

Role of humic substances as refractory organic matter in sustainable water quality assessment and management

Maoqing Duan, Xia Du, Wenqi Peng, Cuiling Jiang and Shijie Zhang

ABSTRACT

In northern China, river water originating from or flowing through forests often contains large amounts of oxygen-consuming organic substances, mainly humic substances. These substances are stable and not easily biodegradable, resulting in very high detection values of chemical oxygen demand. However, under natural conditions, the dissolved oxygen demand is not as high. Using experimental values to evaluate river water quality and the impact of human activities on water quality is thus unscientific and does not meet national development goals. In this study, the potential sources of high-concentration chemical oxygen demand in river water in two areas exposed to virtually no anthropogenic activities and strongly affected by humic substances, were analysed. The chemical oxygen demand contributed by humic substances (COD-HSs) was quantified using three methods. The results of water quality monitoring in 2017 and 2018 revealed that the chemical oxygen demand concentrations (5–44 mg/L) predominantly exceeded the standard (15 mg/L). The study results suggest that COD-HSs should be considered separately for objective evaluation and management of water quality, particularly in areas that are seriously affected by COD-HSs, to provide a scientific basis for formulating sustainable water quality management policies.

Key words | chemical oxygen demand, humic substances, surface water quality, sustainable water quality, water quality management

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INTRODUCTION

Oxygen-consuming organic substances in natural rivers mainly comprise humic substances (HSs). The two primary sources of HSs in surface water flowing through forestland, in particular, can be characterised as endogenous and exogenous. Endogenous inputs mainly constitute primary and secondary plant litter, phytoplankton, and benthos, whereas exogenous inputs comprise mostly the process of recharge through external water sources, such as runoff, groundwater, and tides, which bring in granular and dissolved humus (Wada *et al.* 2015; Johnson *et al.* 2018). In rivers seriously polluted by human activities, oxygen-consuming organic substances mainly include proteins, lipids, and sugars.

HSs are high-molecular-weight (300–30,000 Da) compounds that can be divided into three types according to

their dissolution properties: fulvic acids (FAs), which are soluble in acidic and alkaline solutions; humic acids (HAs), soluble in alkaline but insoluble in acidic solutions; and humins, insoluble in both acidic and alkaline solutions (Helles 2010). Research on HSs has mainly focused on soil because of their effect on its physical and chemical properties, such as fertility, permeability, adsorption, and complexation with heavy metals, organic compounds, and other pollutants (Anna *et al.* 2017; Hayes & Swift 2017). Although there are some studies on aquatic humus, its removal and separation from water or its functional group spectral characteristics, few studies on its concentration detection and oxygen-consumption capacity have been conducted because it has no fixed molecular structure (Palomeque & Ortiz 2013). Aquatic HSs mainly originate

from the decomposition of terrestrial and aquatic organisms (Palomeque & Ortiz 2013). Because of their complex structure and undetermined molecular weight, HS content in water is relatively lower than that in soil, and detection methods are limited, even though aquatic HSs have been recognised since the 1970s (Ghassemi & Christman 1968; Palomeque & Ortiz 2013).

Chen *et al.* (2003, 2004a, 2004b) have repeatedly discussed whether the chemical oxygen demand (COD) value in the Yellow River truly reflects the degree of water pollution, and the authors considered that most of the organic matter in sediments are natural HSs that are rather stable. Most rivers in Heilongjiang Province, China, originate from or flow through forestland in mountainous areas. The recharge of river water through runoff brings a large amount of HSs into the river channels, which is structurally stable and not easily degradable (Kästner & Hofrichter 2005; Fisher 2015). However, in water quality management and evaluation, a high concentration of COD was measured in laboratory experiments and the evaluation results did not accurately represent the water pollution. In China, with increasingly stringent water resources management policies, less objective evaluations reflect the imperfections in the water quality management system.

To correctly reflect the status of water pollution by COD value, it is necessary to quantify the COD contributed by HSs (COD-HSs). However, there is no universally accepted method to detect the concentration of HSs in water. Moreover, HSs formed in different regions have different oxygen-consumption capacity (corresponding COD value) due to their different functional groups. Therefore, we reference the methods recommended by the International Humic Substances Society (HISS) for the separation, extraction, and removal of HSs from water, as well as the spectral characteristics of HSs, to study the background value of COD supplied by HSs. The aims of this study were as follows. (1) To analyse the primary sources of oxygen-consuming organic substances in surface water in different periods under natural conditions in order to clarify the process and mechanism of surface water pollution. (2) To establish that the background value of COD can be expressed by determining the oxygen-consumption capacity of HSs in water. The methods include extracting, separating, and removing HSs from water, and establishing

the relationship between the absorption characteristics of HS and its oxygen-consumption characteristics. The anti-interference ability of these methods is also analysed. (3) To evaluate the surface water quality considering the COD-HSs, calculated via three methods using water from relatively undisturbed river sources. The proposed method can provide a scientific basis for water quality evaluation and aid in the formulation of sustainable water quality management policies.

MATERIALS AND METHODS

Sampling

The river source water reserve is defined according to the standard for water function zoning (GB/T 50594-2010). In areas specified for water function zoning, water quality standards are high and human activities do not have a significant impact on water quality. A total of 20 samples of water, ice, snow, soil, and litter were collected to study the possible sources of COD background values (Table 1). The sampling area comprised the Kamalan River, the largest tributary of the river source reserves of the Huma River, and Nanweng River in Heilongjiang Province, China (Figure 1). Samples were collected in March (dry season), May (spring flood season), and August (rain season) 2018.

The land in the study area is mainly woodland with a little grassland and farmland, the proportions of woodland, grassland and farmland are 87.8%, 3.91% and 0.56% in Huma and 88.6%, 5.6% and 3.7% in Nanweng, respectively. The COD of eight sampling sites (B1–B8) was monitored monthly in the Huma and Nanweng Rivers from November to December 2017 and from March to August 2018 (Figure 1). Fifty three monitoring data of COD were measured; the COD background values of only 42 monitoring data elements out of the 53 measurements were used because there is little addition to the background COD level in Huma River during the dry season.

Experiments

The standard samples of HA and FA were purchased from the Guangfu Precise Chemical Industry Institute in Tianjin,

Table 1 | Samples and sampling areas in the Huma and Nanweng river source reserves, Heilongjiang, China

Reserve	Sampling	Latitude	Longitude	Notes
Huma River Source Reserve	H _{1a}	52°4'23.81"	123°29'41.09"	H _{ij} and S _{ij} – H means Huma River Source Reserve, N means Nanweng River Source Reserve, i means sampling site, j means sampling types (a: Surface water in river, b: Water in river bottom, c: Rain through the canopy, d: Ice in river, e: Snow under the canopy, f: snow in a non-forested area, g: Litter soaked in distilled water, h: Soil humus layer, i: Soil rock base)
	H _{1d}	52°4'23.81"	123°29'41.09"	
	H _{1e}	52°4'9.11"	123°29'39.82"	
	H _{1f}	52°4'9.70"	123°29'40.15"	
	H _{1g}	52°4'9.11"	123°29'39.82"	
	H _{1i}	52°4'9.11"	123°29'39.82"	
	H _{1h}	52°4'9.11"	123°29'39.82"	
	H _{2c}	52°4'18.71"	123°29'0.74"	
	H _{2d}	52°4'18.71"	123°29'0.74"	
	H _{2f}	52°4'18.71"	123°29'0.74"	
	H _{3a}	52°0'58.09"	123°35'45.42"	
	H _{3b}	52°0'48.78"	123°36'3.88"	
	H _{3d}	52°0'45.4"	123°36'8.33"	
	Nanweng River Source Reserve	N _{1a}	50°54'55.32"	
N _{1d}		50°54'55.32"	124°44'24.72"	
N _{1h}		50°54'55.32"	124°44'24.72"	
N _{2a}		50°57'40.92"	124°46'7.15"	
N _{2b}		50°57'40.92"	124°46'7.15"	
N _{2d}		50°57'40.92"	124°46'7.15"	
N _{2i}		50°57'40.92"	124°46'7.15"	

China (HA1 and FA1), Hewu Biotechnology Company in Shanghai, China (HA2 and FA2), and Anpel Laboratory Technological Company in Shanghai, China (HA3 and FA3).

Index detection

The surface water samples were collected in acid-cleaned, 2 L plastic buckets that were rinsed with surface water; 1 kg of solid samples was collected and packed in sealed bags. Water samples (water, ice, snow, and litter leachate) were used for the determination of COD, permanganate index (COD_{Mn}), total organic carbon (TOC), 5-day biochemical oxygen demand (BOD₅), ammonia nitrogen (NH₃-N), total phosphorus (TP), total nitrogen (TN), and heavy metal (Fe, Mn); soil samples were used for the determination of soil organic matter (SOM), HA, FA, and humins. Litter leachate was obtained by blending litter from under forests and distilled water at a ratio of 1:2 (v/v) for 2 days. The details of the methods and instruments used for the water and soil chemistry analyses can be found in the environmental quality standards for water (GB3838-2002) and environmental quality standards for soil (GB15618-1995).

Isolation of HSs from water

Isolation and extraction of HSs from water were performed according to the methods proposed by the International Humic Substances Society (<http://humic-substances.org/>) and those recommended in previous studies (mixed solution extraction method (Chen *et al.* 2004b; Anna *et al.* 2017)). Water samples (500 mL) were dried in a water bath at 100 °C, and the solid residue was extracted with a 50 mL mixture of 0.1 mol/L sodium pyrophosphate solution mixed with 0.1 mol/L NaOH solution in a ratio of 1:1 (v/v). Filtration was carried out with qualitative filter paper; the filtrate was subsequently diluted to 500 mL in distilled water, and the COD value was determined.

Adsorption experiments

XAD-8 resin is usually used for the isolation of HSs, and this study employed the processing method described in previous studies (Kida *et al.* 2016; Zherebker *et al.* 2016). XAD-8 resin was repeatedly extracted in acetonitrile and ethanol until the COD value of the filtrate was below the detection limit (4 mg/L). After extraction, the pH of the sample was lowered to 2.0 with concentrated HCl and

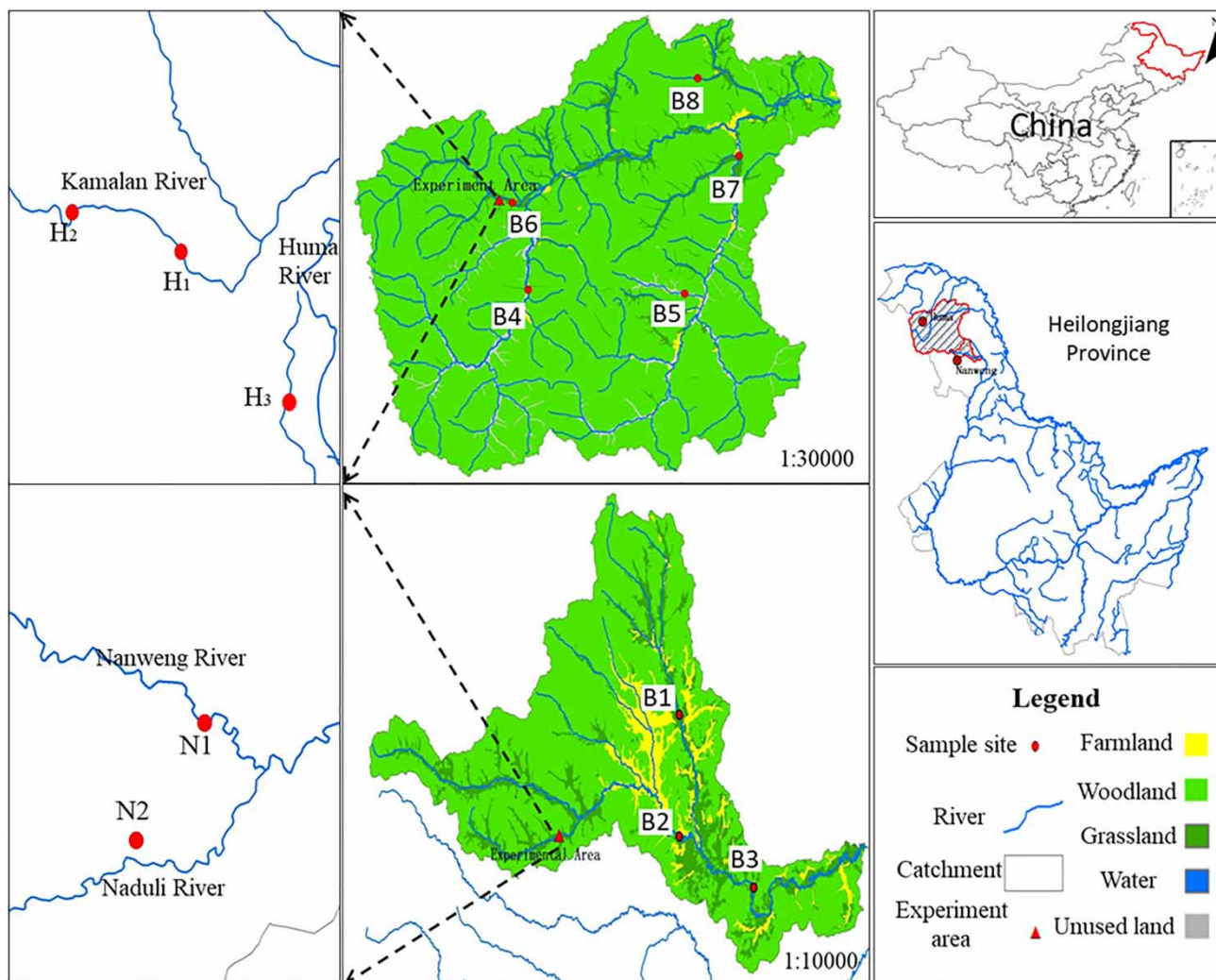


Figure 1 | Schematic diagram of the sampling areas and site locations in the Huma and Nanweng River Source Reserves, Heilongjiang, China.

pumped through a column of XAD-8 resin at 5 mL/min. The COD value of the filtrate was determined. During the process, the background value of COD was filtered out by resins; the background value of COD should be determined by subtracting the filtrate COD value from COD in the raw water sample's COD value.

Relationship between absorbance and COD

The HSs in water were isolated as described above, and the absorbance value was measured. The pH of the sample was lowered to 2.0 with concentrated HCl and filtered to separate HA and FA solutions. The absorbance values of HA and FA were measured at 315 and 250 nm, respectively. The

COD background values were obtained according to the regression equation between absorbance and COD.

Interference experiments

Other organic substances including proteins (bovine serum albumin (BSA)), lipids (nutrient agar) at known concentration and the corresponding COD concentration were added to HA/FA aqueous solutions with different concentrations to investigate the effect of other oxygen-consuming organic matter on the three methods. The sensitivity and applicability of the methods were judged by comparing the changes in COD concentration of the solution before and after adding other organic substances.

RESULTS AND DISCUSSION

Analysis of source of COD background values

In the dry season, the river is mainly recharged by groundwater. Because of the reduction in rainfall-runoff, litter and humus are slowly decomposed and accumulate in ice, snow, and soil, which are consequently the main carriers of humus (Ni *et al.* 2014). Analyses of COD of ice, snow, and soil organic matter content during the dry season indirectly reflect the cumulative effect of humus in different carriers and determine the main contributor of river humus during the snow- and ice-melting period driven by runoff.

Sampling data from March, May, and August showed that water, ice, snow, and rain were mainly acidic, and sample H_{1g} (litter leachate) had the lowest pH (4.57), followed by sample H_{2c} (rain), at 5.9. The litter layer was the main source of HSSs, and the leachate thus had the lowest pH. Sample H_{1g} had a high TOC concentration, followed by sample N_{2d}. This is related to the slow humification of litter in snow (Cleveland *et al.* 2004; Shibata *et al.* 2013; Ni *et al.* 2014). The TOC values of samples N_{1a}, N_{2a}, N_{2b}, N_{1d}, N_{2d}, H_{1e}, and H_{1g} exceeded 20 mg C/L. TOC directly reflects the content of oxygen-consuming organic matter in water. The snow samples showed that TOC varied between under the canopy (H_{1e}) and snow in empty (H_{1f}, H_{2f}). Forest canopy cover creates favourable storage conditions for organic matter in snow, which flows into rivers with snowmelt. Figure 2 shows that COD, COD_{Mn}, NH₃-N, TP, TN, Fe, Mn, and other substances were consistent with changes in organic matter. This indicates that the pollution sources are identical for different indicators in the river source reserve.

A comparison of all water samples (H_{1a}, H_{3a}, H_{3b}, N_{1a}, N_{2a}, and N_{2b}) collected from Huma and Nanweng Rivers is shown in Figure 2. The indexes in the Nanweng River were significantly higher than those in the Huma River; this was also found for ice samples (H_{1d}, H_{2d}, H_{3d}, N_{1d}, and N_{2d}). The observed differences are attributable to different hydrodynamic processes related to the different characteristics (Laudon *et al.* 2004). The rainfall-runoff and melting snow flow erode the underlying surface and directly transfer from basin to river in the Huma River. However, Nanweng

River is a wetland river, rainfall or snowmelt accumulates easily on surface depressions, so as to have a lasting soaking effect on litter, during which the litter layer immersed in water influences the accumulation of oxygen-consuming organic matter with high concentration of COD and it can be washed into the river until the next runoff. Because of this difference, there are great differences in the values of each index between all samples from the different sampling areas. The samples similar to those from the Nanweng River Source Reserve provide more oxygen-consuming organic pollutants to the river in the wet season.

Relationship between HSSs and COD

Mixed solution extraction method

According to the mixed solution extraction method, the HS concentration in the filtrate was taken as the COD background value. The COD in the filtrate was determined as the COD background value in surface water. This method did not require the separation of humus from HA and FA to achieve this aim.

Table 2 summarises the extraction effect of the mixed solution on different samples. Component 1 was a mixture of HA and FA prepared with the standard sample. This component indicated that there were no significant changes in the COD value of HSSs before and after extraction of the mixed extract, showing that the extraction efficiency was high. Component 2 was a result of selection of six random samples (industrial waste, domestic sewage, urban river 1, urban river 2, urban river 3, and urban river 4). These six samples contained not only humus but also other organic substances from human activities. These types of organic pollutants in water are more complex. COD values before and after extraction showed that the extract had selectivity for organic substances. Component 3 comprised two water samples from the Kamalan and Nanweng Rivers where there was no human disturbance. Organic matter in the water originated from terrestrial organic matter (HSSs). There were no significant changes in the COD value of HSSs before and after extraction.

The effect of other oxygen-consuming organic matter on mixed solution extraction was determined (Table 3). The

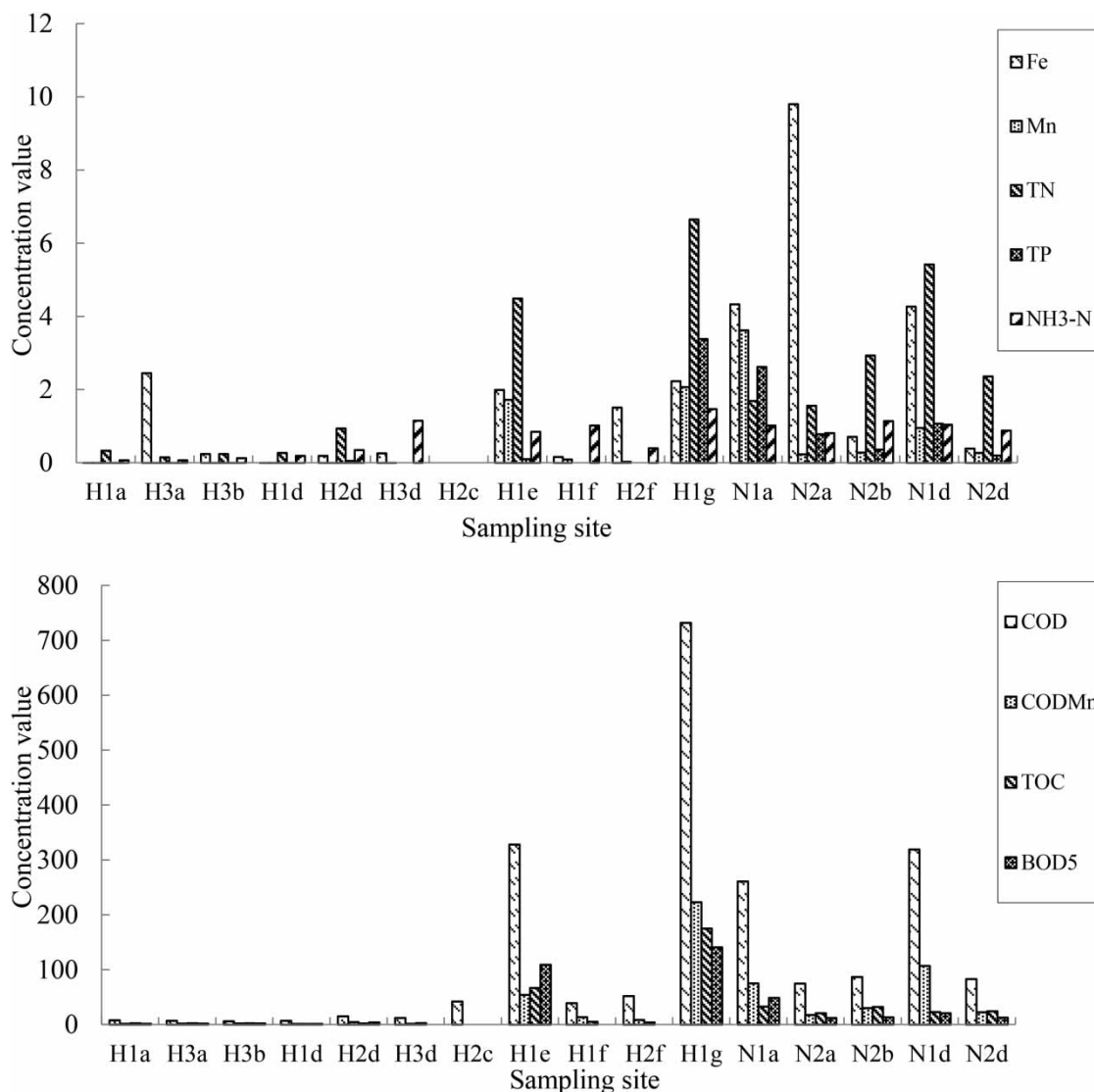


Figure 2 | Value of each indicator in the sampling sites; TOC (mgC/L): total organic carbon; COD (mg/L): chemical oxygen demand; COD_{Mn} (mg/L): Permanganate index; BOD₅ (mgO/L): biochemical oxygen demand; TN (mg/L): total nitrogen; TP (mg/L): total phosphorus; NH₃-N (mgN/L): ammonia nitrogen; Fe (mg/L); Mn (mg/L). Only COD was detected in H_{2c}.

high concentration of interfering organic substances caused a significant decrease in the selective extraction effect of mixed extracts. Under certain conditions, mixed extracts had higher extraction efficiency not only for HSs but also for other organic substances. However, this effect was less than that of the extraction of HSs (Bao *et al.* 2018).

The standard sample experiment shows that the oxygen consumption of HSs did not change after the extraction (Table 3). The organic matter interference test was carried out with a high concentration of proteins, lipids, and glucose in the extraction process. The results show that the extract

did not affect the oxygen consumption of HSs. Although the extract had an extraction effect on high-concentration organic interferents, it was significantly lower than the extraction efficiency of HSs.

XAD-8 resin adsorption method

XAD-8 macroporous resin can effectively adsorb HSs, and the filtrate obtained contained little or no HSs. The COD value of the filtrate was measured and was subtracted from the COD value of the raw water sample, which is the

Table 2 | Extraction effect of mixed solution on different samples; COD: chemical oxygen demand

Component	Sample	After extraction (mg/L)		Before extraction (mg/L) COD	Remarks
		COD1	COD2		
1	Mixed extract	2.9	1.1	/	Improved extraction efficiency for humic substances; H20: concentration of HA is 20 mg/L in solution; F40: concentration of FA is 40 mg/L in solution.
	H20 + F40	30.9	26.6	28.6	
	H70 + F10	26.5	22.2	25.9	
	F15 + H60	20.5	22.2	25.9	
	H10 + F70	48.4	39.9	43.2	
2	Industrial waste	14.6	17.7	51.8	HSs makes up part of organic matter in surface water; Industrial waste and domestic sewage from Zhongfei water quality monitoring company; Urban river from water environment monitoring centre in Beijing, 1-Yongding river, 2-Chao river, 3-Beiyun river, 4-Xun river.
	Domestic sewage	32.5	/	103.5	
	Urban river 1	23.7	18.6	41.2	
	Urban river 2	22.2	27.8	70.3	
	Urban river 3	26.6	24.9	51.6	
3	Urban river 4	11.6	16.7	21.8	Most of the organic matter in surface water was humus.
	Kamalan	19.74	/	22.18	
	Nanweng	51.58	/	54.72	

Notes: COD1 and COD2 mean repetitive detection result of filtrate after extraction; HA, humic acid; FA, fulvic acid.

Table 3 | Effect of non-humic substances on extraction experiment; F50/H50: concentration of FA or HA is 50 mg/L in solution

Pre-treatment	Sample	After extraction (mg/L)	Before extraction (mg/L)
Extraction after evaporation	Nanweng + 100 mg/L protein	73.5	105.3
	Kamalan + F50	59.2	61.2
	100 mg/L protein	24.7	61.7
	100 mg/L nutritive agar	25.8	48.8
	100 mg/L glucose	36.9	79.9
	100 mg/L nutritive agar + F50	73.9	98.5
	100 mg/L glucose + H50	69.8	106.5

COD background value of surface water. Table 4 shows that XAD-8 resin had a strong adsorption effect on HSs. The removal rate of HSs from the filtrate was more than 70%. Similarly, XAD-8 resin can adsorb interfering organic substances (proteins and lipids), and the removal efficiency was 30–40%. However, the adsorption efficiency is obviously lower than that of HSs, and the COD in the water sample of Kamalan and Nanweng Rivers decreased after adsorption by resin. Therefore, this method reflects

Table 4 | XAD-8 resin adsorption experiment; samples were filtered by XAD-8 resin; F50/H50: concentration of FA or HA is 50 mg/L in solution

Sample	After filtering (COD mg/L)	Before filtering (COD mg/L)	Removal efficiency (%)
H20 + F40	8.4	28.6	70.6
H70 + F10	7.4	25.9	71.4
F15 + H60	3.7	25.9	85.7
H10 + F70	10.4	43.2	75.9
100 mg/L nutritive agar	34.4	48.8	29.5
100 mg/L protein	52.2	79.9	34.6
F50 + 100 mg/L nutritive agar	16.3	91.7	82.2
H50 + 100 mg/L protein	45.8	139	67.1
Kamalan	3.4	21.07	88.8
Nanweng	8.9	52.1	82.9

the COD background concentration of surface water to a certain extent.

Absorbance method

The UV–vis absorbance spectral parameters were applied to the study of HSs (Pospíšilová *et al.* 2015). The full scan in the UV–vis region revealed that there was no correlation between the HS standard sample concentrations from

different sources and absorbance of the same HS concentration (FA and HA) standard samples from three companies. However, there was a positive correlation between the absorbance and COD value. Five concentration gradients (15, 30, 50, 60, and 80 mg/L) were set for FA (FA1, FA2, FA3) and HA (HA1, HA2, HA3) and the corresponding COD concentration was tested. Twenty-seven correlation curves were established at intervals of 5 nm in the wavelength range of 220–350 nm. The highest correlation coefficient was 0.961 at 250 nm, and those of the other 26 curves ranged from 0.69 to 0.99. Therefore, there was a high correlation between the absorbance of FA and COD at specific wavelengths. Similarly, the highest correlation (0.9902) between HA and COD was at 315 nm (Figure 3).

HA and FA were effectively separated by adjusting the pH. The respective liquids were subsequently used to calculate the COD background value under the optimum COD wavelength according to the relationship curve. The mixed extract had extraction efficiency for proteins, lipids, and sugar. To explore the interference degree of other organic substances on the absorbance of HSs, FA was used as an example. This interference experiment showed that the interference of other organic substances on the absorbance of FA at 250 nm does not cause an obvious deviation in the calculated value of COD, which was acceptable to some extent (Table 5). Therefore, the influence of other

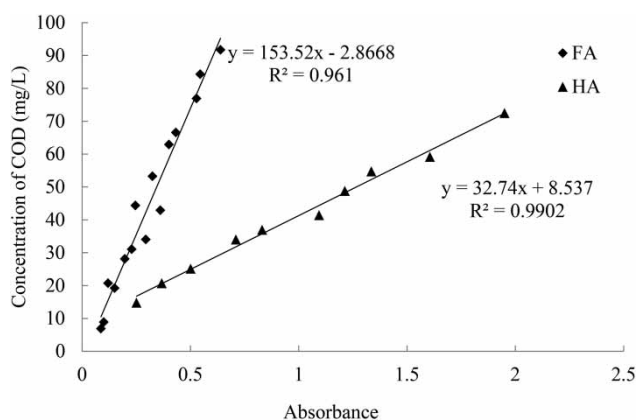


Figure 3 | Relationship between fulvic acid (FA) and humic acid (HA) absorbance and COD at specific wavelengths; the correlation curve between COD concentration and absorbance of FA was established at 250 nm. The correlation curve between COD concentration and absorbance of HA was established at 315 nm.

Table 5 | XAD-8 resin adsorption experiment on the COD of fulvic acid (FA); F15, F30, F50, etc.: concentration of FA is 15, 30, 50, etc., mg/L in solution

Sample	COD (mg/L) detection value		COD (mg/L) calculated value		COD (mg/L) interference value	
	FA1	FA2	FA1	FA2	FA1	FA2
F15	20.7	6.9	17.4	9.5		
F15 + Protein 50 mg/L					16.4	9.5
F30	44.3	19.2	41.2	17.7		
F30 + Protein 80 mg/L					37.9	19.2
F50	62.9	31.05	60.1	27.4		
F50 + Glucose 50 mg/L					59.1	32.7
F65	76.9	34.01	78.4	35.3		
F65 + Agar 50 mg/L					74.1	41.7
F80	91.6	42.8	95.7	43.5		
F80 + Agar 80 mg/L					92.4	46.4

Calculated value: according to the absorbance in the relationship curve at 250 nm.

Interference value: according to the absorbance in the relationship curve at 250 nm after interfering substances were added.

FA1 and FA2 are solutions prepared with standard samples of FA purchased from the Guangfu Precise Chemical Industry Institute and Hewu Biotechnology Company in Shanghai, China.

organic substances on the relationship between HS absorbance and COD is not significant.

Application

The contribution of different sources to the COD background value in the Huma and Nanweng Rivers during the wet and dry seasons has been discussed. Leaching from the litter layer was the main source of organic matter in river water, and snowmelt and rainfall runoff were the main driving forces for land-based organic matter entering the river (Zhrebker et al. 2016). Results showed that the surface water quality of the Huma River was not affected by the COD-HSs in the dry season, but the COD value of the water increased due to non-human pollution in the wet season under the influence of rainfall-runoff and snowmelt. Because of the characteristics of stagnant water in the Nanweng River Wetland Reserve, HSs accumulated in the water during the dry season. Therefore, the COD-HSs was considered only in the wet season for the Huma River and in both seasons for the Nanweng River.

Monitoring data

The monitoring data for COD were collected from November to December 2017 and from March to August 2018; only 32.1% of them met the water quality standard (COD < =15 mg/L) with a range of 5–44 mg/L. This shows that the degree of COD exceeding the standard in the wet season is serious in both rivers (Figure 4), but the degree of B4 exceeding the standard is small. In the dry season, the water quality of the Huma River is better than that of the Nanweng River because of the different formation mechanisms of COD background values (Colina-Tejada *et al.* 2010). In contrast to previous research on background values (Rodríguez *et al.* 2016; Reimann & Caritat 2017), the methods in this study focused on the formation mechanisms of the background values, and the determination method did not involve statistics for monitoring results (Juchen *et al.* 2014; Gałuszka *et al.* 2016). The surface water COD value during the study period was evaluated according to environmental quality standards for surface water (GB3838-2002) for the study area.

Assessment of water quality considering COD background values

The COD background values of 42 monitoring data elements from all 53 measurements were measured according to three methods (Figure 5); the influence of COD background values was neglected in the Huma River during the dry season, for reasons stated above. The results showed that the background values obtained by the mixed

solution extraction and XAD-8 resin adsorption methods were similar. The background values calculated by the absorbance method, using the relationship between HS absorbance and COD, were greater than those calculated by the first two methods. This may be due to the low concentrations of HSs in surface water. The corresponding absorbance values were also higher than those calculated by the extraction and XAD-8 resin adsorption methods. However, the relationship between HS absorbance and COD concentration was neglected in the range of low-concentration HSs, which rendered the relationship curve less precise in the range of low concentration. Therefore, the deviation from the actual COD background value is larger when the HS concentration is low (in the case of low absorbance values).

Zoback (2001) pointed out that changes in natural systems cannot be understood if the environmental background values are not understood. Therefore, elucidating regional environmental background values is essential for successful environmental assessment and legislation (Fukue *et al.* 2006). Figure 6 shows the degree of pollution after considering the COD background values for B1–B8. The water quality at each monitoring site was relatively good according to the COD background values calculated with the three methods and were not significantly different. The assessment of the degree of HS pollution considered the impact of the natural environment on water quality. By deducting natural environmental factors, water quality assessment can more accurately reflect the impact of human activities on water quality in the study area. The three abovementioned methods aimed to determine the

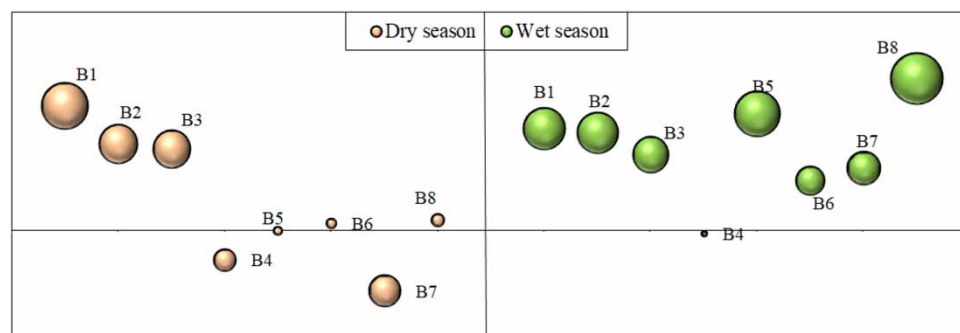


Figure 4 | Diagram of COD in the monitoring sites over the study period (above the horizontal ordinate, the bigger the circle and higher the position, the greater the degree of water pollution; below the horizontal ordinate, the bigger the circle and lower the position, the better the water quality is throughout the year).

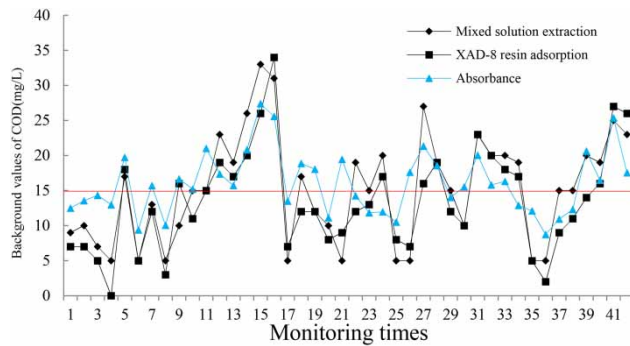


Figure 5 | COD background values calculated with the three methods; the red line represents the permissible maximum value of COD in the study area.

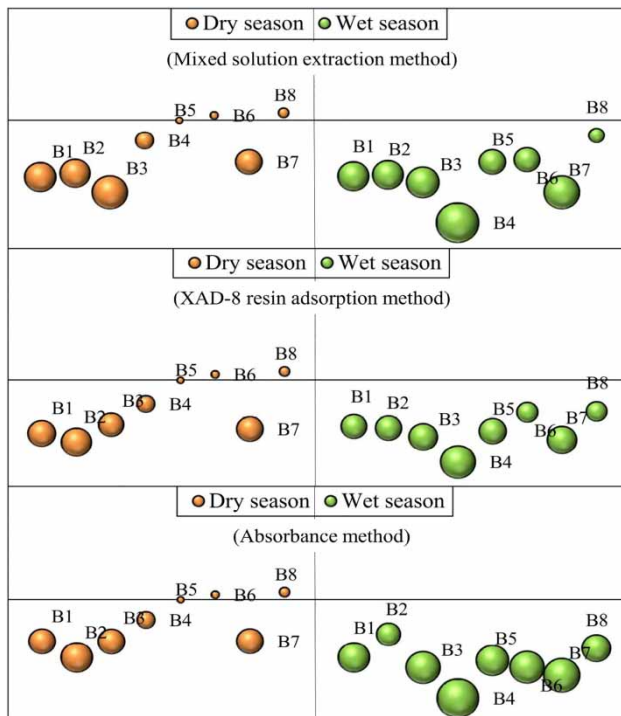


Figure 6 | Excess COD in monitoring sites after deducting background value (above the horizontal ordinate, the bigger the circle and higher the position, the greater the degree of water pollution; below the horizontal ordinate, the bigger the circle and lower the position, the better the water quality is throughout the year).

COD background value as influenced by HSs. Although the three methods had some shortcomings, they reflected the impact of background pollutants on water quality to a certain extent as well as providing a basis for effective scientific evaluation of water quality.

CONCLUSIONS

HSs, as a type of refractory oxygen-consuming organic matter, is input into the rivers via snowmelt and rainfall. It does not consume dissolved oxygen in water under natural conditions. Under strong oxidation conditions (in the laboratory), high COD concentrations in river water were detected and the evaluation results of water quality under natural conditions was found to be poor. This phenomenon is not conducive to the formulation of regional sustainable development plans in water resources management and economic development. Our study suggests that HSs should be considered separately for evaluating oxygen-consuming organic matter in water because it is different from other compounds that are easily degradable in water. In this paper, rivers in typical areas (Huma and Nanweng River Source Reserves) with high concentrations of COD-HSs that are considered as potential sources of COD-HSs in rivers (rain, snow, ice, and, litter leachate) were analysed. Litter leachate was the main contributor to river COD, and snow in winter was also an important carrier of background pollutant accumulation.

Three methods were used for the quantification of the COD-HSs based on separation, extraction, and removal of HSs in water, as well as the spectral characteristics, namely, mixed solution extraction, XAD-8 resin adsorption, and absorbance methods. Three standard HS samples were used to test the methods and interference tests were carried out on the three methods. The results reflected that the three methods for determining COD-HSs have a certain degree of reliability. Taking the Huma and Nanweng Rivers, the natural environment in the study area is better and human activities are fewer. However, the pollution degree of COD (5–44 mg/L) was much higher than the water quality standard (≤ 15 mg/L) of the study area. The COD-HSs in each sample are determined by three methods. The results show that the COD-HSs obtained with the three methods are close to each other. After considering the COD-HSs values, the water quality is evaluated. The results show that the water quality in the study area was good and not affected by pollution; the evaluation results are objective and fair. Therefore, this study suggests that regions with high COD-HSs should be objectively evaluated for the

assessment of water quality. Furthermore, this study provides a scientific basis for sustainable management of regional water quality and guide water pollution control, so as to guarantee the water environment and maximise the development of the regional economy.

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AUTHOR CONTRIBUTIONS

Supervision, W.P.; Formal analysis, X.D. and S.Z.; Resources, C.J.; Writing – original draft, M.D.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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