The characteristics of dissolved organic matter (DOM) in storm sewer sediments and the binding interaction with Cu(II) in four typical regions in Beijing, China
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ABSTRACT
In this work, dissolved organic matter (DOM) was extracted from storm sewer sediments collected in four typical regions (residential, campus, traffic and business regions) in Beijing, China. The basic characteristics of DOM were analyzed by UV–visible spectroscopy (UV–Vis), excitation-emission matrix Fluorescence Spectroscopy and Fourier Transform Infrared Spectroscopy. Furthermore, the complexation between DOM and Cu(II) were investigated. The results showed that there were large amount of aromatic structure in the DOM extracted from storm sewer sediments. The microbial activities had also made a contribution to the DOM in storm sewer sediments. The composition of DOM influenced the complexing capacity of Cu(II) greatly, which may be attributed to the protein-like and humic-like substances in storm sewer sediments. This study demonstrated valuable information on the structure present in the DOM of storm sewer sediments and provided new insight for exploring the relationship between DOM and co-existing heavy metals in storm sewer sediments.

Key words | complexation, Cu(II), dissolved organic matter, storm sewer sediment

INTRODUCTION
The urban expansion has made a great contribution to the quantity of the urban impervious area, leading to increasing runoff pollution (Qin et al. 2016). The urban storm sewers, which act as intermediates between storm water runoff and the key receiving waters, are not only essential infrastructures in modern cities but also an important passageway for introducing non-point source pollutants into receiving waters (Zgheib et al. 2012). With the increase in runoff pollution, a large amount of pollutants existing in runoff will be deposited in urban storm sewers (Seco et al. 2014). Furthermore, the microorganisms in storm sewer sediments not only decompose some pollutants into water or carbon dioxide, but may also change the structure of the pollutants. New pollutants may be produced under microbiological degradation in urban storm sewers (Jin et al. 2015). These pollutants would be discharged into water bodies without any further treatment, leading to the deterioration of the water quality.

Dissolved organic matter (DOM), as an important group of organic compounds, largely exists in storm sewer sediments. Playing a very important role in ecosystems and significantly affecting the quality of the sediments’ environments (Sakrabani et al. 2009). Previous studies have shown that many pollutants (such as organic/inorganic matter, and heavy metals) in other sediments (such as rivers, lakes, soils) could be combined with DOM (Li & Zhou 2010; Zhang et al. 2016). After complexation with DOM, the structure, transport, transformation, toxicity, bioavailability and stabilization of pollutants are changed, especially for the heavy metals. Additionally, the difference in the properties of DOM (molecular weight, structure, compound, etc.) would make some different impacts on the targeted pollutants (Zhou et al. 2016). Many studies showed that both DOM and other pollutants were found in storm sewer sediments and may be interacted with each other (Zgheib et al. 2012; Liu et al. 2015). Meanwhile, DOM properties of storm sewer sediments in different functional urban areas may be different because of the differences in runoff pollution levels (Zhao et al. 2015). However, up to now, few studies have focused on the nature, properties, structure and potential sources of DOM in storm sewer sediment, not to mention its interactions with other pollutants.

In this study, DOM was extracted from storm sewer sediments collected in four typical regions (residential,
campus, traffic and business regions) which the sampling sites were completely separate drainage system in Beijing, China. The chemical composition, structural characterization and potential sources of DOM in storm sewer sediments were systematically characterized via UV–visible spectroscopy (UV–Vis), excitation emission matrix (EEM) fluorescence spectroscopy and Fourier transform infrared spectroscopy (FTIR). Furthermore, to confirm the impact of DOM on the migration and transformation of heavy metals in storm sewer sediment, Cu(II) was chosen to investigate the binding interaction with DOM due to the high concentration in storm sewer sediments. This paper can provide useful information on the structure present in the DOM of storm sewer sediment and the interactive relationship between DOM and the co-existing heavy metals in storm sewer sediment.

MATERIALS AND METHODS

The sampling sites and sample preparation

To investigate the properties of sediment DOM without stormwater runoff, the storm sewer sediment samples were collected in the dry season during April 2015 before the first rainfall. The samples were located in Xicheng District (39°2’ N–39°94’ N, 116°33’ E–116°36’ E) of Beijing, China (Figure 1), with a completely separate drainage system. The sampling sites located at four typical functional regions (Residential area, Campus, Business area and Traffic area) and each region contained four sampling sites. Each sample was labeled by the sampling sequence of the corresponding regions (R#, C#, B# and T#), where R, C, B and T represented residential, campus, business and traffic area, respectively. The information for some sampling sites is listed in Table 1.

The surface sediments (0–5 cm) in the storm sewers with 2–3 m distance to the stormwater inlet were taken using a metallic shovel. All sediment samples were transported to the laboratory in sealed plastic bags and were put in ice-boxes within a few hours (<6 h), and were then freeze-dried with a freeze drier (−30 °C) and griddled (149 μm).

Each sediment sample (3 g) was extracted with 30 ml ultra-pure water (18.2 MΩ, Milli-Q) in an orbital shaker at 220 rpm for 16 h at 20 °C. The mixed sample was centrifuged at 12,000 g for 20 min, and was then filtered through 0.45 μm polysulfone membranes (Whatman, GF/F). The filtered solution was analyzed for sediment DOM.

The measurement of dissolved organic carbon

The contents of dissolved organic carbon (DOC) were measured as the difference concentration of total carbon (TC) and total inorganic carbon (TIC). The concentrations...
Ultra-pure water was used as the blank. Samples were measured with a PerkinElmer lambda 650S UV–Vis spectrophotometer (Japan) with a 700 voltage Xenon flash lamp, using 1 cm quartz cells. The emission wavelengths ($\lambda_E$, nm) from 250 to 600 nm every 5 nm, with 10 nm slit width, a PMT voltage of 700 V and scanning speed of 1,200 nm min$^{-1}$. The ultra-pure water blank was subtracted to eliminate the water scattering peaks.

Quinine sulfate in 0.1 N $\text{H}_2\text{SO}_4$ was selected as the reference standard with its minimum detection limit of 0.4 ppb in this fluorescence spectrophotometer. The relative fluorescent intensities of samples were expressed in terms of standard quinine sulfate units ($\text{QSU}$, 1 QSU = 1 ppb quinine sulfate in 0.05 mol L$^{-1}$ $\text{H}_2\text{SO}_4$).

The difference in fluorescence properties of DOM from four regions were assessed by three indices, the fluorescence index (FI), the humification index (HIX) and the biological index (BIX) (Huguet et al. 2009). FI is the ratio of fluorescence intensity at an emission wavelength of 450 nm to that at 500 nm at excitation wavelength 370 nm (Cory & McKnight 2005). BIX is calculated at an excitation of 310 nm, by dividing the fluorescence intensity emitted at the emission wavelengths of 380 nm and 430 nm. HIX is the ratio $H/L$ of two spectral region areas from the emission spectrum scanned for an excitation at 254 nm. The two areas are calculated between emission wavelengths 300 and 345 nm for L and between 435 and 480 nm for H (Huguet et al. 2009; Zhang et al. 2010).

The complexation of DOM and Cu(II)

The metals binding capacities of DOM samples have been assessed using a fluorescence quenching towards constant metal concentrations. The adjustments of pH values were performed by adding small volumes of 0.1 M of NaOH or HNO$_3$ solutions to the desired levels ($\text{pH} = 5.0 \pm 0.1$, $T = 20 \pm 0.2$ °C). Prior to measuring the complexation capacity of Cu(II), the DOM samples were adjusted to a low concentration (15 mg L$^{-1}$). Fluorescence quenching was carried out by adding Cu(II) solutions into the DOM samples, which the concentrations were consistent with before showing in EEM fluorescence spectroscopy analysis. In order to avoid a concentration effect, the amount added was less than 5% of the solution. All samples were continuously shaken for 18 h at room temperature (20 °C) to ensure equilibrium.

**RESULTS AND DISCUSSION**

**UV–Vis spectroscopy**

The correlation of the contents of DOC and $a_4$ is shown in Figure 2 ($P < 0.01$) for all 16 sampling sites. It shows that
the contents of DOC increase with the increase of \( a_\lambda \), which mainly attributes to the change of the contents of TC (Fichot & Benner 2011). The results indicate that \( a_\lambda \) (254, 275, 295, 350 nm) can be used to monitoring the contents of DOM, which offer a simple and useful method for the monitoring of DOM in storm sewer sediments. Combined with the characteristics of 16 sampling sites, the sediment depth and catchment area of R2, C5, B9 and T13 are much larger than those in the other sites in four regions. Hence, these four sampling sites were selected for the detailed analysis.

To investigate the sources of DOM in storm sewer sediments, SUVA\textsubscript{280} (specific ultraviolet absorbance at 280 nm) values are used to characterize the aromaticity of sediment DOM (Weishaar et al. 2003). As shown in Table 2, SUVA\textsubscript{280} values of the sediment exhibit a broad range from 1.23 to 3.46 mg C L\(^{-1}\) m\(^{-1}\), which suggests that a greater amount of aromatic structures is present in storm sewer sediment. The SUVA\textsubscript{280} value of the campus is relatively higher than the other three areas, which demonstrates that the more aromatic structures in the campus.

In this study, the spectral slopes (\( S_{240-400} \)) and slope ratios (\( S_R \)) are used to investigate the molecular weight (MW) of sediment DOM in storm sewer sediment (Fichot & Benner 2011). The \( S_{240-400} \) values of DOM in storm sewer sediment are in the range of 13.96–16.85 for different
samples (Table 2). The \( S_R \) values of DOM in four storm sewer sediments are consistent with the \( S_{240-400} \) values and range from 0.51 to 1.13, which indicates that the contents of the autochthonous components of sediment DOM follow the order: B9 > T13 > C5 > R2. A previous investigation has suggested that an inverse relationship existed of DOM molecular weight with the values of \( S_R \) (Zhao et al. 2018). Hence, it can be deduced that the MW of DOM in storm sewer sediments follows the order: B9 < T13 < C5 < R2. Combined with the analytical results of \( S_{240-400} \) and \( S_R \), it indicates that the sediment DOM in storm sewer with lower MW shows a stronger autochthonous component character. These differences are mainly attributed to the impact of different pollution resources and components of DOM in storm sewer sediments (Hur et al. 2009).

**FTIR spectra**

To providing more information about the change of structure and functional groups of DOM in storm sewer sediments, the FTIR spectrum of DOM is shown in Figure 3 and the main absorption bands and corresponding assignments are presented in Table 3.

As shown in Figure 3, the FTIR spectra of the R2 and C5 sampling sites show an obvious band around 3,400 cm\(^{-1}\), which are less broad than the band of the B9 and T13 spectrum, probably due to the loss in hydrogen bonding (Abdulla et al. 2010). As shown in the B9 and T13 sampling sites, the band around 1,650 cm\(^{-1}\) can be attributed to C = O stretching of the carbonyl bond in the amide functional group. Additionally, the FTIR spectra of the T13 sampling sites shows obvious band around 1,630 cm\(^{-1}\), which identifies the major vibrational modes of de-protonated (−COO\(^-\)) carboxyl groups. Most importantly, the disappearance of the band around 1,630 cm\(^{-1}\) in R2 and C5 is attributed to the fact that autochthonous inputs strongly affect the sediment DOM (Abdulla et al. 2010). According to previous studies (Hay & Myneni 2011), the bands at 1,100–1,050 cm\(^{-1}\) can be assigned to aliphatic ester. In all the FTIR spectra of four samples, aliphatic ester vibration bands are just shown in R2 and C5 (Figure 3). It suggests that the sediment DOM of the two sampling sites is affected more by microbially rather than terrestrially derived compounds.

The differences of the FTIR spectra between R2, C5 and B9, T13 indicates that the microbial activities also make a contribution to the sediment DOM and the enriched existence of autochthonous components.

**EEM fluorescence spectroscopy**

EEM fluorescence spectroscopy is suggested to be very useful to distinguish the types of DOM, which can determine the specific fluorescent fractions in organic matter from different sources. As shown in Table 4, EEM can identify humic-like (designated as A, C) and protein-like fluorescence peaks (designated as T1, T2).

All four samples were characterized by EEM to gain insight into the nature of the structure of DOM, and the results are depicted in Figure 4. It is clear that the peak A occurred in the EEM spectra in all samples collected from the four typical regions. Especially in B9 and T13, Peak A shows great dominance, which indicates lots of humic-like substances existed in the storm sewer sediments. Different from the DOM in urban runoff (just shown Peak A), Peaks T1 and T2 are prominently observed in R2 and C5 samples, which suggests lots of protein-like substances (tryptophan, autochthonous DOM) are present in the residential and campus areas (Zhao et al. 2015). Furthermore, most of the intensities of Peak A in four areas (varying from 159 to 1572 QSU) are higher than that in urban runoff (most of which varied from 118 to 1216), which is mainly caused by the presence of more chromophoric molecules (Zhao et al. 2015).

As the weak fluorescence signals of some components can be masked by the strong fluorescence signals (Huguet et al. 2010), the differences in fluorescence properties of DOM are further assessed by three fluorescence indices (FI, BIX and HIX).

FI is used to distinguish sources of aquatic fulvic acids in DOM. As presented in Table 5, the values of FI (1.68–1.87)
are in the range of 1.4–1.9, which suggests that the sources of DOM in storm sewer sediments are influenced more by both autochthonous and allochthonous origins (Zhang et al. 2011). The BIX can be used as an indicator for investigating the organic matter source, which can reflect autochthonous biological activities (Huguet et al. 2009; Salve et al. 2012). In this study, the BIX values stay relatively constant (between 0.85 and 0.91) in all samples.

Table 3 | The major FTIR vibration modes for the functional groups of DOM

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Vibration</th>
<th>Type</th>
<th>Compound class</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,400</td>
<td>O–H stretching</td>
<td>/</td>
<td>The overlap of phenol, carbohydrate and carboxylic acid groups</td>
<td>a,b</td>
</tr>
<tr>
<td>~1,650</td>
<td>C = O stretching</td>
<td>/</td>
<td>Amide I, carboxylate</td>
<td>a,c</td>
</tr>
<tr>
<td>1,600 ± 40</td>
<td>Asymmetric stretching</td>
<td>–COO(^-)</td>
<td>Carboxylic acid</td>
<td>a,c,d</td>
</tr>
<tr>
<td>1,065 ± 35</td>
<td>O–C–C stretching</td>
<td>Aliphatic</td>
<td>Ester</td>
<td>a,c</td>
</tr>
</tbody>
</table>

\(^a\)Abdulla et al. (2010).
\(^b\)Li et al. (2011).
\(^c\)Hay & Myneni (2007).
\(^d\)Michalska et al. (1984).

Table 4 | The major fluorescence peaks of DOM in storm sewer sediment

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Sources</th>
<th>Ex/Em (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak C</td>
<td>Visible humic-like, more aromatic</td>
<td>320–360/420–460</td>
</tr>
<tr>
<td>Peak A</td>
<td>UV humic-like, less aromatic</td>
<td>&lt;260/380–460</td>
</tr>
<tr>
<td>Peak T(_1)</td>
<td>Visible protein-like tryptophan</td>
<td>270–280/340–370</td>
</tr>
<tr>
<td>Peak T(_2)</td>
<td>UV protein-like tryptophan</td>
<td>225–235/340–345</td>
</tr>
</tbody>
</table>

Figure 4 | The EEM fluorescence spectroscopy of four sampling sites.
which confirms the strong autochthonous characteristic of DOM. Furthermore, the results also demonstrate that the sediments’ DOM in storm sewers are influenced by higher biological productivity. The HIX is usually used to evaluate the degree of humification and source property of DOM (Salve et al. 2012). In this study, the values of HIX in the samples vary from 3.18 to 3.88 with a mean of 3.62, which illustrate that the degree of aromaticity of DOM in storm sewer sediments is much higher than that of urban runoff (mostly in the range of 1.72–3.49) (Zhao et al. 2015).

The influenced of the DOM on the complexing capacity of Cu(II)

Heavy metals are a type of important pollution in storm sewer sediments. The characteristics and content of DOM can greatly influence the complexing capacity of Cu(II). The DOM extracted from four regions are used to investigate the complexation with Cu(II), and the results are listed in Table 6. The DOM in R2 sampling sites exhibits the largest complexing capacity with Cu(II), followed by C5, T13 and B9. According to the previous research (McIntyre & Guéguen 2015; Kulikowska et al. 2015), compared with humic-like substances, protein-like substances can be combined further with heavy metals and form large amount of metal complexes. As shown in Figure 4, the DOM in R2 and C5 contains large amount of protein-like substances that induce a higher complexing capacity than B9 and T13. Furthermore, Peaks T1 (1372 QSU) and T2 (981 QSU) of sediment DOM in R2 show higher intensity than C5 (T1-1028 QSU, T2-837 QSU), demonstrating the higher complexing capacity of R2. As shown in Figure 4, the humic-like substances show great dominance in B9 and T13, which is consistent with the combining capacity of 341 and 412 mg g⁻¹, respectively. These results may be attributed to the lower interaction between humic-like substances and Cu(II). The fluorescence intensity of T13 (Peak A-1372) is relatively higher than B9 (Peak A-828), confirmed by the higher complexing capacity for T13. Furthermore, these results are also consistent with the MW of DOM showed in Table 2.

To investigate the complexing mechanism of DOM and Cu(II), the EEM fluorescence spectroscopy of DOM after the interaction with Cu(II) is presented in Figure 5. Compared with the prior fluorescence, the signals of EEM fluorescence spectroscopy have been obviously changed. The fluorescence intensity of DOM is much weaker than before due to the effectively quenched humic- and protein-like fluorescence caused by Cu(II) (McIntyre & Guéguen 2015). For R2, the fluorescence intensity of T1 and T2 peaks decreases from 1188 to 200 QSU, and 914 to 136 QSU, respectively. For C5, the fluorescence intensity of T1 and T2 peaks decreases from 1219 to 347 QSU, and 1024 to 105 QSU, respectively. These results indicate the strong complexing capacity between the protein-like substances of DOM and Cu(II). Additionally, Peak A (humic-like substances) of R2 has appeared, due to some humic-like matter not being effectively combined with Cu(II) (Zhao et al. 2016). However, for B9 and T13, the fluorescence intensity of peak A is nearly unchanged after thecomplexing, which may be caused by and is mainly consistent with humic-like substances (Zhang et al. 2016).

The characteristics of DOM in storm sewer sediments are influenced by both allochthonous pollution and microbial activities. Due to the different components, the interaction of DOM and Cu(II) differ greatly in the four regions. The complexation will make more heavy metals be fixed in storm sewer sediments, and these heavy metals will be more stable than in their prior existence in sewer sediments. When the surface sediments are washed off into natural water via the erosion of stormwater runoff, the binding heavy metals would be deposited for a long time in the sediments of the aquatic environment and be more difficult to remove from storm sewer sediments (McIntyre & Guéguen 2015).

| Table 5 | The fluorescence indices for storm sewer sediments in four sampling sites |
|---------|--------------------------|----------------|----------------|----------------|
| Sampling sites | R2 | C5 | B9 | T13 |
| FI370 | 1.87 | 1.68 | 1.70 | 1.73 |
| BIX | 0.91 | 0.85 | 0.90 | 0.90 |
| HIX | 3.86 | 3.18 | 3.88 | 3.56 |

| Table 6 | The complexing capacity of DOM with Cu(II) |
|---------|--------------------------|----------------|----------------|----------------|
| Sampling sites | R2 | C5 | B9 | T13 |
| Combining capacity (mg/g) | 876 ± 12 | 463 ± 9 | 341 ± 15 | 412 ± 13 |

CONCLUSIONS

To investigate the features of DOM in storm sewer sediment, four typical regions in Beijing were selected and the properties of DOM were analyzed. Furthermore, the interactions of...
DOM with Cu(II) were studied to confirm the relationship between DOM and co-existing heavy metal. Some conclusions can be proposed as follows. (i) The sediment DOM in storm sewers contained lots of aromatic structure. The MW of sediment DOM in different regions follows the order: residential region < campus < traffic area < business region. (ii) The autochthonous components showed great dominance in sediment DOM, which could be attributed to the microbial activities in storm sewer sediments. (iii) The characteristics of DOM influenced the complexation of Cu(II) greatly, which could be ascribed to the humic- and protein-like substances in storm sewer sediments. Additionally, it could be demonstrated that the interaction between protein-like substances and Cu(II) is much stronger than with humic-like substances. This study can provide useful information for the structure present in the DOM of storm sewer sediments and offers new insight into the relationship between DOM and the co-existing heavy metals in storm sewer sediment.

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