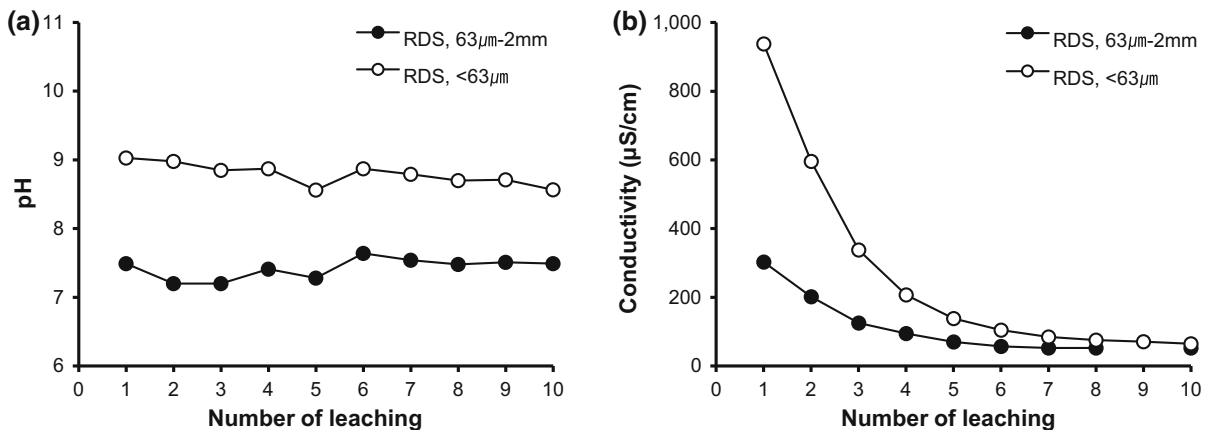


Fig. 2 a pH and b electric conductivity of the leachants and the leaching of the RDS using synthetic precipitation (the pH and conductivity of the synthetic precipitation was 5.0 and 0.06 $\mu\text{S}/\text{cm}$, respectively)

enrichment (Yuen et al. 2012). Zn was the most mobile, i.e., the leached fraction out of the total amount associated with the larger and the smaller RDS was 12.36% and 21.11%, respectively. The leached amount and the fraction leached differed from each other. The metal content was not correlated with the leached amount, indicating that the form of the metals in RDS, i.e., water soluble, weak acid soluble, reducible, oxidizable, and environmentally persistent (Świetlik et al. 2015), was different each other. The leaching of NO_3^- -N and PO_4^{3-} -P was significant, while the leached amount of NH_4^{+} -N was relatively lower (Table S3, Fig. S2). The higher leaching of NO_3^- -N than NH_4^{+} -N might be attributed to the NO_x -rich vehicle exhaust, which is one of the most important sources of N in RDS (Otterson et al. 2014). The leaching of the metals and nutrients needs to be further investigated.

Leaching of DOM

The accumulated leached amount of COD, BOD, and DOC after 10 leachings is presented in Fig. 3. The total content of TOC of larger and smaller RDS was 16,807 and 35,726 mg C/kg, respectively, and the leached amount after 10 leachings was 1811.3 and 2301.7 mg C/kg, i.e., 8.2% and 4.6% of the total TOC, respectively. The total content of BOD was 2182 and 3617 mg/kg, and the leached amount after 10 leachings was 1460.2 and 1640.8 mg/kg, i.e., 66.9% and 45.4% of the total BOD, for larger and smaller RDS, respectively. The fraction of BOD leached from the

RDS was higher than that of DOC, possibly because BOD was induced by readily soluble and bioavailable DOM (Hosen et al. 2014).

The leaching of dissolved organic compounds from RDS has not been reported so far, although the contribution of the RDS to the organics load on the road surface has been calculated to be 9.24–845.22 mg TOC/m², by measuring the TOC concentration of the wet-sieving effluents of the RDS, which contained fine particles of RDS (Deletic and Orr 2005). Thus, the results in this study firstly confirmed that RDS is an important source of DOM in runoff for a long period of time when they intermittently contact with rainfall.

The first leaching of COD, BOD, and DOC was higher than the leachings afterward. The initial leaching rate from the smaller RDS was higher than from larger RDS. Note that the leached amount increased continuously as the leaching was repeated, and none of the indicators of organics, i.e., COD, BOD, and DOC, reached a plateau after 10 leachings. This indicates that more DOM can be leached with more contacts between the RDS and rainfall.

UV/Vis absorption and fluorescence characteristics of the leached DOM

Figure 4 shows that the absorbance was higher for smaller RDS than larger RDS, and that it was increased as the leaching was repeated regardless of the size of RDS. The specific UV absorption at 254 nm (SUVA_{254}) at the first and the eighth leaching was 1.67

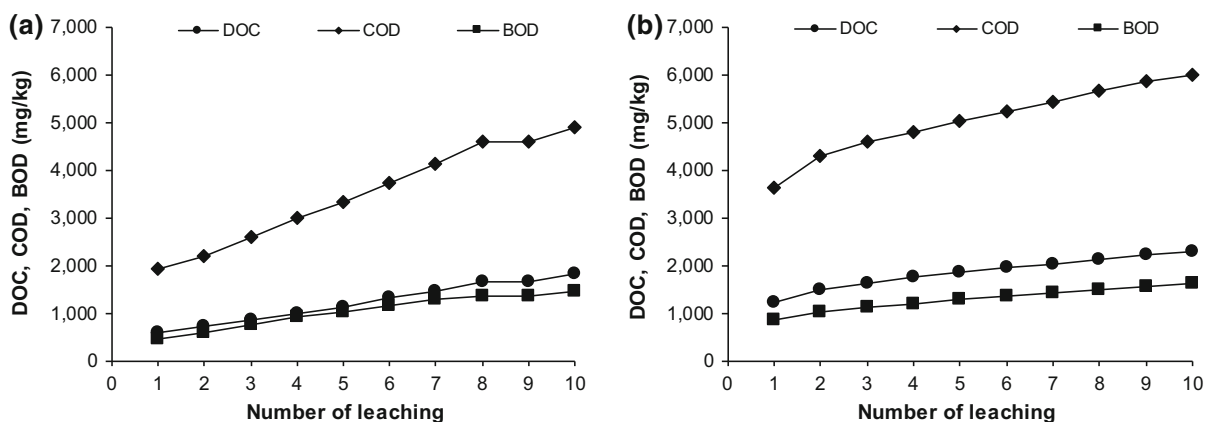


Fig. 3 The accumulated leached amount of COD, DOC, and BOD after the leaching of **a** larger (63 μm –2 mm) and **b** smaller (< 63 μm) RDS using synthetic precipitation

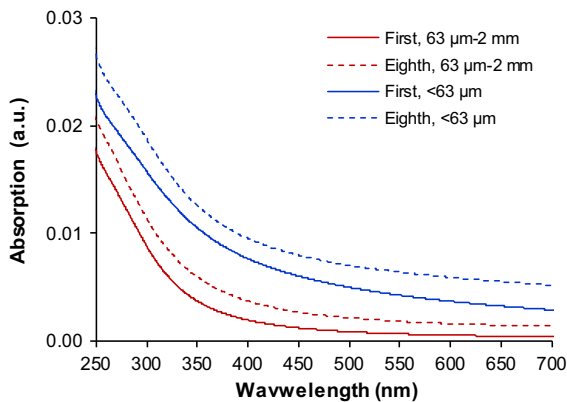


Fig. 4 UV/Vis spectra of the DOM leached from RDS at the first and eighth leachings (DOC 1 mg/L)

and 1.98 L mg/C m for larger RDS and 2.19 and 2.55 L mg/C m for smaller RDS, respectively. The ratio of the absorption at 250 nm to at 365 nm ($E2/E3$) was 5.86 and 4.03 for larger RDS and 2.41 and 2.33 for smaller RDS. The ratio of the absorption at 250 nm to at 365 nm 465 nm to 665 nm ($E4/E6$) was 2.40 and 1.73 for larger RDS and 1.80 and 1.41 for smaller RDS.

It is generally accepted that $SUVA_{254}$ is a direct indicator of MW and aromaticity, while the $E2/E3$ and $E4/E6$ are inversely proportional to MW (Rodríguez et al. 2016). Therefore, the results indicate that the DOM of relatively lower MW was leached in advance to that higher MW and that the DOM leached from smaller RDS has higher MW and aromaticity than larger RDS. The $SUVA_{254}$ in this study suggests that the DOM from RDS can be one of the sources of the DOM in runoff, because it is comparable to that in stormwater runoff, which are significantly lower than that of natural organic matter (NOM). The $SUVA_{254}$ of stormwater runoff from highly impervious surfaces was less than 2 (Hosen et al. 2014), while that of Suwannee River NOM was 3.55 L mg/C m (Li and Hu 2018). It also indicates that the chromophoric DOM leached from the RDS has a low aromaticity and a low degree of humification, and therefore, it was associated more with of abiotic/anthropogenic origins, than NOM.

The EEMs of the DOM of the first leaching of both larger and smaller RDS showed strong peaks centered at Ex/Em 335/450 and 245/430 nm, which could be assigned to the peaks C (Ex/Em 300–350/400–500 nm) and A (Ex/Em 237–260/400–500 nm),

respectively. The shoulders of the peak T1 (Ex/Em ~ 225/~ 350 nm) and T2 (Ex/Em ~ 280/~ 350 nm) were also observed (Goldman et al. 2012) (Fig. 5a, c).

The peaks suggest that the DOM was originated from anthropogenic and/or industrial sources as suggested by previous works. The PARAFAC components at Ex/Em 250(345)/450 nm were found in coke wastewater containing phenols, polycyclic aromatic hydrocarbons, and heterocyclic compounds (Ou et al. 2014). Pyrene-like components (the Ex/Em maxima at 280 (375, 350, 270, 245)/384 (402) nm) were found solely in a wastewater treatment plant influent, where 50% of it was originated from an electronic components factory (Cohen et al. 2014), which were not observed in municipal wastewater. A unique component (Ex/Em 275 (330)/436 nm) was found in the pulp mill effluents (Cawley et al. 2012). The components at Ex/Em 335/413, < 250/445, and 250(285)/347 nm were identified in the treated wastewater from the industries of non-alcoholic drink, electronic device, food, meat, pulp and paper, petrochemical, steel, steam-power, and textile dyeing (Yang et al. 2015). Specifically, components at Ex/Em < 250/445 and 250 (285)/347 nm were dominant in the treatment effluents from the industries of organic chemical, pulp and paper, non-alcoholic drink, food, meat, petrochemical, resin and plastic, leather and fur, and textile dyeing. In addition, it has been shown that the peaks at Ex/Em ~ 225 or ~ 280/~ 350 nm and 300–350/400–500 nm can be used as fluorescent tracer of non-specific industrial pollution (Borisover et al. 2011; Yang et al. 2015). It was also shown that the peaks of Em < 380 nm, i.e., peaks T1 and T2, are associated with fluorophores of lower aromaticity and tryptophan, while those of Em > 380 nm, i.e., peaks C and A, are associated with polycyclic aromatic hydrocarbons, lignins, humic acids (HA), quinones, aromatic ketones, and pharmaceutically active compounds (Stedmon and Cory 2014).

The EEMs in Fig. 5a, b also strongly suggest that RDS can contribute to the anthropogenic DOM ubiquitous in stormwater runoffs (Ernst et al. 2016). Zhao et al. (2015) showed that the peaks C and A were commonly found in the stormwater runoff collected in Beijing, China. Chen et al. (2017) investigated the EEMs of the DOM in runoff from a catchment of a 92% impervious road surface in Changzhou, China. They showed that the largest portion of the DOM

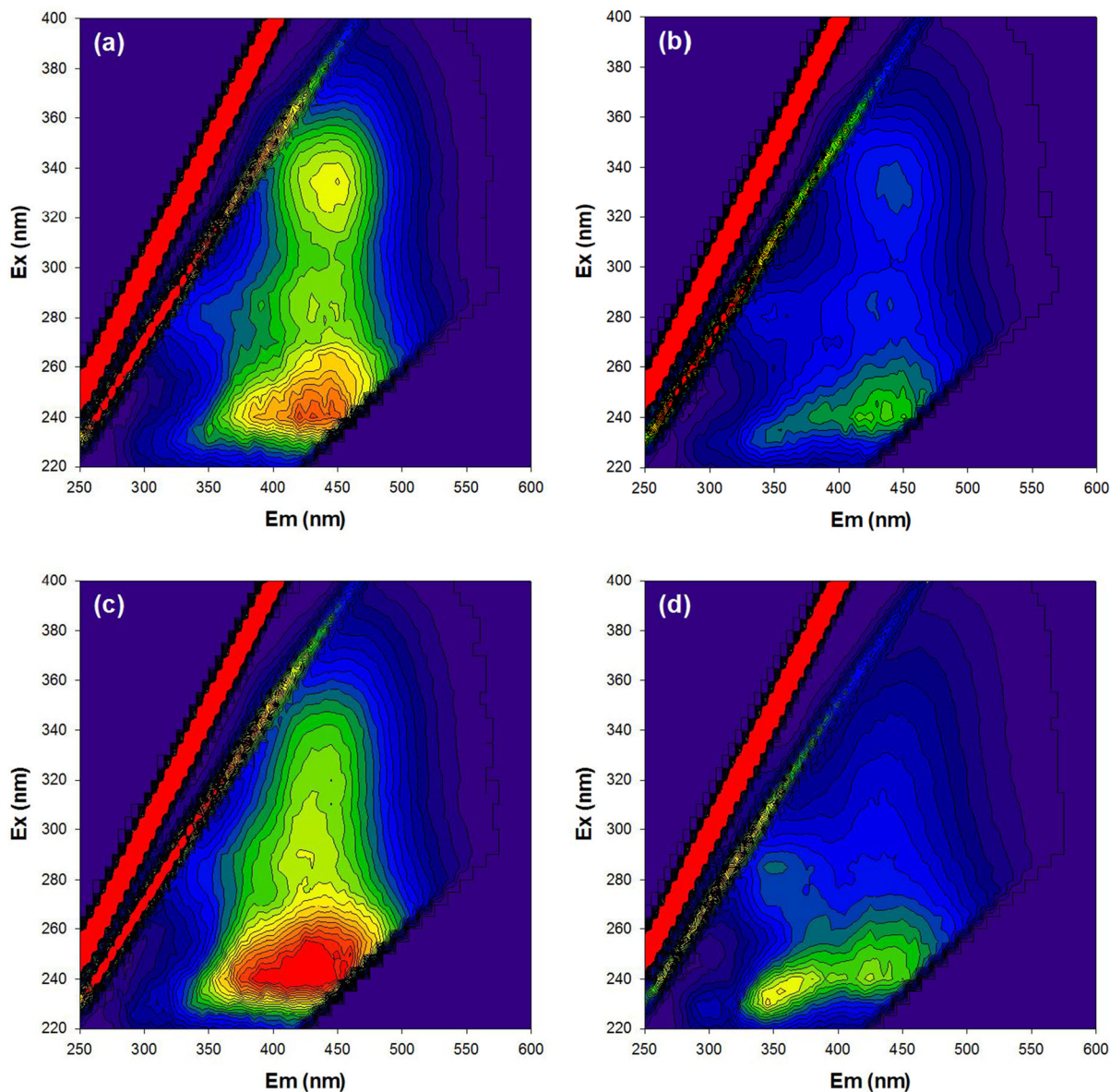


Fig. 5 Fluorescence EEMs of the DOM leached from larger (63 μm –2 mm) RDS at the **a** first and **b** eighth leachings, from smaller (< 63 μm) RDS at the **c** first and **d** eighth leachings

consisted of anthropogenic HA-like substances (peaks C). In addition, Hosen et al. (2014) found terrestrial and anthropogenic HA- and fulvic acid (FA)-like fluorophores and protein-like substances in the streams in Maryland, USA.

It should be noted that the leached DOM would pose significant effects on the chemistry and quality of receiving water. The fluorophores of peaks C, A, and T1/T2 can be assigned to HA-like (Ex/Em 330–350/

440–450 nm), FA-like (Ex/Em 230–250/400–450 nm), and tryptophan-like (Ex/Em 220–240/340–350 nm, 270–290/330–350 nm) substances, respectively (Yang et al. 2015; Chen et al. 2017). HA-, FA-, and tryptophan-like substances, either anthropogenic or terrestrial, can greatly affect the fate of dissolved metals because they are environmental chelators with various complexation sites. It has been reported that the mobility of Cu(II), Ni(II), Pb(II),

Zn(II), and Al(III) was significantly affected by the binding to those components (Cabaniss 2011; Ernst et al. 2016). This suggests that RDS could enhance the mobility of metals. Therefore, the removal of metals from runoff using filtration or infiltration devices could be inhibited. In addition, humic substances compete with target pollutants for adsorption sites on activated carbon and contribute to the fouling of membranes and disinfection by-products formation (Murray and Örmeci 2018).

The intensity of peak A was the strongest for both larger and smaller RDS, while the peak C was also strong for the larger RDS (Fig. 4a, c). It suggests that FA-like substances were dominantly leached from smaller RDS, while both FA- and HA-like substances were leached from larger RDS. Compared to HA-like substances, FA-like substances are more soluble, have lower MW, and are unique in easy diffusion through membranes and uptake to plants (Canellas et al. 2015; Huang et al. 2016). Therefore, FA-like substances can pose serious hazards because they efficiently carry toxic compounds and because disinfection by-products, such as trihalomethanes and halo-acetic acids, are formed mostly from FA-like substances (Richardson et al. 2007; Zhang and Yang 2018).

The fluorescence intensity greatly decreased after the eighth leaching, indicating fluorophores were leached significantly at the first contact of the RDS and the leachant (Fig. 5b, d). Especially, the peaks of T1 and T2 were relatively stronger, along with peak A, for the eighth leaching of the smaller RDS (Fig. 5d). Synchronous fluorescence spectra also showed that the

fluorescence intensity decreased as the leaching was repeated (Fig. 6). It suggests that the DOM containing electron-donating groups, which increase in fluorescence intensity, was leached more at the first leaching (Nakashima et al. 2008). For larger RDS, the intensity at $E_m < 350$ nm was reduced more significantly, while the intensity at $E_m > 350$ nm was greatly reduced for smaller RDS. This indicates that the DOM of lower conjugation degree and MW was leached in advance and then more condensed DOM was leached afterward, from larger RDS. It was also indicated that the DOM of higher conjugation degree and MWs was leached at the first leaching of the smaller RDS.

Three indices were obtained from the EEMs as shown in Fig. 5 and presented in Fig. 7: the fluorescence index (FI), which is defined as the ratio of the fluorescence intensity at Ex/Em 370/450 nm to that at Ex/Em 370/500; the humification index (HIX), which is defined as the ratio of the spectral area at Ex/Em 254/300–345 nm to that at Ex/Em 254/435–480; and the biological index (BIX), which is defined as the ratio of the fluorescence intensity at Ex/Em 310/380 to that at Ex/Em 310/430 nm (Huguet et al. 2010; Zhao et al. 2015). FI can be used to discriminate the potential sources of DOM, i.e., higher and lower values indicate autochthonous and allochthonous DOM, respectively. HIX indicates the degree of maturation and structural complexity of DOM. A high BIX value (> 1.0) corresponds to a biological origin, and a low value (< 1.0) indicates low DOM content from biological origins.

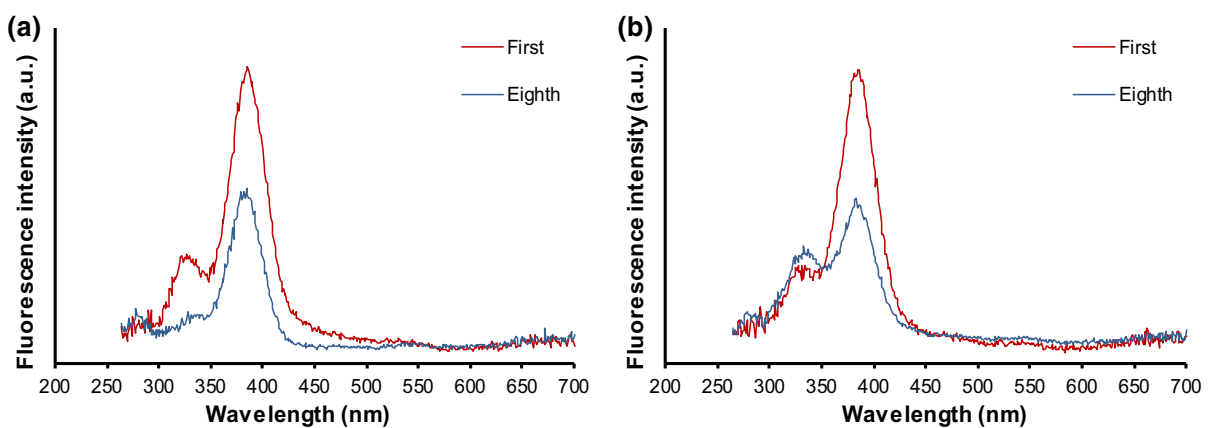


Fig. 6 Synchronous fluorescence spectra ($\Delta\lambda = 44$ nm) of the DOM leached from **a** larger (63 μm –2 mm) and **b** smaller (< 63 μm) RDS at the first and eighth leachings

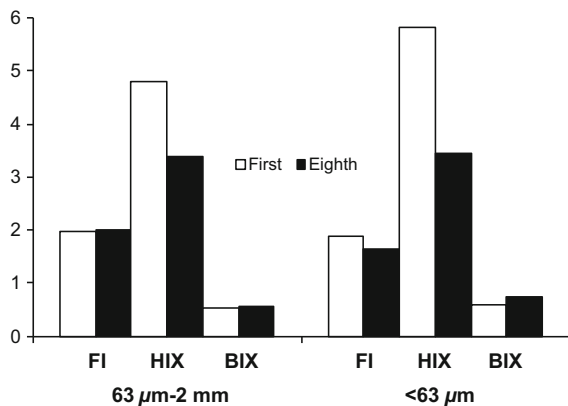


Fig. 7 **a** FI, **b** HIX, and **c** BIX of the DOM leached from RDS at the first and eighth leachings (DOC 1 mg/L, FI fluorescence index, HIX humification index, BIX biological index)

The FI was 1.98 and 1.89 at the first leaching of larger and smaller RDS, respectively, and changed slightly at the eighth leaching. FI values near to or higher than 2.0 indicate the possible existence of non-humic, autochthonous DOM (Korak et al. 2015). The high FI could be associated with the impervious surface of the expressway because the FI in runoff increased from ≈ 1.3 to ≈ 1.6 when the imperviousness of the surface increased from 1 to 50% (Hosen et al. 2014). It suggests that the FI would be higher when the imperviousness is $> 50\%$. Lower FIs of 1.24–1.65 were shown in the runoffs from the areas where the input of humic substances were highly possible, i.e., a forested watershed in Maryland, USA (Inamdar et al. 2011) and the residential, and campus areas in Beijing, China (Zhao et al. 2015). The HIX was 4.79 and 5.81 for larger and smaller RDS, respectively, at the first leaching, and decreased substantially to 3.39 and 3.44, respectively, at the eighth leaching. The HIXs suggest that the DOM is less humified ($\text{HIX} < 10$) and autochthonous ($\text{HIX} < 4$), and that a relatively more humified fraction leached preferentially (Huguet et al. 2010). The low HIX might be attributable to the lack of sources of humified OM along expressways. The HIXs in the runoff in a business area (1.72–9.21) were lower than those in a residential area (3.49–22.86), where more humified OM can be introduced to runoffs (Zhao et al. 2015). The BIX was 0.54 and 0.58 for larger and smaller RDS, respectively, at the first leaching. It did not show a notable change after more leachings. The BIXs were < 1.0 , regardless of the number of leaching

or the size of RDS, suggesting that RDS could be an important source of low aromaticity, abiotic, autochthonous, and non-humic DOM in runoff (Zhao et al. 2015).

The values of high FI, low HIX, and low BIX indicate that a significant anthropogenic influence (He et al. 2016) on the leached DOM, i.e., OM associated with the RDS.

The MW_w , polydispersity, and molecular size distribution of the chromophoric and fluorophoric DOM from the RDS are presented in Table 1 and Fig. 8. The MW_w and polydispersity of the chromophoric DOM from larger RDS were 325.1 Da and 89.2, respectively, at the first leaching. They were increased greatly to 794.9 Da and 244.8, respectively, at the eighth leaching, due to a significant increase in 6–30 kDa molecules. On the other hand, the chromophoric DOM from smaller RDS showed much higher MW_w and much lower polydispersity, i.e., a narrower MW distribution, than larger RDS. The MW_w and polydispersity were 2172.5 Da and 2.71, respectively, at the first leaching, and increased to 2616.4 Da and 5.17, respectively, at the eighth leaching.

The results indicate that the DOM from larger RDS is associated with abiotic sources, while that from smaller RDS was relatively less influenced by abiotic sources. McElmurry et al. (2014) reported that the average MW of the DOM was the highest in the runoff from vegetative cover and forested area (around 2000 Da), followed by agricultural (1440 Da) and urban (1220 Da) areas. It indicates that the DOM of anthropogenic sources consists of low MW chromophores. It was also reported that the DOM of 0.2–5 kDa dominated in the runoff in summer when the biological reactions were enhanced, while the DOM of < 0.5 kDa dominated in winter (Huang et al. 2016), in a semi-urban catchment in Mannum, South Australia.

Since larger RDS was dominant, it seems reasonable that the MW_w of the DOM leached from the total RDS, i.e., the mixture of 93.8% larger RDS and 6.2% smaller RDS, is similar to that of larger RDS, i.e., 325.1–794.9 Da. It is compatible with the MW_w of the DOM in runoffs from impervious, urban areas. The MW_w was 918.1 ± 82.9 and 730.6 ± 88.4 Da, for the chromophoric DOM in the runoff from a 92% impervious road surface in China for a couple of rainfalls (Chen et al. 2017), and that of the DOM in the

Table 1 Weight averaged molecular weight (MW_w) and polydispersity of the DOM leached from the RDS

Component	Number of leaching	63 μm –2 mm		< 63 μm	
		MW_w (Da)	Polydispersity	MW_w (Da)	Polydispersity
UV/Vis (chromophores)	First	325.1	89.19	2172.5	2.71
	Eighth	794.9	244.75	2616.4	5.17
Peak C (fluorophores)	First	7790.2	40.38	–	–
	Eighth	8641.8	86.65	–	–
Peak A (fluorophores)	First	11,789.2	24.10	118,076.5	3.14
	Eighth	15,279.3	28.00	107,046.8	3.41

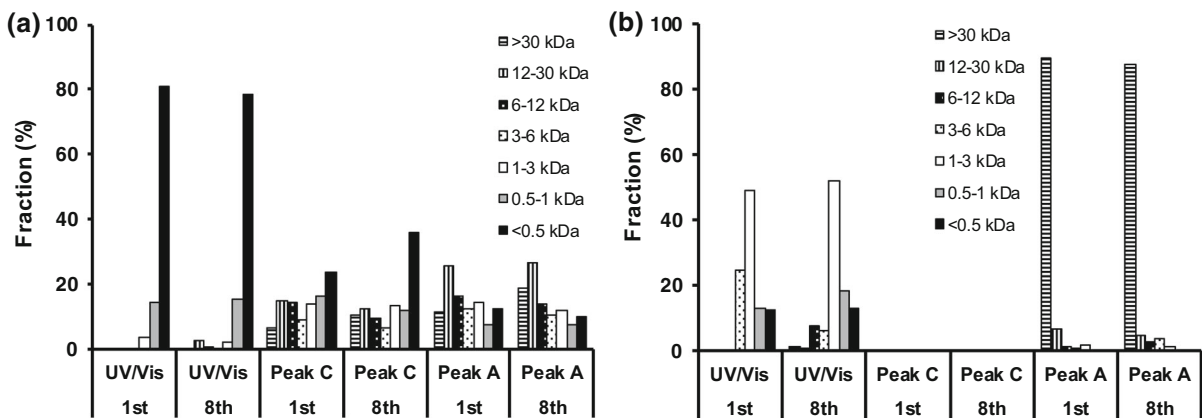


Fig. 8 Molecular size distribution of chromophoric (UV/Vis) DOM and, HA-(peak C) and FA-(peak A) like fluorophoric DOM leached from the RDS of **a** 63 μm –2 mm and **b** < 63 μm (HA humic acid, FA fulvic acid)

runoff from urban area was 1220 Da (McElmurry et al. 2014). It strongly suggests that a significant fraction of the DOM in runoff is originated from RDS. In addition, the MW_w of the DOM in this study was significantly lower than that of SRNOM, i.e., 23.3 kDa (Louie et al. 2013). It indicates that the DOM from RDS is poorly humified, conjugated, or aged, which was supported by the low HIX (Fig. 6).

The MWDs of fluorophores were analyzed because the DOM in runoff contains both chromophores and fluorophores (Zhao et al. 2015; Chen et al. 2017). Both the MW_w and polydispersity of peaks C and A fluorophores from larger RDS were increased as the leaching was repeated. The increase in the DOM of > 30 kDa contributed to the increase in the MW_w of peaks C fluorophores, while the increase in the MW_w of peaks C fluorophores was attributed to the increase in the DOM of > 12 kDa. For smaller RDS, MW_w of the peaks A fluorophores was decreased

slightly from 118,076.5 Da at the first leaching to 107,046.8 Da at the eighth leaching, while the polydispersity was slightly increased. The increase and decrease in MW_w of the fluorophores from larger and smaller RDS, respectively, agreed with the synchronous fluorescence spectra (Fig. 6).

Collectively, the results in Table 1 and Fig. 8 suggest that lower MW DOM molecules were leached within a short contact between RDS and the leachant and that it took a longer contact for the leaching of relatively higher MW DOM, regardless of the size of the RDS. It was supported by the increased $SUVA_{254}$ (Fig. 4) and the decreased fluorescence intensity (Fig. 5) at the eighth leaching, compared to the first leaching, because $SUVA_{254}$ is proportional to MW (Rodríguez et al. 2016) and fluorescence intensity is inversely proportional to MW (Chen et al. 2017).

Weight averaged molecular weight (MW_w) and polydispersity of the DOM leached from the RDS.

The results in this study may not represent all of the situations regarding the pollutants release from RDS during rainfall events because of the great diversity in the composition and load of RDS (Wei and Yang 2010; Hu et al. 2011; Bian and Zhu 2009; Bourliva et al. 2017; Kim et al. 2019), and the rainfall characteristics, i.e., intensity, duration, and composition (Göbel et al. 2007; Iavorivska et al. 2016; Wang et al. 2017). However, the results in this study strongly suggest that RDS can act as a mediator to transfer OM to stormwater runoff to contribute to the OM in runoffs, especially for the OM of anthropogenic origins which is autochthonous, less humified, low aromaticity, and of abiotic origins. It is also suggested that the OM in the runoff can be reduced by sweeping of RDS. The sweeping efficiency of RDS increased with the increase in the particle size (Public Utilities & Herrera Environmental Consultants 2009; Calvillo et al. 2015). For example, it was $47.1 \pm 11.1\%$, and $25.8 \pm 37.6\%$, for $63 \mu\text{m}$ – 2 mm and $< 63 \mu\text{m}$ particles, respectively (Kim et al. 2019). It indicates that sweeping would be more beneficial where large particles are dominant in the RDS. Therefore, the application of sweeping can be encouraged for the reduction of RDS and the OM associated with RDS, which can be transferred to stormwater runoff.

Conclusion

This study investigated the leaching of dissolves pollutants from RDS. The results showed that significant amounts of alkalinity, dissolved ions, metals, nutrients, and DOM leached out of the RDS. The leaching of the DOM was still significant even after 10 leachings, suggesting that the leaching could affect runoff quality for a long period of time. The DOM leaching per unit mass of RDS was higher for smaller RDS than larger RDS. The leached DOM had higher FI, while it had and lower SUVA_{254} , HIX, BIX, and MW_w , compared to NOM, suggesting that the DOM is anthropogenic, autochthonous, less conjugated, of lower aromaticity, of lower humification degree, and of abiotic origins. The SUVA_{254} , FI, HIX, and BIX, MW_w of the leached DOM was comparable to those of the DOM in the runoffs from highly impervious, urban, and industrial areas. In addition, the fluorophores, which are ubiquitous in industrial discharges and stormwater runoff, were found in the leached

DOM. The results also showed that relatively less humified and lower MW DOM was dominantly leached from larger RDS and it was leached in advance to the DOM of relatively more humified and higher MW DOM.

These strongly indicate that RDS is a sink of anthropogenic OM and a source of the DOM in stormwater runoffs. However, the results in this study also provide an opportunity to reduce risks posed by the DOM in RDS and runoff by removing the RDS, i.e., sweeping.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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