



Characteristics of dissolved organic matter in surface water and sediment and its ecological indication in a typical mining-affected river—Le'an River, China

Wenhui Liu^{1,2} · Teng Ma^{1,2} · Yao Du^{1,2} · Xiancang Wu^{1,2} · Liuzhu Chen^{1,2} · Junqi Li^{1,2}

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Abstract

Dissolved organic matter (DOM) plays an important role in the cycling and toxicity of heavy metals in aquatic systems. However, most studies have focused only on DOM in either water or sediments. This study aimed to analyze the source, composition, and structural characteristics of DOM in both surface water and bottom sediments of the Le'an River and its major tributaries. In addition, the potential ecological risks of three typical heavy metals (Cu, Pb, and Zn) were quantitatively evaluated based on the characteristics of DOM and in situ data. The results showed that sediment DOM is more aromatic and hydrophobic than surface water DOM. Although humic-like components dominated the DOM pool in both surface water and sediments, their sources were different. Surface water DOM is mainly autochthonous, while sediment DOM is controlled by both autochthonous and allochthonous sources. Risk prediction results based on DOM characteristics show that surface water has a higher potential risk of heavy metal release than sediments. Comprehensively considering the ecological risk of water and sediments, high-risk areas were found to be mainly distributed in the upper and middle reaches of the Le'an River. This distribution is attributable to the developed mining and smelting industries in these areas and consistent with the risk assessment results of measured concentrations of heavy metals. This study established a new technique for predicting the ecological risk of aquatic systems based on the characteristics of DOM in surface water and sediments.

Keywords Le'an River · Dissolved organic matter · Ecological risk · Heavy metals

Introduction

Heavy metal pollution has been an issue of wide concern because heavy metals are highly toxic, persistent, resistant to degradation, and they can easily enter the food chain (Cui et al. 2021; Yu et al. 2021). It is reported that large amounts of heavy metals are discharged into rivers and

lakes worldwide every year (Li et al. 2020b). For example, Zijiang River, a mining-affected river, releases large amounts of heavy metal pollutants to Dongting Lake every year (Liu et al. 2021). Previous studies show that dissolved organic matter (DOM) can form DOM-metal complexes with heavy metals and strongly affect the spatial distribution and even ecotoxicity of heavy metals (Huang et al. 2019; Luo et al. 2021; Xia et al. 2008). Interestingly, DOM, as a small but reactive fraction, can change the speciation and bioavailability of heavy metals by affecting the complexation and adsorption process of heavy metals (Cheng and Wong 2006; Xu et al. 2013). Therefore, insight into DOM and its effects on ecological toxicity of heavy metals is essential for reducing the ecological risk of heavy metals in aquatic environments.

The complexation of DOM with heavy metals is key to evaluating the potential ecological risk of heavy metal release, which is affected by the characteristics of DOM. In general, DOM of low molecular weight have a strong complexing ability to heavy metals. It was found that DOM

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✉ Teng Ma
mateng@cug.edu.cn

¹ State Environmental Protection Key Laboratory of Source Apportionment and Control of Aquatic Pollution, Hubei Key Laboratory of Yangtze Catchment Environmental Aquatic Science, China University of Geosciences, Wuhan 430078, China

² School of Environmental Studies, State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Lumo Road 388, Wuhan 430078, China

concentrations in polluted seawater affect the toxicity of Cu and Pb (Sánchez-Marín et al. 2010). Huang et al. (2019) suggested that protein-like and humic-like substances have strong affinity for Cu. In their study on DOM in Nansi Lake, Ren et al. (2020) found that protein-like substances exhibit a higher binding potential with metals than humic-like substances. Thus, studying the components and characteristics of DOM in the aquatic environment may help in determining the potential ecological risks of heavy metals, and effectively guide water treatment and protection.

Previous studies on DOM in heavy-metal-polluted aquatic systems generally focused on DOM in either surface water or sediments rather than in both. For example, some researchers evaluated the potential ecological risk of heavy metal release by studying the source, content, and structural characteristics of DOM in surface sediments (Dong et al. 2020; Li et al. 2020a). However, the potential ecological risks of heavy metals in aquatic systems cannot be accurately reflected by considering only sediment DOM. Luo et al. (2021) found that the source, content, and photo-degradation potentials of DOM differ between surface water and sediments. Xu et al. (2013) indicated that DOM extracted from macrophyte-dominated sediments exhibit more heavy-metal-binding sites and higher conditional stability constants than DOM extracted from algae-dominated sediments. These differences in the nature and origin of the DOM may affect the evaluation results of the ecological risk of heavy metal release, attributable to differences in binding properties between DOM and heavy metals. Therefore, when evaluating the potential ecological risk of heavy metal release, the influence of DOM in water and sediments should be considered simultaneously.

Thus far, various spectroscopic techniques have been applied to characterize DOM. One such technique is ultraviolet–visible spectrophotometry (UV–vis), which is a common method for studying the properties of aromatic or unsaturated compounds (Sellami et al. 2008). With the advantages of high sensitivity, good selectivity, large amounts of information, and fast and accurate detection (Zi et al. 2016), the combination of three-dimensional excitation-emission matrix (3D-EEM) and parallel factor analysis (PARAFAC) has been widely applied to study the components and structural characteristics of DOM (Hao et al. 2017; Yamashita et al. 2008). Wang et al. (2015) used UV–vis and 3D-EEM to investigate soil DOM in the Three Gorges Reservoir and found that the aromaticity and humification characteristics of DOM widely vary between different land uses types (forest, cropland, vegetable field, and residence). Analyzing the characteristics of DOM and its correlation with heavy metals in Ningbo City using 3D-EEM, Liang et al. (2018) found a significant positive correlation between DOM and Cu, Pb, Zn, As, Mn, and Cr in urban rivers. Therefore, the characteristics and source of DOM can be effectively analyzed by

combining UV–vis and 3D-EEM, which may help understand the complex relationship between DOM and heavy metals and provide more accurate results of risks associated with heavy metal release.

The safety of the aquatic ecological environment of rivers is controlled by local anthropogenic activities within the entire drainage area (Xu and Xu 2018). Dexing Copper Mine in the upper reach of the Le'an River is the largest open-pit copper mine in Asia and the first one in China. It has been exploited for more than 50 years for ores containing chalcopyrite (FeCuS_2), sulfide pyrite (FeS_2), galena (PbS), and sphalerite (ZnS) (Lin et al. 2019). At the same time, the serious heavy metal pollution of the Le'an River has attracted wide attention. Studies have shown that the concentration of Cu in the soil of the Le'an River Basin exceeds the background value by 8.82 times on average and sediments are heavily contaminated by Cu, Pb, and Zn (Ji et al. 2018; Yu et al. 2016). Most studies on heavy metal pollution and ecological risk in the Le'an River Basin have been based on the content of heavy metals in the soil and sediments. However, the effect of aquatic environmental factors, particularly DOM, on the ecotoxicity of heavy metals was not considered. Considering this issue, our study aimed to (i) use UV–vis and 3D-EEM to study the contents and structural characteristics of DOM in both surface water and sediments of the Le'an River Basin; (ii) quantitatively estimate the potential ecological risk of heavy metals based on the characteristics of DOM and on-site sampling data.

Materials and methods

Study area

The Le'an River, the southern branch of the Rao River, is located northeast of Jiangxi Province. It merges with the Changjiang River in Poyang County to form the Rao River and then flows into Poyang Lake. The main tributaries are the Dawu River, Jishui River, Chexi River, and Panxi River. The basin has numerous mines, including Yinshan Lead–Zinc Mine and Dexing Copper Mine in Dexing City in the upper reaches. In addition, some abandoned small mines are scattered in the northeastern part of Leping City in the middle reaches. The Le'an River is not only the source of water for residents but also the main source of industrial and agricultural water along the river. Therefore, it has important ecological functions and economic value.

Sample collection and preparation

In September 2020, we selected 21 sampling sites (including 17 sites in the mainstream and one site in each of the 4 tributaries) in the Le'an River Basin to collect surface water

and sediment samples. The locations of the sampling points are shown in Fig. 1. The sampling points were divided into four parts according to their location in the basin: source (sampling sites LA01–LA03), upstream (sampling sites LA04–LA10, including DX05 and JS09), midstream (sampling sites LA11–LA17, including CX14 and PX16), and downstream (sampling sites LA18–LA21).

In situ water samples were collected through a 0.45- μm membrane filter and stored in brown glass bottles and polyethylene terephthalate bottles at 4 °C, acidified with HPO_4 and HNO_3 to $\text{pH} < 2$. The sediment samples were naturally air-dried in the laboratory and ground through a 200-mesh sieve before storage for later use.

DOM was extracted from the mixtures of sediments and ultrapure water with a ratio of 1:10. The mixtures were placed in a shaking bath for 24 h (200 r/min), then centrifuged for 25 min at 4000 r/min, filtered through 0.45- μm organic fiber membrane, and finally stored at 4 °C for testing (Xu et al. 2013).

For the determination of heavy metal contents in sediments, a 0.1 g soil sample was weighed accurately in a Teflon digestion tube. Subsequently, the following steps were followed: (1) add 1.6 mL HNO_3 , shake for 2 min, and increase the temperature to 120 °C for 30 min; (2) add 0.8 mL HClO_4 and 1.2 mL HF, shake for 2 min, and increase the temperature to 150 °C for 180 min; (3) open the digestion tube and heat it up to 190 °C for 120 min, carry out complete digestion, and rush the acid until the sample is jelly viscous; (4) add 1 mL aqua regia, shake for 15 min, and heat it up to 120 °C for 20 min. Finally, after cooling, the entire sample was transferred into a 10-mL volumetric flask and brought to volume with ultra-pure

water. This method was formulated by the Experimental Center of the School of Environment, China University of Geosciences (Wuhan), and referred from the national standard of Soil and sediment—Digestion of total metal elements—Microwave assisted acid digestion method (HJ832-2017).

Analytical methods

The DOC concentration of samples was measured with a total organic carbon analyzer (Elementar Vario TOC, Germany) as DOM concentration, and the measurements were repeated twice for each sample. UV spectral analysis was carried out a full-wavelength scan from 200 to 700 nm stepped with 1-nm increments using a UV-vis spectrophotometer (U-3900, China).

Fluorescence EEM spectroscopy of all diluted samples were conducted using a fluorescence spectrometer (F-4500; Hitachi, Japan) with a scan speed of 12,000 nm/min. The excitation (E_x) wavelength was from 200 to 500 nm with 5 nm increments, and the emission (E_m) wavelength was from 250 to 600 nm with 2 nm increments. The above experimental tests were completed in the School of Environment, China University of Geosciences (Wuhan).

The Cu, Pb, and Zn concentrations in water and sediment samples were determined at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Wuhan). The analytical instrument was ICP-MS (Thermo Scientific ICAP Q, USA) with an accuracy of 0.001 $\mu\text{g/L}$.

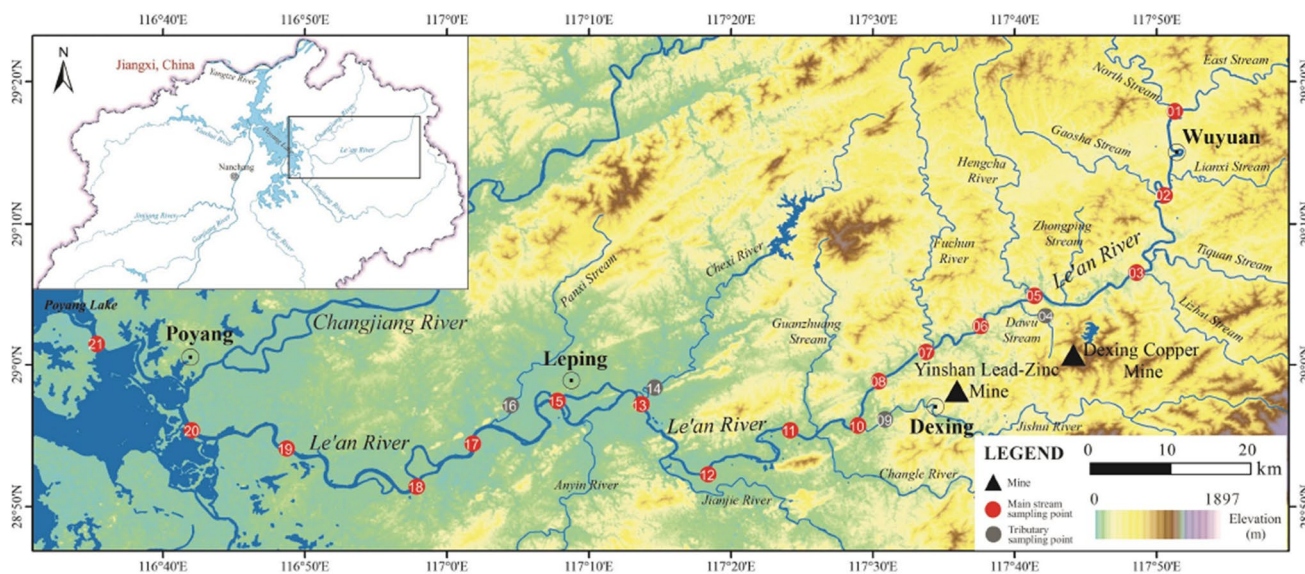


Fig. 1 Location of the study area and distribution of sampling sites in the Le'an River Basin

Data analysis

PARAFAC modeling

All EEM spectra of DOM in surface water and sediments in the Le'an River were analyzed by PARAFAC modeling on MATLAB 7.0 combined with the DOMFluor toolbox. Leverage comparison was carried out to assess the occurrence of outlier samples. In addition, residual and split-half analyses were performed to determine the correct number of components.

Calculation of optical indicators

SUVA₂₅₄ reflects the aromaticity of DOM, the value of which is the ratio of UV absorbance at 254 nm and DOC content (Niloy et al. 2021). Fluorescence index (FI) is the fluorescence intensity of emission wavelengths at 470 and 520 nm divided by that at an excitation of 370 nm (Huguet et al. 2009). Biological index (BIX) is the fluorescence intensity of emission wavelengths at 380 and 430 nm divided by that at an excitation of 310 nm (Huguet et al. 2009).

Potential ecological risk of heavy metals

The potential ecological risk factor of a given metal (E_r^i) initially introduced by Hakanson (1980) is calculated as follows:

$$E_r^i = T_r^i \times (c_i/c_0)$$

The potential ecological risk of heavy metals based on the characteristics of DOM (RI_{DOM}) is calculated with the following equation (Li et al. 2020a):

$$RI_{DOM} = T_r^i \times (1/A_s \cdot C_s)$$

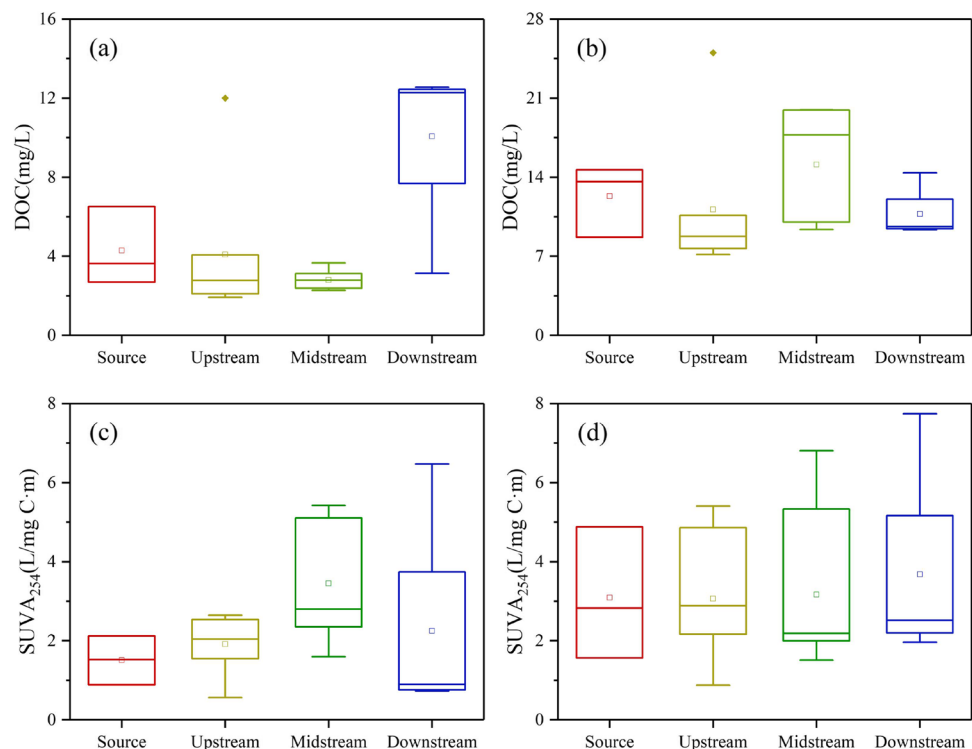
where c_i is the content of metal i in sediments, c_0 is the background soil heavy metal content in Jiangxi Province (Cu = 20.30 mg/kg, Pb = 32.30 mg/kg, Zn = 69.40 mg/kg (Yu et al. 2020)), T_r^i is the biological toxicity factor of an individual element (Cu = Pb = 5, Zn = 1 (Chen et al. 2016)), A_s is the complexation ability at sites, and C_s is the concentration of DOM in sites.

Results and discussion

Spatial distribution and UV-vis spectrum characteristics of DOM

The concentration of DOC is often used to analyze and characterize the content and distribution of DOM (Niloy et al. 2021). Figure 2a and b shows that the average DOC concentration in surface water (4.829 mg/L) was lower than that in sediments (12.564 mg/L). DOC content in surface water exhibited a decreasing trend from the source to midstream, which can be mainly attributed to the source

Fig. 2 DOC content and SUVA₂₅₄ value of DOM in surface water and sediment samples (**a, b** DOC content of surface water and sediment samples; **c, d** SUVA₂₅₄ value of surface water and sediment samples)



section (in Wuyuan County) being an area with developed tourism. Site LA09 in Jishui River exhibited an unusually high concentration over other upstream sites, which may be attributable to the random discharge of domestic wastewater from residents and rotting branches at the bottom of the river (Wen et al. 2021). The highest DOC concentration in surface water was recorded at downstream sites, which agrees with the results of previous studies (Liu et al. 2021). In other words, this may be explained by the distribution of cities and industrial areas in the downstream area. Another possible reason is the wider river surface, slower water flow, and widespread aquaculture near the river in the downstream area (Luo et al. 2021; Stanley et al. 2012).

DOC contents of sediments ranged from 7.167 to 25.013 mg/L, indicating a relatively high level. The content fluctuated significantly compared with DOC in surface water. The highest DOC content was recorded at site LA10, which is located at a confluence with a tributary as well as near a sand bar containing a large amount of biomass. The decrease in river flow rate and the abundant biomass of the sand bar may explain the deposition of large amounts of organic matter and higher organic matter content in the sediments (Pinney et al. 2000). Unlike surface water DOC, sediment DOC was higher in the midstream than in the other reaches, which suggests that the sources of DOM in surface water and sediments may be different. Suspended matter with a large specific surface area will absorb many organic compounds and be deposited at the river bottom by gravity (Luo et al. 2021; Viguri et al. 2002). Moreover, some animal and plant residues remaining in bottom sediment will generate DOM through microbial decomposition (Luo et al. 2021). This could explain the generally higher DOM in sediments, and hydrodynamic conditions along with physicochemical properties of water bodies may also be important factors affecting the distribution characteristics of DOC.

The $SUVA_{254}$ index, regarded as a proxy for aromaticity, is usually applied to reflect the source and degree of humification of DOM (Helms et al. 2008; Jaffrain et al. 2007; Niu et al. 2021). According to previous studies, $SUVA_{254} > 4$ L/mg C·m indicates that DOM is mainly composed of macromolecules and hydrophobic organics, while $SUVA_{254} < 4$ L/mg C·m indicates hydrophilic organics as the major components (Zhang et al. 2010). As presented in Fig. 2c and d, the average $SUVA_{254}$ value of surface water was 2.435 L/mg C·m, ranging from 0.560 to 6.471 L/mg C·m, which was generally lower than that of sediments (3.221 L/mg C·m on average, ranging from 0.881 to 7.742 L/mg C·m). Moreover, the proportions of $SUVA_{254} > 4$ L/mg C·m in water and sediments were 19.05% and 28.57%, respectively, suggesting the occurrence of more aromatic and hydrophobic substances in sediments than in surface water. Except downstream, the surface water $SUVA_{254}$ values in all other river sections were less than 4 L/mg C·m, indicating that hydrophilic organics

were the major components of surface water DOM. Furthermore, it can be inferred that the molecular weight of sediment DOM is higher than that of surface water DOM.

Optical characteristics of DOM by PARAFAC

The emission (E_m) and excitation (E_x) of different components determine the basic properties of individual fluorophores (Zhou et al. 2017). Different fluorescent components can be identified through PARAFAC analysis using EEM data. Two effective fluorescence components were identified via PARAFAC analysis of the three-dimensional fluorescence spectra of water and sediment DOM (Fig. 3). However, in the analysis of the EEM data of water samples, the data of site LA21 was excluded because it was identified as an outlier during initial data analysis and outlier identification.

Two distinct fluorescent components in surface water and sediment samples were humus components, which shows that the fluorescent components in water and sediments are similar to some degree. The excitation wavelengths of components W-C1, W-C2, and S-C1 were between 320 and 350 nm, and the emission wavelengths were between 380 and 520 nm, which fitted with the fluorescence peaks of humic-like compounds (Dong et al. 2020). Component W-C1 displayed a peak at 345/474 nm (E_x/E_m), which was close to the visible fluorescence peak C (Coble 1996; Zhang 2019; Zhu et al. 2017). This component was considered as a humic-like acid, which is believed to be microbially transformed and widespread in wetlands (Fellman et al. 2010; Williams et al. 2010). Component W-C2 exhibited a peak at 330/392 nm (E_x/E_m) as a UVA humic-like substance with low molecular weight, which approached the fluorescence of fulvic-like acid and is believed to have two types of sources: terrestrial input and autochthonous production (Fellman et al. 2010; Zhang 2019). Component S-C1 located at 335/428 nm (E_x/E_m) was considered a UVC humic-like substance related to high-molecular-weight humic substances, which contacted with the fluorescence of visible fulvic-like acid (Fellman et al. 2010; Li 2012; Murphy et al. 2008; Zhang 2019). Component W-C2 and S-C1 were similar to C2 reported by Zhu et al. (2017) and C3 covered by Yang et al. (2015), which were analyzed in a river affected by anthropogenic activities and wastewater. Thus W-C2 and S-C1 were considered anthropogenic humic materials of agricultural sources. Component S-C2 with a peak at 200/394 nm (E_x/E_m) was identified as UV fulvic-like acid, associated with autochthonous production and microbial processing of DOM (Fellman et al. 2010; Jia et al. 2012).

Figure 4 illustrates the relative proportion of fluorescence components. In surface water, the proportion of the fulvic-like acid component was higher than that of the humic-like

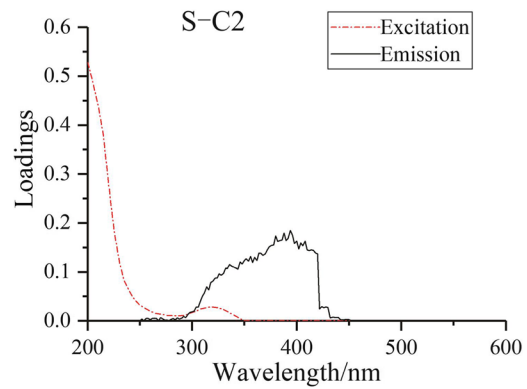
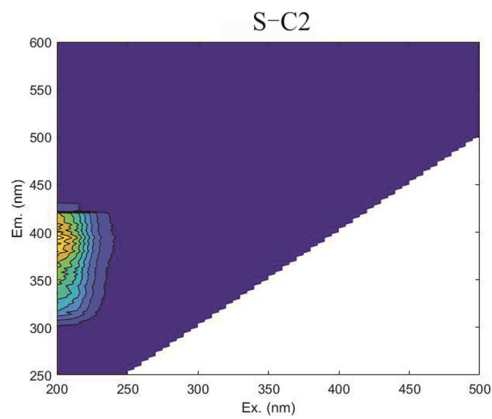
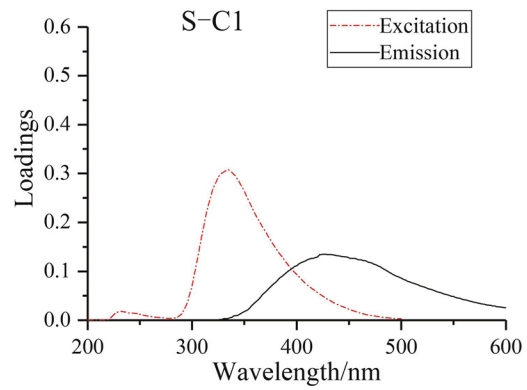
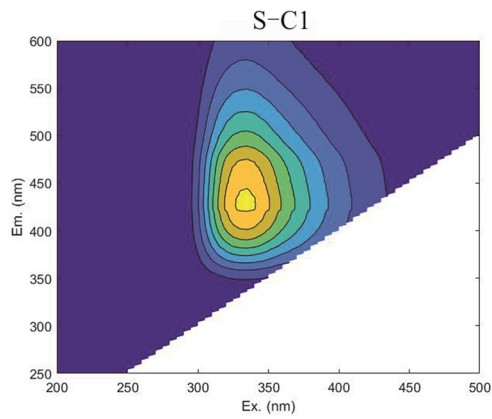
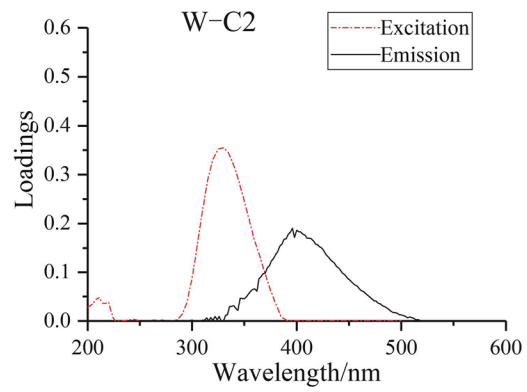
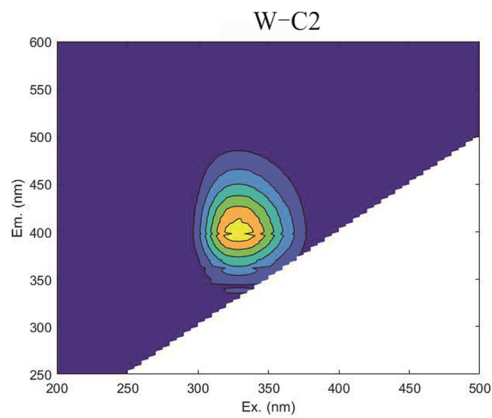
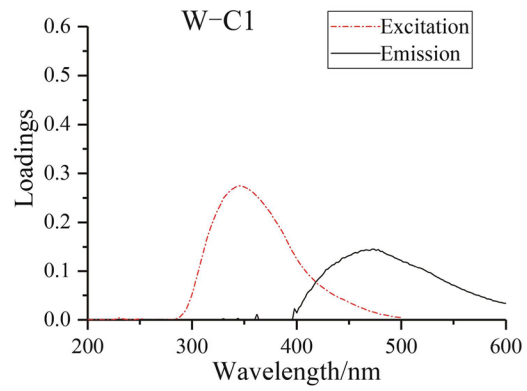
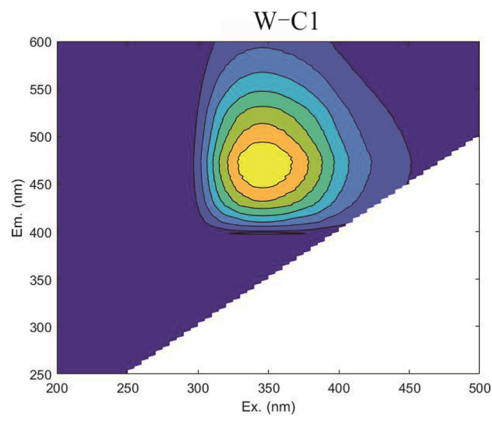


Fig. 3 Contour plots and E_m/E_x loadings of the two fluorescent components in surface water and sediments obtained via PARAFAC analysis. W-C1 and W-C2: the two components of surface water samples; S-C1 and S-C2: the two components of sediment samples

acid component, and the proportions appeared to remain constant. On the contrary, the proportions of the visible fulvic-like acid and UV fulvic-like acid components in sediments widely fluctuated, with the visible fulvic-like component reaching the largest proportion at 91%. Such a wide spatial variation indicated that sediment DOM has complex sources, and the specific contribution of individual sources could not be ascertained. In addition, the fluorescence index (FI) and biological source index (BIX) were selected to further analyze the source of DOM.

FI as a characteristic parameter can indicate the source of DOM humus components. $FI > 1.8$ reflects a microbial source and $FI < 1.2$ reveals land and soil origins (Fellman

et al. 2010). FI between 1.2 and 1.8 ($1.2 < FI < 1.8$) suggests a mixed source with DOM humus being affected by the combined effects of terrestrial and endogenous materials (Lu 2018). According to Fig. 5, the FI of all sites of the Le'an River was between 1.2 and 1.8, indicating the contribution of terrestrial and authigenic sources to DOM at these sites, except for site DW05. The FI values of surface water were universally higher than those of sediments and closer to 1.8, showing more autochthonous production input to DOM in surface water. Thus, autochthonous production caused by microbial processes may be the main source of W-C2.

BIX is an important indicator reflecting the relative contribution of the self-generating source of DOM. $BIX > 1$ indicates significant self-generating characteristics and strong microbial activity, while a low BIX value ($BIX < 0.8$) suggests small authigenic input and large terrestrial input (Birdwell and Engel 2010). The BIX value of 19.04% of the surface water sampling points was less than 0.8, suggesting

Fig. 4 Percentages of fluorescence components of DOM in surface water and sediments

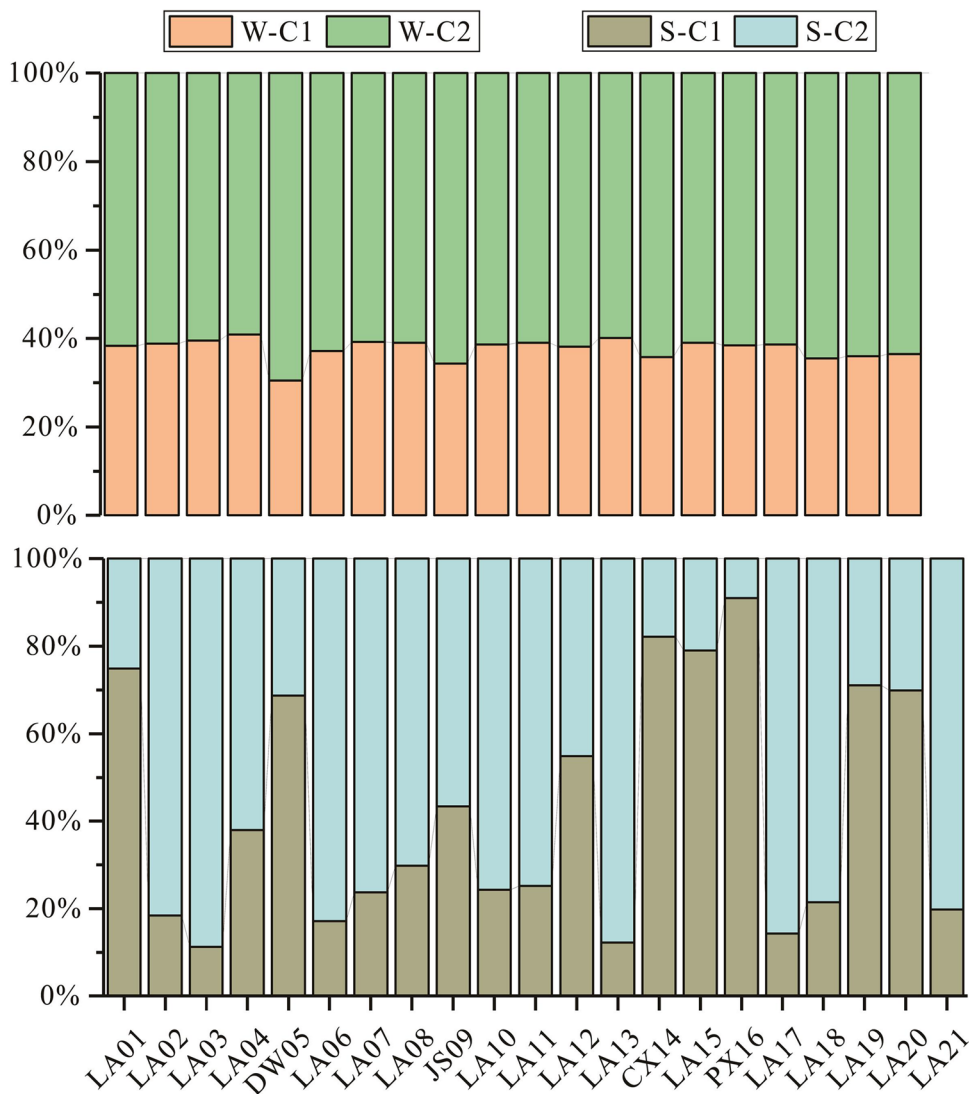
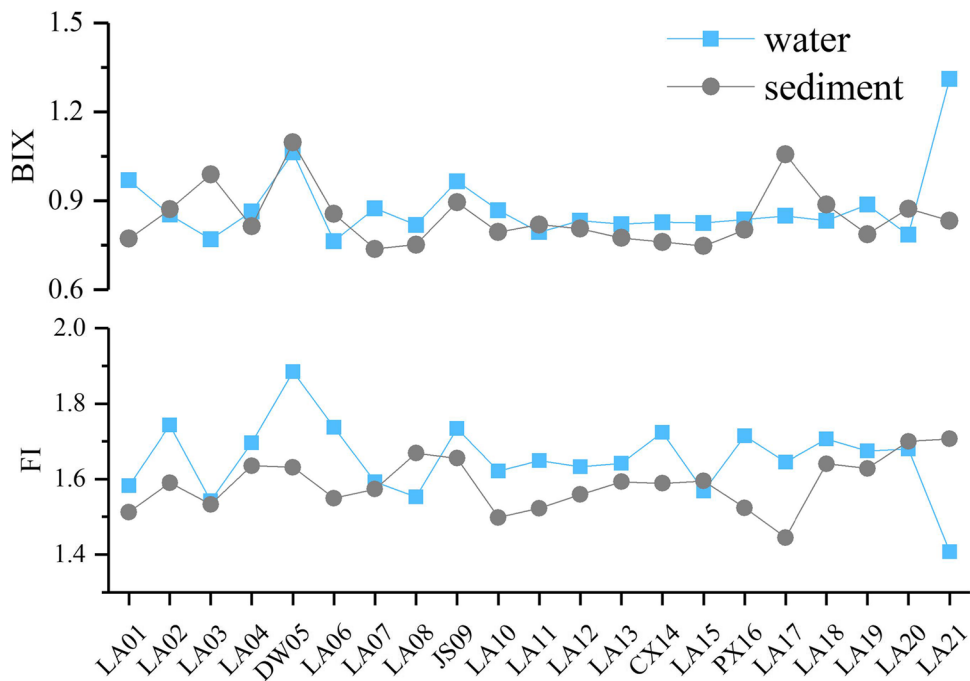


Fig. 5 Fluorescence spectral index (FI and BIX) of DOM in surface water and sediment



terrestrial input. This further showed that DOM in surface water was mainly autogenous. While the BIX value of 33.33% of sediment sampling sites was less than 0.8, 9.52% of the BIX values were higher than 1.0 indicating multiple sources of sediment DOM. Furthermore, the BIX values in the water and sediment samples of the tributaries were larger than 0.8, suggesting a large contribution of autogenic sources. Among them, the BIX values of surface water and sediment samples of the Dawu River (sampling site DW05) were larger than 1.0, indicating that the DOM is mainly derived from biological and bacterial activities—showing significant self-generating characteristics.

Table 1 shows the relationship between the components, content, and spectral characteristics of DOM. There was a significant relationship between W-C1 and W-C2, proving their autochthonous source. DOC concentration was positively correlated to BIX and negatively correlated to SUVA₂₅₄, suggesting that the DOM component with higher organic carbon in surface water tended to have the characteristics of autochthonous source and lower aromaticity. In addition, component S-C1 had a significant positive correlation with DOC and a negative correlation with BIX, indicating its allochthonous sources with higher organic carbon, which appeared to be the opposite of that in surface water.

Table 1 Relationship between DOM components, content, and spectral characteristics

		W-C1	W-C2	DOC	FI	BIX	SUVA ₂₅₄
Water	W-C1	1.000	0.890**	0.242	0.015	-0.280	0.299
	W-C2		1.000	0.418	0.254	-0.074	0.325
	DOC			1.000	0.226	0.517*	-0.466*
	FI				1.000	0.004	-0.164
	BIX					1.000	-0.182
	SUVA ₂₅₄						1.000
	Sediment	S-C1	1.000	-0.299	0.711**	-0.247	-0.543*
S-C2			1.000	-0.045	-0.269	0.148	0.662**
DOC				1.000	-0.363	-0.410	-0.369
FI					1.000	0.077	0.017
BIX						1.000	0.203
SUVA ₂₅₄							1.000

*Relationship is significant at $p < 0.05$; **relationship is significant at $p < 0.01$

Table 2 Potential ecological risk values of heavy metals based on the characteristics of DOM at sampling points in the Le'an River Basin (non-dimensional)

	W-Cu	W-Pb	W-Zn	W-sum	S-Cu	S-Pb	S-Zn	S-sum	Sum
LA01	24.68	49.37	19.74	93.79	20.88	41.77	21.45	84.10	177.89
LA02	13.71	27.43	10.97	52.11	16.42	32.84	6.15	55.40	107.51
LA03	33.11	66.21	26.48	125.80	39.07	78.14	9.53	126.74	252.54
LA04	46.12	92.24	36.88	175.25	20.47	40.93	13.53	74.93	250.17
DX05	23.17	46.33	18.53	88.02	31.17	62.34	30.45	123.96	211.98
LA06	42.77	85.54	34.20	162.51	29.01	58.02	10.21	97.24	259.75
LA07	32.08	64.16	25.65	121.89	19.66	39.33	9.06	68.06	189.95
LA08	37.87	75.74	30.29	143.90	26.50	53.00	14.61	94.11	238.01
JS09	7.60	15.20	6.08	28.87	17.75	35.49	12.88	66.11	94.99
LA10	26.28	52.56	21.02	99.85	8.26	16.52	3.88	28.66	128.52
LA11	39.16	78.32	31.32	148.80	10.20	20.40	4.92	35.52	184.32
LA12	32.03	64.07	25.62	121.72	17.40	34.80	14.78	66.98	188.69
LA13	31.01	62.03	24.80	117.84	31.86	63.72	8.36	103.93	221.77
CX14	28.87	57.74	23.09	109.70	19.06	38.12	20.63	77.81	187.52
LA15	36.34	72.69	29.06	138.10	18.62	37.23	19.71	75.56	213.65
PX16	24.41	48.82	19.52	92.75	40.12	80.24	45.86	166.23	258.97
LA17	37.52	75.05	30.01	142.58	30.40	60.81	9.16	100.37	242.95
LA18	7.35	14.70	5.88	27.92	23.61	47.22	10.01	80.83	108.76
LA19	7.20	14.40	5.76	27.36	26.21	52.43	26.13	104.77	132.13
LA20	7.37	14.73	5.89	27.99	25.92	51.84	25.58	103.34	131.33
LA21	–	–	–	–	16.04	32.08	6.36	54.48	54.48

Component S-C2 was positively correlated to $SUVA_{254}$, proving its characteristic of high aromaticity.

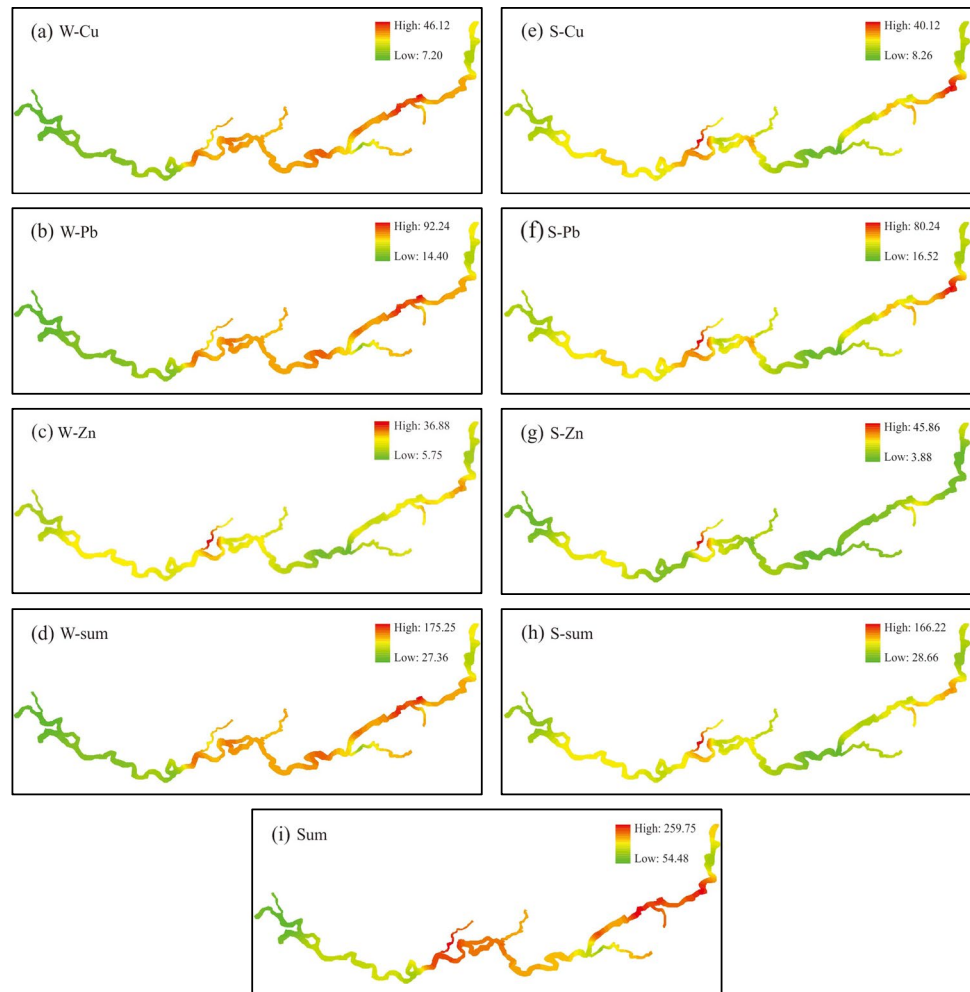
Prediction of potential ecological risk of heavy metals based on DOM structural characteristics

DOM, an important coordination and adsorption carrier in the aquatic environment, can undergo ion exchange and complexation with metals, affecting the migration and transformation, bioavailability, and ultimate fate of heavy metals (Shi 2013). Previous studies have shown that DOM can decrease the content of free metal ions in water environments by combining with heavy metals through complexations, which can reduce the potential biological toxicity of metals to aquatic organisms (Li et al. 2020a; Sánchez-Marín and Beiras 2012). In this research, three heavy metals (Cu, Pb, Zn) with severe contamination were selected. The contamination of these heavy metals is attributable to mining and smelting activities of Dexing Copper Mine and Yinshan Lead–Zinc Mine upstream of the Le'an River. In order to quantitatively characterize the ability of metal binding to DOM, the modified Stern–Volmer equation is usually adopted to determine the complexation parameters between heavy metals and PARAFAC-derived components (Ren et al. 2020; Xu et al. 2013). The combining capacity between the humic-like component and heavy metals follows the order of $Cu > Pb > Zn$ (Huang et al., 2018; Tipping et al. 2011; Xu et al. 2013). Furthermore, the $\log K_M$ value

of complexes of humic-like acid and heavy metals (Cu, Pb, Zn) is higher than that of fulvic acid and heavy metals (Cu, Pb, Zn) (Tipping et al. 2011). Moreover, the relatively long excitation and emission peaks reveal the larger molecular weight of the DOM component (Li et al. 2020c). Xu et al. (2019) found that humic-/fulvic-like components with high molecular weight exhibited higher metal combining potential than their low molecular weight counterparts. Thus, component S-C1 has a higher metal-binding potential than S-C2.

Taking the above factors into consideration, the analytic hierarchy process (AHP) method was applied to calculate the weight of the combining affinities between DOM components and heavy metals (see [supplementary materials](#) for details). The potential ecological risk values of heavy metals in surface water and sediments were calculated (Table 2). For example, the comprehensive ecological risk value of surface water (W-sum) ranging from 27.36 to 175.25 (average of 102.34) is higher than that of sediments, ranging from 28.66 to 166.23 (average of 85.20). Furthermore, the inverse distance weight (IDW) was applied to display the potential ecological risk of heavy metals based on the structural characteristics of DOM in space (Fig. 6). In both surface water and sediments, compared with other metals, the ecological risk of Pb was more serious, and it was higher in the midstream. Accordingly, the degree of ecological risk for individual heavy metals was considerably different at different

Fig. 6 Ecological risk interpolation maps of heavy metals based on the characteristics of DOM at different levels of sampling sites in the Le'an River Basin (**a–d** surface water, **e–h** sediments, **i** surface water and sediments)



sites, but the distribution of high-risk areas was similar between surface water to sediment sampling sites. The grade of comprehensive ecological risk of all heavy metals in surface water and sediments was similar to that of each heavy metal. Further, comprehensively considering the ecological risk value of heavy metals in surface water and sediments, the results indicated that high-risk regions are mainly located in the upper and middle reaches of the river, and the risk is the lowest in downstream areas, fully reflecting the ecological risk status of heavy metals in the Le'an River Basin. This is consistent with the conclusion of in situ sampling to assess the ecological risk of heavy metals. Thus, it is of great practical significance to evaluate the influence of the structural characteristics of DOM on the ecological risk of heavy metals.

These results implied that the characteristics of DOM such as the concentration and components played an important role in the process of migration and transformation of heavy metals. Sites with higher DOM content in sediments showed a lower ecological risk of heavy metals than those

with higher DOM content in surface water. This can be explained by DOM combining with a large amount of heavy metals through complexation. Therefore, in the management of heavy metal pollution in the Le'an River Basin, the water composition should also be taken into consideration in addition to controlling pollution sources.

Levels and potential ecological risk of heavy metals based on measured concentration data

Figure 7 shows the spatial distribution of heavy metal concentrations in surface water and sediments of the Le'an River. In surface water, the levels of Cu, Pb, and Zn appear to increase from the source to downstream, which may be because many tributaries merge into the main stream towards the downstream. These tributaries are affected by anthropogenic activities associated with dense population and developed urban industry. The content of heavy metals in surface water did not exceed the concentration limits of the environmental quality standards for surface water. In

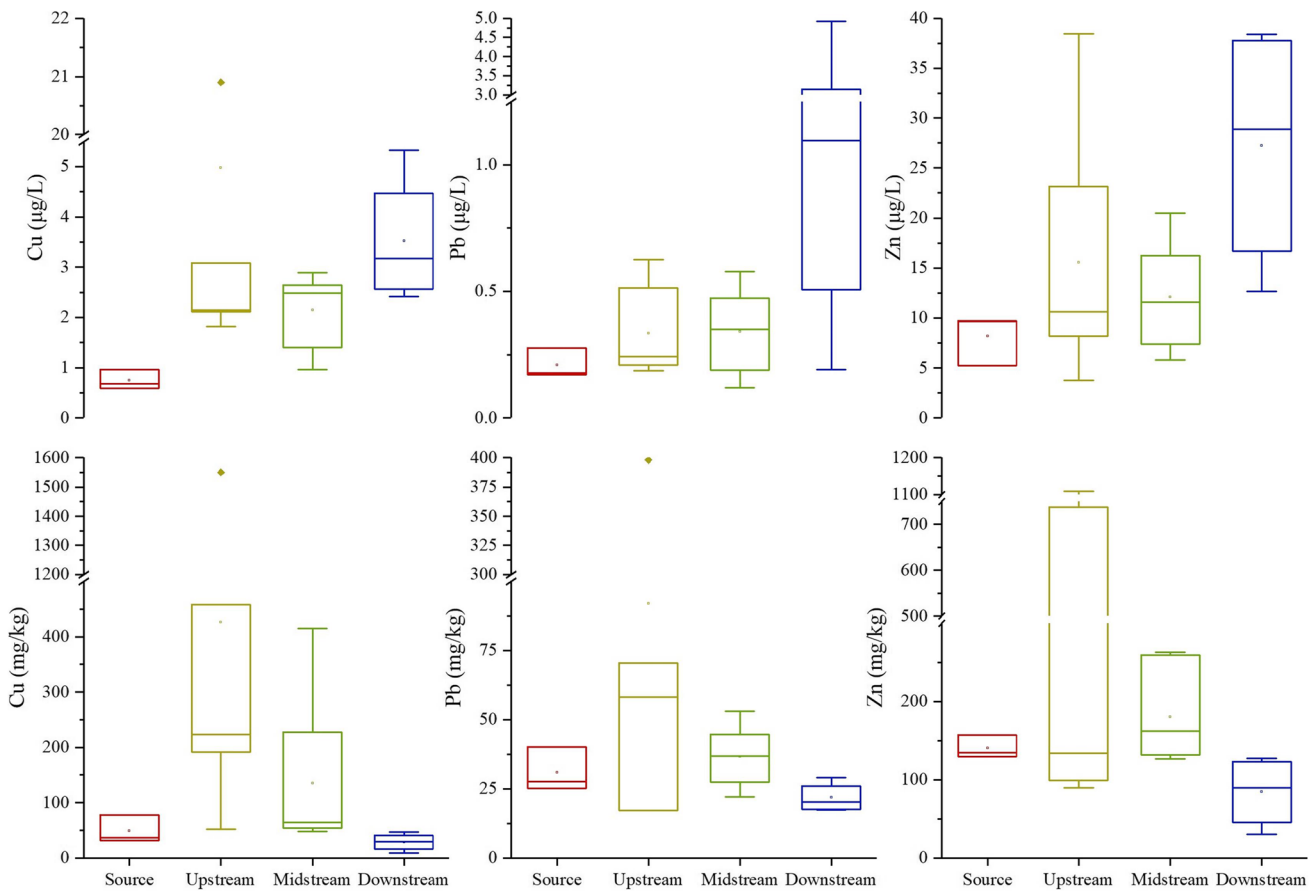


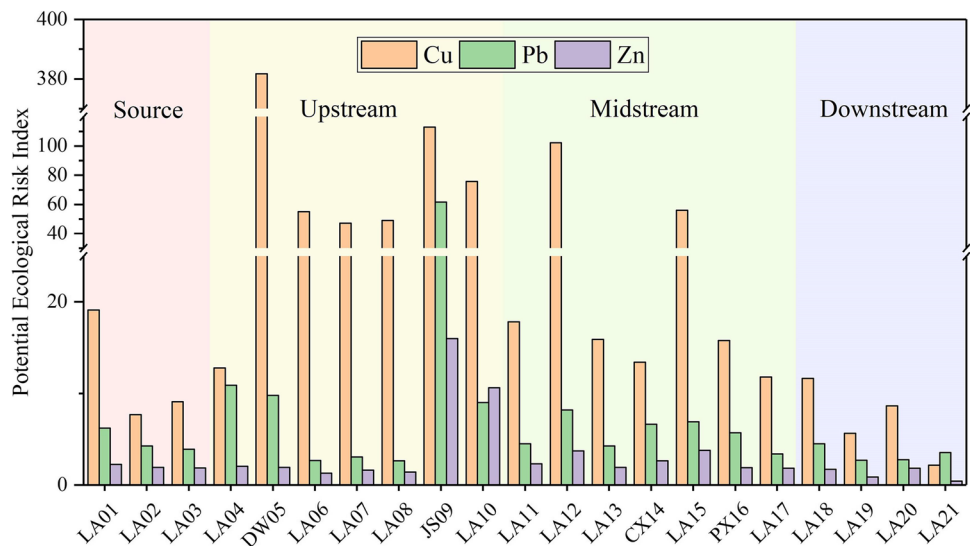
Fig. 7 Levels of heavy metals in surface water and sediments of the Le'an River

contrast, the highest levels of heavy metals were recorded in upstream sediments, which can be attributed to the mining industry in Dexing City. Sampling sites DW05 and JS09, which are directly affected by the mining and smelting activities of Dexing Copper Mine and Yinshan Lead-Zinc Mine,

showed the highest content of heavy metals, which can also explain the higher contents of heavy metals in the upstream and midstream sediments given their proximity to the mines.

The ecological risk index was applied to evaluate the degree of heavy metal pollution in the sediments of the

Fig. 8 Potential ecological risk of heavy metals based on in situ data of sediments of the Le'an River



Le'an River. As shown in Fig. 8, Cu posed a higher ecological risk than other heavy metals. It posed a moderate risk in the upstream, with very high and considerable risk levels at DW05 and JS09, respectively. The ecological risk of heavy metals in the Le'an River was significantly high at the confluence with the Dawu River and Jishui River. In general, the three heavy metals showed higher risk levels in the middle and upper reaches of the Le'an River. Nevertheless, Pb and Zn exhibited a low risk level throughout the Le'an River. The observation of upstream and midstream areas facing a higher potential ecological risk of heavy metals agrees with the result of risk assessment of heavy metal content in previous studies (Chen et al. 2016; Yu et al. 2020). Furthermore, this is in general accord with the assessment result of the potential ecological risk of heavy metals based on the structural characteristics of DOM. The method established in this study achieved more accurate and comprehensive evaluation of the ecological release risk of heavy metals compared to existing methods. The proposed method has important practical significance for river heavy metal risk management and control.

Conclusion

In this study, the content, components, and structural characteristics of DOM in surface water and sediments of the Le'an River were investigated using UV–vis and 3D-EEM. Furthermore, the potential risk of heavy metal release was evaluated on the basis of the structural characteristics of DOM and in situ sampling data. The following main conclusions can be drawn: (i) The DOC content was lower in surface water than in sediments, and the DOM in sediments had more aromatic and hydrophobic substances than that in surface water. (ii) DOM components in surface water and sediments were all humus substances, humic-like acid (W-C1), visible fulvic-like acid (W-C2 and S-C1), and UV fulvic-like acid (S-C2). Moreover, surface water DOM was mainly from autochthonous sources, while sediment DOM was controlled by autochthonous and allochthonous sources. (iii) Surface water has a higher potential ecological risk of heavy metals than sediments. Considering the comprehensive values of surface water and sediments, areas of high risk are mainly located in the upper and middle reaches of the river, attributable to the developed mining and smelting industries. Areas of the lowest risk are located downstream. This spatial distribution of ecological release risk of heavy metals is basically consistent with the risk evaluated using in situ sampling data. This study presents the spatial distribution of the risk of heavy metals in the Le'an River and established an ecological risk assessment system for heavy metals based on DOM, which are of significance for risk management.

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Data availability All data and materials support the published claims and comply with field standards.

Declarations

Ethics approval and consent to participate All authors have read and agreed to the published version of the manuscript.

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Competing interests The authors declare no competing interests.

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