


RESEARCH

Open Access



# Second derivative UV–visible spectroscopy characterizing structural components of dissolved and particulate organic matter in an urbanized river

Weining Xu<sup>1,2</sup>, Huibin Yu<sup>2,3\*</sup>, Fang Yang<sup>2,3\*</sup> , Feng Yang<sup>2,3</sup>, Dongping Liu<sup>2,3</sup>, Koutian Lu<sup>2,3</sup>, Hongjie Gao<sup>2,3</sup> and Yonghui Song<sup>1,2</sup>

## Abstract

**Background:** Spatio-temporal variations of structural components of the POM–DOM fractions exhibit in urban rivers, which is valuable information to reveal dynamic migration and transformation within and between the organic matter pools, also provide important support for river water quality improvement and management measures. Second derivative UV–visible spectroscopy (SDUVS) was applied to simultaneously characterize structural components and spatial variations of dissolved (DOM: Diameter < 0.2 μm) and particulate (POM1: 0.2 < diameter < 0.7 μm; POM2: diameter > 0.7 μm) organic matters in an urbanized river of northeast China.

**Results:** Thirty-six water samples were collected from mainstream and tributaries along a human impact gradient, i.e., rural, town and urban regions. The DOM was a representative fraction for the natural organic matter pool, which was mostly derived from allochthonous and terrestrial sources. Four components C1 to C4 were identified from the POM–DOM fractions by the SDUVS. The C1 associated with phenolic groups and the C2 related to carboxylic groups were dominant for the organic matter pool. The C3 was composed of the primary humified materials, and the %C3 was kept relatively consistent in the organic matter pool. The C4 presented deeply humified organic matter with the increase of aromatic and alkyl structures. The average %C4 of the POM pool was higher than that of the DOM pool, indicating that the humification degree of the POM fractions was higher than that of the DOM fraction.

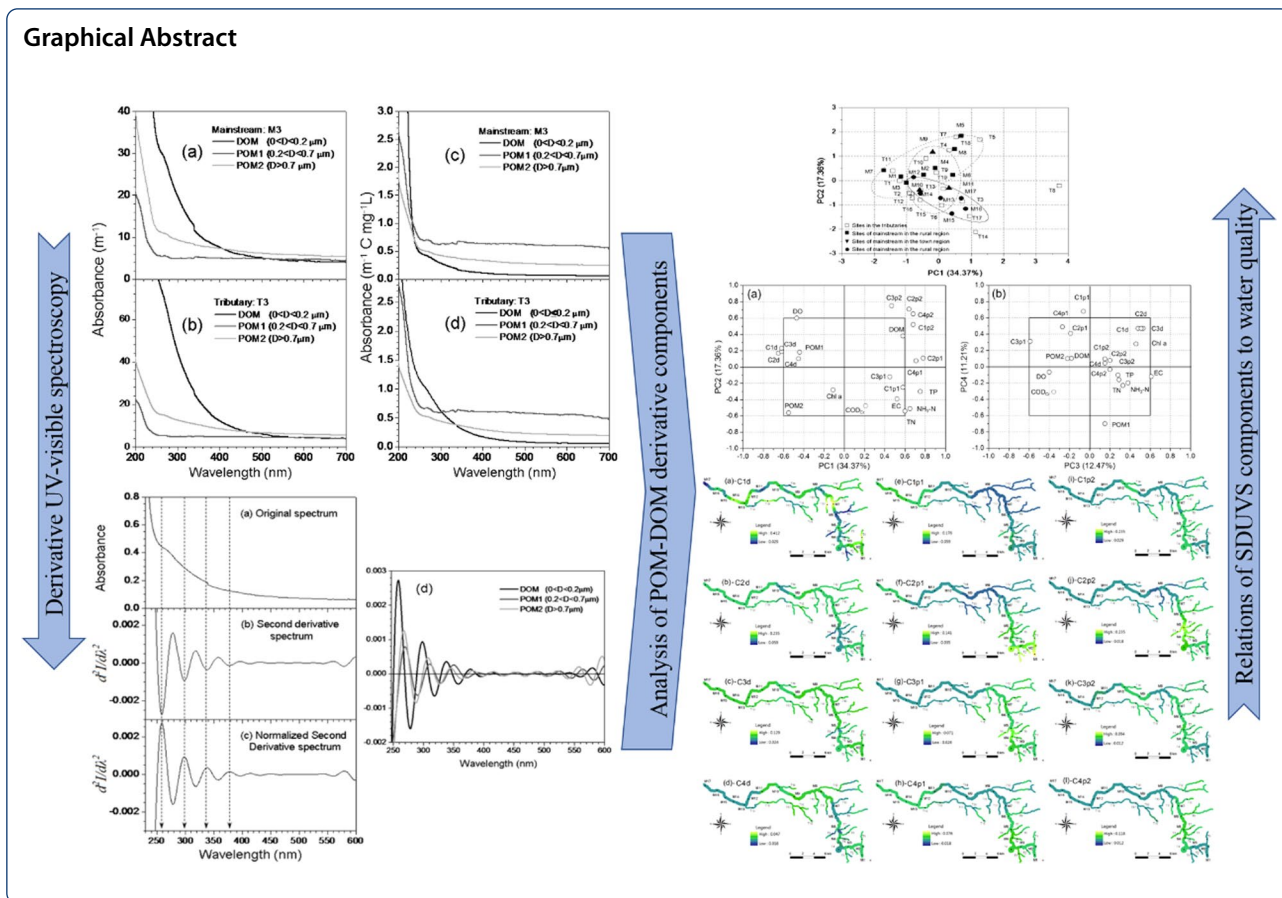
**Conclusions:** Moreover, the tributaries had a higher average %C4 within the DOM than the mainstream, and trends of the POM pool were similar to the DOM pool. The trophic level of the river water decreased in the order of urban region > town region > rural region, while the molecular sizes of the POM–DOM decreased in the order of rural region > town region > urban region.

**Keywords:** Second derivative, UV–visible spectroscopy, Dissolved organic matter, Particulate organic matter, Urbanized river

\*Correspondence: yhbybx@163.com; yang.fang@craes.org.cn

<sup>2</sup> State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

Full list of author information is available at the end of the article



**Introduction**

Urban rivers, as rivers or river sections that originate in or flow through urban areas, are more closely connected to humans than natural rivers [37]. Urban black-odor water bodies are usually formed by domestic sewage, industrial wastewater and other long-term pollution that causes serious pollution of urban rivers [5, 54]. The river DOM is both a source of mineral and organic nutrients for aquatic plants and an energy source for heterotrophic microorganisms, as well as an important component in the formation of organic matter in the aquatic environment [10]. Natural organic matter is an intricate entity with diverse functional groups and molecular sizes and usually occurs in pristine and engineered environmental systems [14, 21, 48]. It can affect species evolution, nutrient cycle and pollutant transport in the aquatic system [4, 24], which mainly responds to regional changes in land use [15, 18]. The natural organic matter pools can be generally divided into particulate (POM) and dissolved (DOM) organic matter by filtration [18, 43, 53]. The POM pool is dominated by fresher materials, whereas the DOM pool is composed of more degraded and recalcitrant

material [41, 63]. River sediments and POM provide sufficient carbon sources for algae, bacteria, etc. [61]. Structural components of the POM–DOM fractions exhibit conspicuously spatio-temporal variations in a stream-dominated system, into which insight can conduce to reveal dynamic migration and transformation within and between the organic matter pools [18, 19]. The functional group characteristics of conversion products often provide us with information on the origin of substances and are an important entry point for environmental management and detection [6, 56].

Diverse spectrophotometric techniques have been successfully applied for characterization of the structural components of the natural organic matter, such as UV–visible, Fourier-transformed infrared, fluorescence and nuclear magnetic resonance spectra [2, 18, 26, 56]. The UV–visible spectroscopy can be widely used to characterize the POM–DOM fractions extracted from the natural and engineering systems due to its simplicity, promptness, low cost and high sensitivity [36]. However, it is featureless and decreases monotonically with increasing acquisition wavelengths, thus a variety of analytic methods such as integration, deconvolution

and derivation, have been applied to the spectral data for obtaining much useful information [1, 20, 56]. Second derivative UV–visible spectrophotometry (SDUVS) involves the differentiating of the instrumental spectrum by calculating and plotting the spectrum curve into a second derivative, which can enhance resolution bands, reduce background and matrix interference, and provide qualitative and quantitative information from overlapping bands of the mixtures containing organic compounds [30, 44]. Moreover, the SDUVS combined with Savitzky–Golay, adjacent-averaging, percentile filter, or Fourier transform filter data-processing technique, has received an increasing focus on in single and multi-component quantitative analyses, especially in the UV–visible matrices [45]. The SDUVS has been utilized as a tool for quantitative analysis, indication and quality control in agricultural, industrial, pharmaceutical and biogeochemical fields [8, 16, 52, 56]. Principal component analysis (PCA) is utilized for splitting overlapping fluorescent signals into independent components, and then reveals the variation in a given study area [58, 66]. However, PCA could only identify UV–visible spectroscopic characteristics of POM–DOM and cluster cases by all spectral data, while it cannot analyze each sample, respectively. The second derivative in spectral technology was a useful tool as PARAFAC to monitor the removal efficiency of DOM fractions from wastewater in the wastewater treatment plant [29, 57]. However few studies have examined structural components of the POM–DOM fractions extracted from an urbanized river using the SDUVS technique.

The study of DOM structural characteristics and influencing factors of small watershed rivers in the complex urban environment is characterized by various land types, complex hydrological conditions and serious human interference in the watershed [2, 35, 54]. The aims of this study were (i) to characterize the structural components of the POM–DOM fractions in an urbanized river located in the northeast of China, implementing the SDUVS technique; (ii) to explore the component variations within and between the POM and DOM pools in the water column, and the spatial dynamics in the whole river; (iii) and to track correlations between the POM–DOM fractions and the water quality. A systematic study on the composition, spatial and temporal distribution and sources of dissolved organic matter in rivers is of scientific significance to reveal the carbon cycle process of the aquatic ecosystem and the migration and transformation law of organic matter [37, 60]. It also provides a scientific basis for the improvement of water quality and ecological environment restoration in urban rivers [5, 54].

## Material and methods

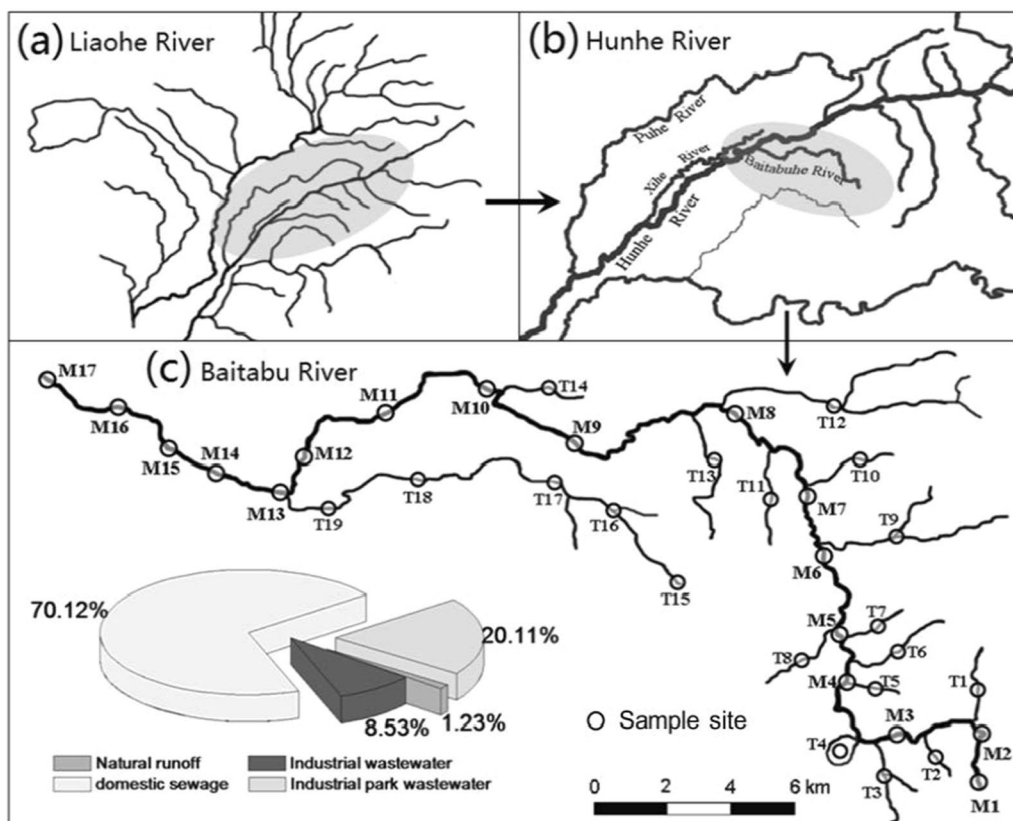
### Study area and sample collection

Hunhe River, the main branch of Liaohe River, is located in the central of Liaoning Province, China (Fig. 1a). The river stretches 415 km with a basin of 11,400 km<sup>2</sup>, where a heavy-industry complex has been developed. There are more than 30 tributary rivers on the left of Hunhe River (Fig. 1b), among which Baitapuhe River with the length of 51.51 km, an urbanized river, flows through Shenyang City. There are 12 tributary streams in the upper reaches, and three streams in the middle reach (Fig. 1c). The runoff volume reaches  $6.92 \times 10^4 \text{ m}^3 \text{ d}^{-1}$  in the medium-flow period, in the low-flow period, about 1.31 times more than that in the low-flow period, and about 1.31 times less than that in the high-low period. Its basin covering 182 km<sup>2</sup> experiences a temperate monsoon climate with an average annual rainfall of 680.43 mm and an average annual temperature of 8.11 °C. The monthly average temperature of −11.64 °C in January is the lowest, while 24.62 °C in July was the highest. The dominant wind directions are south-east in summer and north-west in winter. The continuous expansion of urbanization can lead to large quantities of pollutants loading into the river, which may result in threats to the water quality and river ecosystem.

Based on hydrological characteristics and effects of human activities, 17 sampling sites were in the mainstream and 19 sampling sites were in the tributaries (Fig. 1c). The sites M1 to M7 were located in the rural region, the sites M12 to M17 were located in the urban region, and the sites M8 to M11 were located in the town region (rural-to-city transitional zone) [59]. The sites T1 to T14 were located in the tributaries, and only one sampling site was in a given tributary stream. The sites T15 to T19 were in Shangshenghe Stream. At each sampling site, three water samples were collected along the left, middle and right channels of the section, which were completely mixed with an equal volume. The water samples were obtained in mid-depth of the river using a 10-L Van Dorn water sampler, which was stored and shipped to the lab in a cooled container. Temperature, pH, dissolved oxygen (DO) and electrical conductivity (EC) of each water sample were measured on-site with a YSI 600 multi-probe.

### Physico-chemical analysis and POM–DOM extraction

In the laboratory, the water samples filtered through a 0.45- $\mu\text{m}$  membrane were used to determine ammonia (NH<sub>3</sub>-N), while non-filtered samples were used to determine total nitrogen (TN), total phosphorus (TP), chemical oxygen demand (COD) and chlorophyll a (Chl-a) [38, 51]. TP was determined by the harmonized and validated SMT method developed by European Committee for



**Fig. 1** The study area and sampling sites: **a** Liaohe River system, **b** Hunhe River system, and **c** Baitapu River with the composition of river waters. *M* mainstream, *T* tributary

Standardization. TN was determined by the potassium persulfate oxidation method. COD was evaluated by the potassium dichromate method. Chl-a was gained with ultraviolet spectrophotometry. These parameters were measured following the environmental quality standards for surface water [49]. Details of analytical methods were described by previous publications [11, 23].

The POM was separately extracted from the water sample using the 0.7 μm and 0.2 μm porosity, precombusted glass fiber filters (25-mm diameter; Whatman GF/F) in succession, and the filtrate was used for the DOM solution (diameter < 0.2 μm). The organic matter on the 0.2 μm separate filter defined as the POM1 (0.2 < Diameter < 0.7 μm) was extracted into 10 mL of 0.1 M NaOH for 24 h in the dark. After adjustment for the pH 8.0 ± 0.05 near that of the original sample, the resultant solution was filtered through 0.2 μm polyethersulfone filters (Millipore Sterivex). The organic matter on the 0.7 μm separate filter referred to as the POM2 (diameter > 0.7 μm) was also extracted using the method described for the POM1. After correction for the volume of the base-extracts of the POM1 and the POM2 with the corresponding DOM, the particulate and dissolved organic

carbon concentrations were measured separately using a TOC analyzer (analytic jena multi N/C 3100 TOC, Germany).

**UV-visible spectrum determination**

The UV-visible spectra of the DOM, POM1 and POM2 in the corrected solutions were measured from 200 to 700 nm on a Shimadzu UV-1700 spectrophotometer in a 1-cm quartz cuvette for preventing air. The Milli-Q water and 0.1 M NaOH extraction solution for the POM were measured, respectively, and utilized as the blanks. The absorption values were converted to the Napierian absorption coefficients, α<sub>(λ)</sub>, in units of m<sup>-1</sup>, after all UV-visible spectra were blank-subtracted and corrected [56].

The absorption ratio at 250 to 365 nm (E<sub>2</sub>/E<sub>3</sub>) is used to track variations in the relative sizes of organic matter molecules. The E<sub>2</sub>/E<sub>3</sub> values decrease with the increasing of the molecular sizes, for stronger light absorption by the large molecular sizes of the organic matter at the longer wavebands. The absorption ratio at 240 to 420 nm (E<sub>2</sub>/E<sub>4</sub>) is used as an indicator of the humification degree of the organic matter, for the ratio has been verified to be better correlated with the molecular size, C:N atom ratio,



carboxyl content and total acidity than to aromaticity [22].

#### Derivative UV–visible spectroscopy and principal component analysis

The SDUVS was determined numerically using Oring-inPro 8.0 Software (OringLab Corporation) program for the spectroscopic acquisition and subsequent calculation of the derivative data. The interval of 1 nm was used in the processes. The SDUVS was then subjected to smoothing using a fast Fourier transform algorithm with a 4 cut-off percentage to remove excess noise and improve resolution [27, 30].

Principal component analysis (PCA) was applied to track the correlations between the UV–visible components and the physico-chemical parameters using SPSS 16.0. The loading plots could track factors of the POM–DOM and water quality, while the score plots for the 36 sampling sites could explore their spatial variations.

## Results and discussion

### Organic matter analysis

#### OM characteristics of Hunhe River

The average DOM concentration of  $13.65 \pm 3.42$  mg C L<sup>-1</sup> in the rural region was the highest, followed by the town region ( $11.10 \pm 1.57$  mg C L<sup>-1</sup>) and rural region ( $10.21 \pm 0.71$  mg C L<sup>-1</sup>) (Fig. 2a). The decreasing order of the average POM1 concentrations was town region ( $1.76 \pm 0.30$  mg C L<sup>-1</sup>) > rural region ( $1.67 \pm 0.63$  mg C L<sup>-1</sup>) > urban region ( $1.42 \pm 0.28$  mg C L<sup>-1</sup>) (Fig. 2b). The average POM2 concentration of  $3.39 \pm 0.60$  mg C L<sup>-1</sup> in the town region was higher than those in the rural region ( $3.03 \pm 1.26$  mg C L<sup>-1</sup>) and urban region ( $3.02 \pm 1.14$  C mg L<sup>-1</sup>) (Fig. 2c). The spatial variations of the organic matter concentrations are linked to the combination of the socio-economic development and land use in the basin, which has a marked effect on the organic matter contents of the river system [12, 28, 55]. Baitapuhe River could mainly receive the farmland return water, “grey water” from the household appliances, and the livestock wastewater in the rural region, received the domestic sewage, livestock wastewater, and wastewater effluent from the industrial parks in the town region; and received the treated domestic sewage and industrial wastewater in the urban region. This could deeply influence the allochthonous and terrestrial organic matter contents [18]. Moreover, the autochthonous organic matter could be generated or transformed from the terrestrial sources resulting from the enhanced microbial and biochemical activities [55, 63]. Therefore the hydrological and biogeochemical processes, which could dominate the spatial variations of the POM–DOM concentrations

in the mainstream and tributaries, were worthy of further investigation.

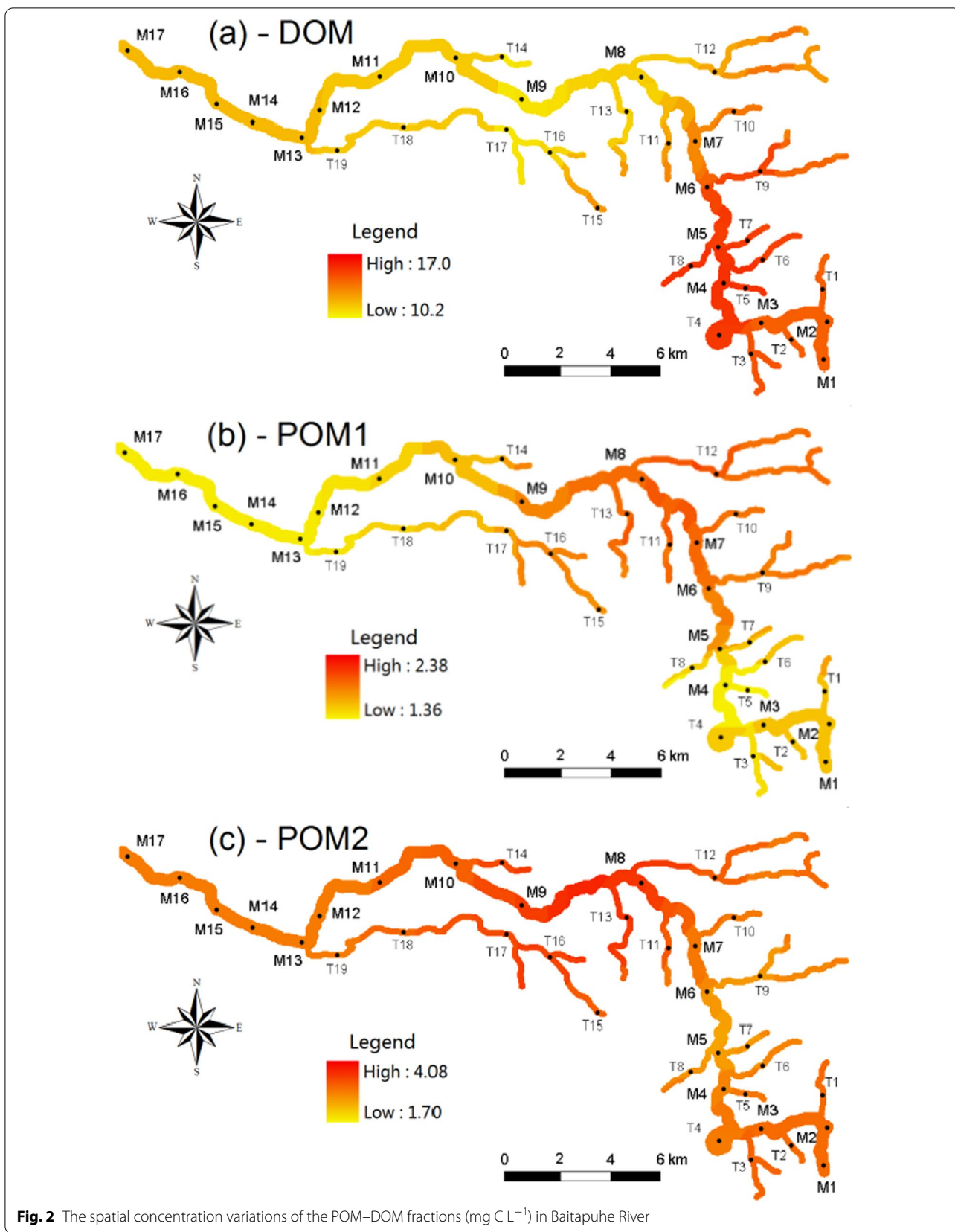
#### Relations of DOM to water quality

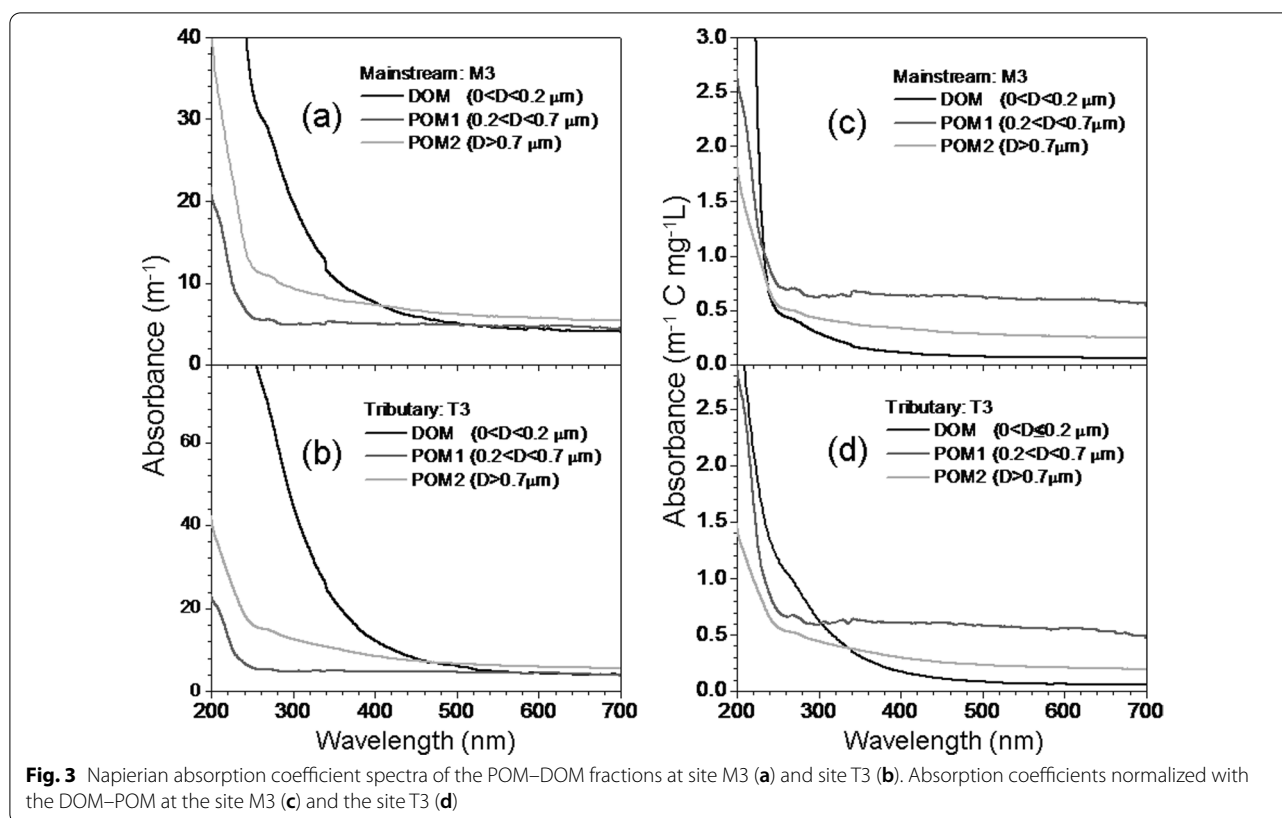
Eutrophication has been a lingering problem in the urbanized rivers, into which excess anthropogenic-derived nutrients are being loaded with rapidly increasing urbanization [41, 42]. The TEMP, pH, DO, EC, COD, NH<sub>3</sub>-N, TN, TP and Chl-a were determined and analyzed in the previous studies on the same samples, and the trophic level of the river was the highest in the urban region, followed by the town and rural regions [58, 59]. The noticeably different NH<sub>3</sub>-N and Chl-a occurred among the mainstream as well as the tributaries. The average NH<sub>3</sub>-N concentration in the mainstream ( $2.09 \pm 2.07$  mg L<sup>-1</sup>) was less than that in the tributaries ( $3.04 \pm 4.71$  mg L<sup>-1</sup>), which suggested that the NH<sub>3</sub>-N should be partially derived from the tributaries. The mainstream exhibited the average NH<sub>3</sub>-N concentration of  $4.26 \pm 1.87$  mg L<sup>-1</sup> across the urban region, approximately 2.71 times more than that across the town region, and 7.99 times more than that across the rural region. The average NH<sub>3</sub>-N concentration of the tributaries in the town region was  $3.32 \pm 3.10$  mg L<sup>-1</sup> more than that in the rural region ( $2.84 \pm 5.76$  mg L<sup>-1</sup>). The average Chl-a concentration in the mainstream was  $24.99 \pm 27.14$  mg L<sup>-1</sup>, about 2.16 times more than that in the tributaries. The increasing order of the Chl-a means in the mainstream was urban region ( $59.02 \pm 13.32$  mg L<sup>-1</sup>) > town region ( $11.93 \pm 3.32$  mg L<sup>-1</sup>) > rural region ( $4.39 \pm 1.58$  mg L<sup>-1</sup>), indirectly indicating that the river in the urban region showed higher eutrophication levels than those in the town and rural regions. The average Chl-a concentration of tributaries was  $20.72 \pm 19.98$  mg L<sup>-1</sup> in the town region, about 4.24 times more than that in the rural region.

The DOM showed the positive correlations with the NH<sub>3</sub>-N ( $r=0.34$ ,  $p<0.05$ ,  $n=36$ ) and TP ( $r=0.41$ ,  $p<0.05$ ,  $n=36$ ), while the negative correlations with the Chl-a ( $r=0.39$ ,  $p<0.05$ ,  $N=36$ ) and COD<sub>Cr</sub> ( $r=-0.29$ ,  $p>0.05$ ,  $n=36$ ). This proved that the DOM might have mainly originated from the domestic sewage accounting for 70.12% runoff of the River (Fig. 1c), for the NH<sub>3</sub>-N and TP are considered as the representative compounds for the domestic sewage [18, 47].

#### Variation characteristics of POM–DOM

In the whole river system, the average DOM concentration was  $12.24 \pm 3.07$  mg C L<sup>-1</sup>, roughly 7.65 times more than the average POM1 concentration, and 3.99 times more than the average POM2 concentration. It indicated that the DOM could be considered as a representative fraction for the natural organic matter pool, which was





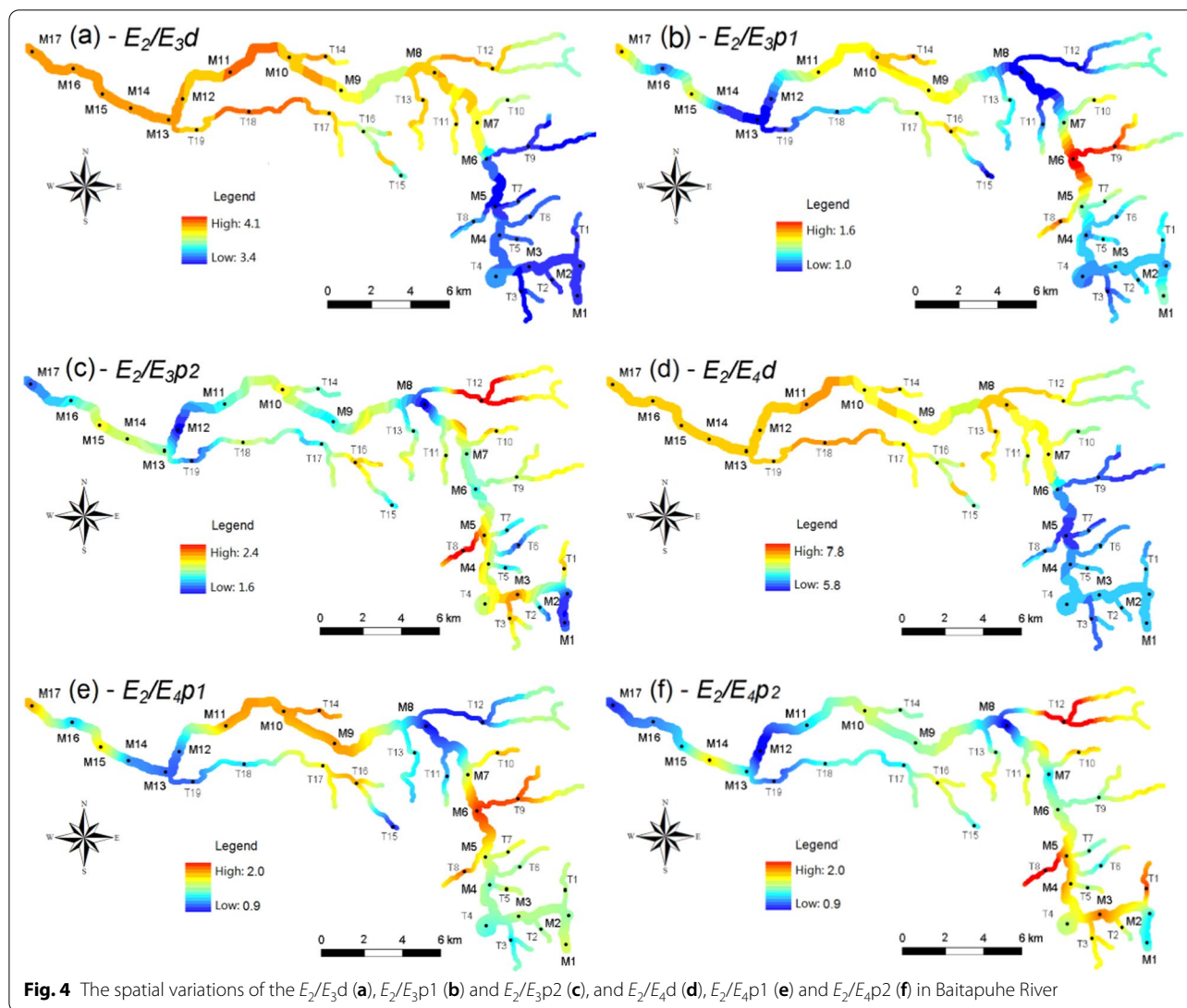
similar to many rivers and estuaries [31, 41, 43]. Thus the DOM had an allochthonous source from the domestic sewage instead of an autochthonous (and fresher) source from phytoplankton cultures subjected to microbial degradation. Interestingly, the average DOM concentration in the mainstream was similar to that in the tributaries, so were the means of the POM1 and POM2 concentrations.

#### UV–visible spectroscopic characteristics of POM–DOM

The UV–visible absorption corrected spectra for all sampling sites exhibited the familiar monotonous decrease with the increasing wavelengths between 200 and 700 nm (Fig. 3a, b, only sites M3 and T3 were shown). According to Domeizel et al. [13] and Rosa et al. [46] studies, the presence of shoulders in the range of 240–400 nm can be associated with aromatic or unsaturated compounds that have conjugated double bonds (C=C, N=N and C=O). The shoulder increasing and widening highlights the high concentration of the aromatic compounds, as well as the modification of the organic function groups [1, 46]. The wavelengths lower than 240 nm are well known to produce a prominent UV–visible absorption by inorganic ions such as bromide and nitrate [9, 39]. The absorption intensities can be determined by the solution pH, organic carbon content, and molecule structure and size [14, 22,

33]. The absorption intensities of the spectroscopy normalized with the organic carbon were mainly affected by the molecular structure and size in this study, for the pH could be almost similar in all water samples. At site M3, the spectroscopy of the POM1 showed the strongest absorption between 240 and 700 nm, followed by the POM2 and DOM (Fig. 3c). Fascinatingly at site T3, the absorption of the DOM was the strongest in the range of 240–300 nm, followed by the POM1 and POM2, while the decreasing order of absorptions from 340 to 700 nm was similar to that at the site M3 (Fig. 3d).

In the whole river system, the average  $E_2/E_3$  value of the DOM ( $E_2/E_3d = 3.78 \pm 0.77$ ) was highest, decreasing to  $1.81 \pm 0.22$  of the POM2 ( $E_2/E_3p2$ ) and  $1.23 \pm 0.19$  of POM1 ( $E_2/E_3p1$ ), verifying that the molecular size of POM1 or POM2 was larger than that of the DOM. The  $E_2/E_3d$  values increased in the order of rural region ( $3.56 \pm 0.71$ ) < town region ( $3.77 \pm 1.33$ ) < urban region ( $4.20 \pm 0.33$ ) (Fig. 4a), revealing that the decreasing order of the DOM molecular sizes was rural region > town region > urban region. This may be related to a large amount of industrial wastewater discharged into the town section and urban section [64]. However, the  $E_2/E_3p1$  values exhibited a non-regular variation in the three regions, so was the  $E_2/E_3p2$ . In the whole river, the mean  $E_2/E_4$  value of the DOM ( $E_2/E_4d$ ) ( $6.89 \pm 1.85$ )



was obviously higher than that of the POM1 ( $E_2/E_{4p1}$ ) ( $1.45 \pm 0.31$ ) or POM2 ( $E_2/E_{4p2}$ ) ( $2.25 \pm 0.30$ ), illustrating that humification degree of the POM1 or POM2 was higher than that of the DOM. The  $E_2/E_{4d}$  values increased in the order of rural region ( $6.36 \pm 1.75$ ) < town region ( $6.91 \pm 3.04$ ) < urban region ( $7.84 \pm 0.96$ ) (Fig. 4d), indicating that humification degree of the DOM decreased in the order of rural region > town region > urban region. DOM originated from endogenous metabolites produced by microbial decomposition are mainly distributed in the river of the rural region [65]. The trends of the  $E_2/E_{4p1}$  and  $E_2/E_{4p2}$  values were similar to the  $E_2/E_{3p1}$  and  $E_2/E_{3p2}$ .

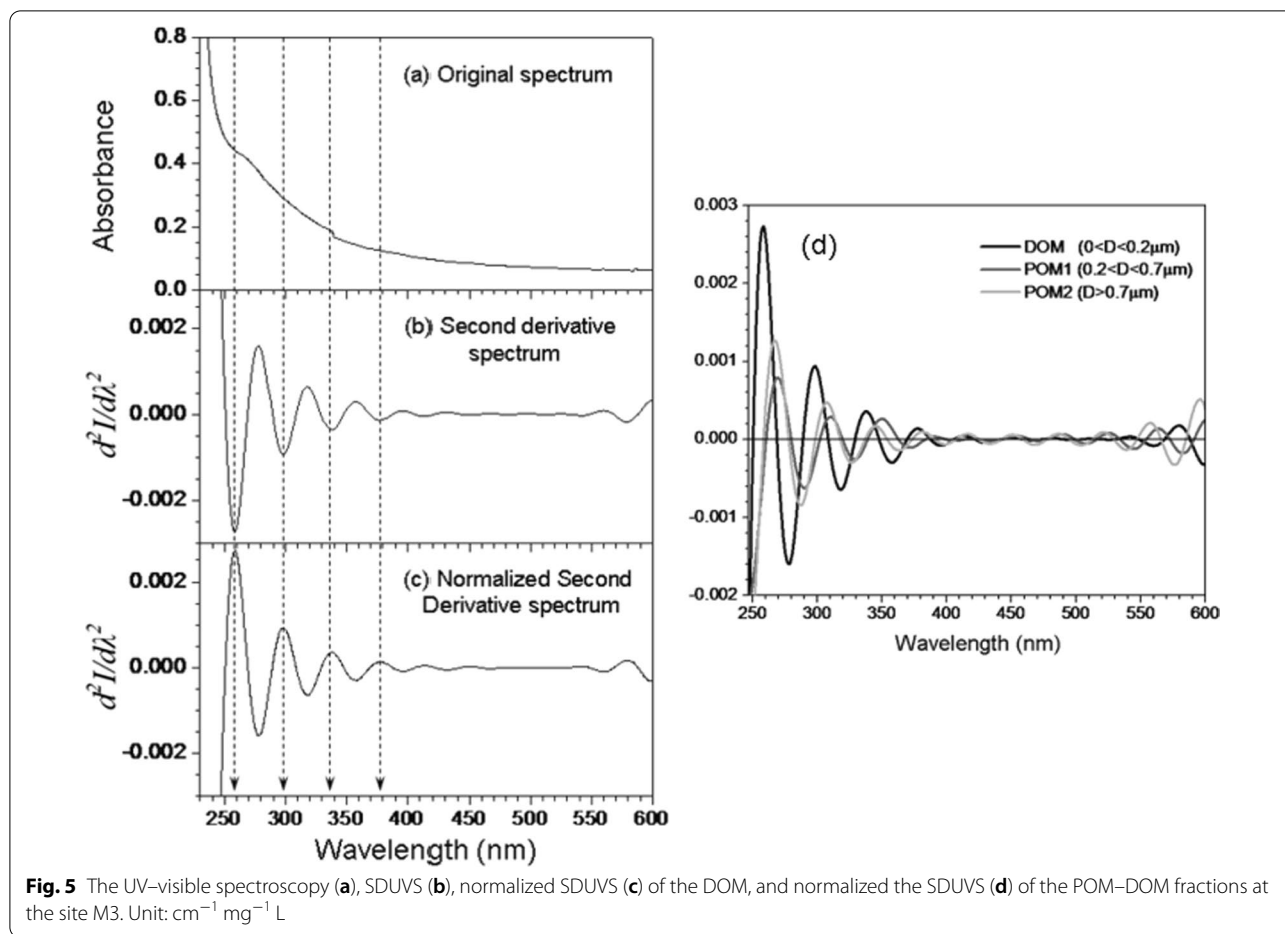
A high trophic level of the river water with a low DO concentration exhibits a strong microbial heterotrophic processing of DOM, which may conduce to the strong degradation of the large organic molecular sizes into

the small molecular sizes [12]. Since the trophic level in the Baitapuhe River decreased in the order of urban region > town region > rural region, the molecular sizes of the DOM decreased in the order of rural region > town region > urban region. This was consistent with the result of the  $E_2/E_{3d}$ .

#### Analysis of POM–DOM derivative components

Four relatively meaningful absorption bands are defined as the first band: 245–270 nm, the second band: 270–320 nm, the third band: 320–400, and the fourth band: 400–560 nm [1, 17]. The first band is mainly relative to phenolic groups (lignin and quinine moieties), defined as the component 1 (C1), and the second band presents major carboxylic groups (carboxylic acid), referred to as the component 2 (C2) [1, 14, 56]. The third band reflects the organic matter at the beginning of humification,



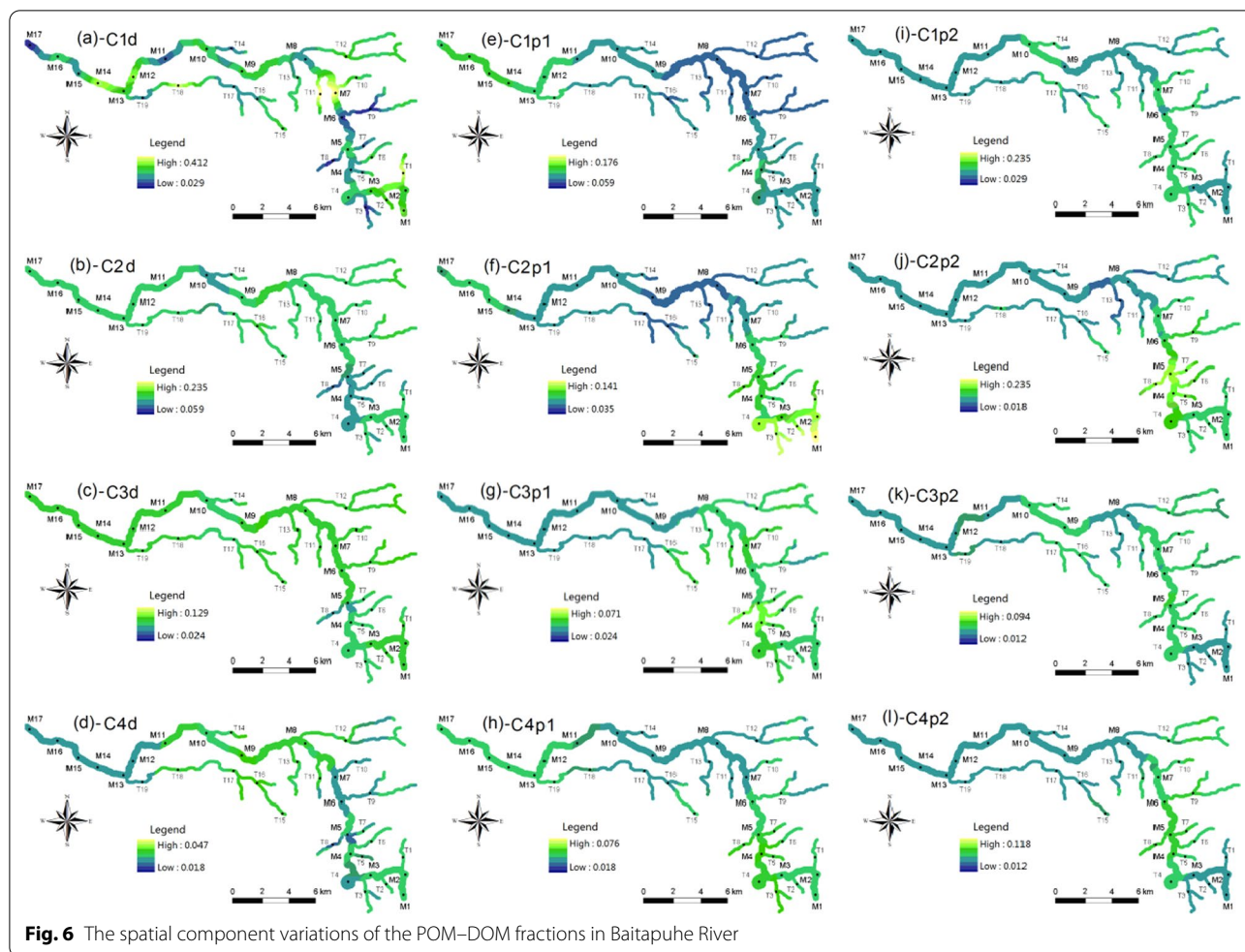


which contains microbial products (primary humified organic materials), considered as the component 3 (C3) [17, 50]. The fourth band is concerned with deeply humified organic materials with a high degree of aromatic and alkyl groups, regarded as the component 4 (C4) [1, 62].

The C1, C2 and C3 exhibited a single broad shoulder in the UV-visible spectroscopy of the DOM for the site M3, while the C4 represented a broad and low absorption platform. This could be attributed to the strong overlaps between the four bands (Fig. 5a). After the second derivative transformation of the spectroscopy, the shoulder was clearly separated into four peaks: the first peak at around 260 nm corresponding to the C1, the second peak at around 300 nm corresponding to the C2, and the third/fourth peaks at 340 nm and 380 nm with corresponding to the C3 (Fig. 5b, c). Additionally, the platform was separated into several weak shoulders corresponding to the C4. There were several peaks at 560–700 nm which were attributed to the random noise effect on the smoothing arrays of the Fourier transform [32, 40]. Similar to the DOM, the derivative spectra of the POM1 and POM2 for the site M3 showed distinctly

four peaks (Fig. 5d). However, these peaks were red-shifted to longer wavelengths compared to those peaks of the DOM. This resulted from the larger molecular sizes of the POM1 and POM2 than those of the DOM [41], which was consistent with the above analysis of the  $E_2/E_3$ .

The absolute peak-area integral was performed using the OringinPro 8.0 Software (OringLab Corporation) program, which could be considered to be proportional to the true concentration of the corresponding component [7, 25]. Hence the peak area could indicate the molecular structure and size of the component. Positive relationships occurred between the DOM components ( $r \geq 0.36$ ,  $p < 0.05$ ,  $N = 36$ ), so was the POM1 ( $r \geq 0.45$ ,  $p < 0.01$ ,  $N = 36$ ) or POM2 components ( $r \geq 0.75$ ,  $p < 0.01$ ,  $N = 36$ ). Negative relationship existed between the C2d and the C2p1 ( $r = -0.37$ ,  $p < 0.05$ ,  $N = 36$ ) or between the C3d and the C3p1 ( $r = -0.40$ ,  $p > 0.01$ ,  $N = 36$ ). This indicated that the carboxylic acid and primary humified materials in the DOM could sorb onto the POM1, for these compounds could aggregate in the large molecular

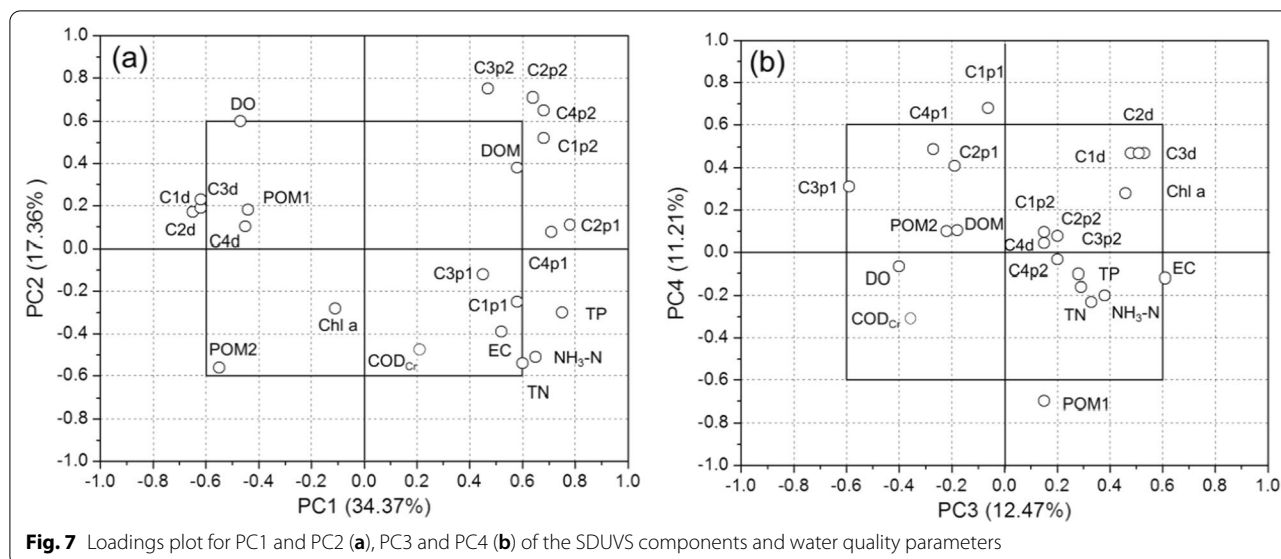


size DOM and particles in rivers, potential through the formation of Schiff base derivatives [3, 41].

In the whole river system, the decreasing order of the average C1d was urban ( $0.042 \pm 0.021$ ) > rural ( $0.039 \pm 0.022$ ) > town ( $0.034 \pm 0.017$ ) (Fig. 6a). The trends of the C2d and C3d were similar to the C1d, while the trend of the C4d was opposite to the C2d (Fig. 6b–d). The decreasing order of the average C1p1 was urban ( $0.022 \pm 0.005$ ) > rural ( $0.016 \pm 0.005$ ) > town ( $0.015 \pm 0.003$ ), so was the C2p1 (Fig. 6e, f). The decreasing order of the average C3p1 was rural ( $0.009 \pm 0.006$ ) > urban ( $0.007 \pm 0.002$ ) > town ( $0.006 \pm 0.001$ ), while the decreasing order of the average C4p1 was rural ( $0.008 \pm 0.003$ ) > town ( $0.007 \pm 0.002$ ) > urban ( $0.006 \pm 0.002$ ) (Fig. 6g, h). The decreasing order of the average C1p2 was rural ( $0.021 \pm 0.021$ ) > town ( $0.020 \pm 0.015$ ) > urban ( $0.014 \pm 0.007$ ), so were the C2p2 and C4p2 (Fig. 6i, j, l). Hence the decreasing order of the average C3p2 was town ( $0.009 \pm 0.008$ ) > rural ( $0.008 \pm 0.007$ ) > urban ( $0.006 \pm 0.003$ ) (Fig. 6k). Interestingly, the urban region

had the lower C4 of the POM–DOM fractions than the rural and town regions, indicating that the deeply humified organic materials in the urban region were much less than those in the rural and town regions.

The amount of each component, measured as % of the total peak areas for the four components (%C) varied substantially among the POM–DOM fractions. The %C1 ranged from 36.06 to 45.29%, and the %C2 ranged from 27.11 to 30.06% in the POM–DOM fractions. The %C3 stayed relatively consistent (15.17–18.38), while the %C4 largely varied (6.89–20.69). Obviously the C1 and the C2 have dominated the POM–DOM fractions. The average %C4 in the POM was higher than that in the DOM. This proved that the humification degree of the POM was higher than that of the DOM, which was consistent with the above analysis of the  $E_2/E_4$ . Interestingly, the average %C4d in the tributaries was higher than that in the mainstream, so were the C4p1 and C4p2. This suggested that the relative content of the deeply humified organic materials in the tributaries should be much more than that in the mainstream.



**Relations of SDUVS components to water quality**

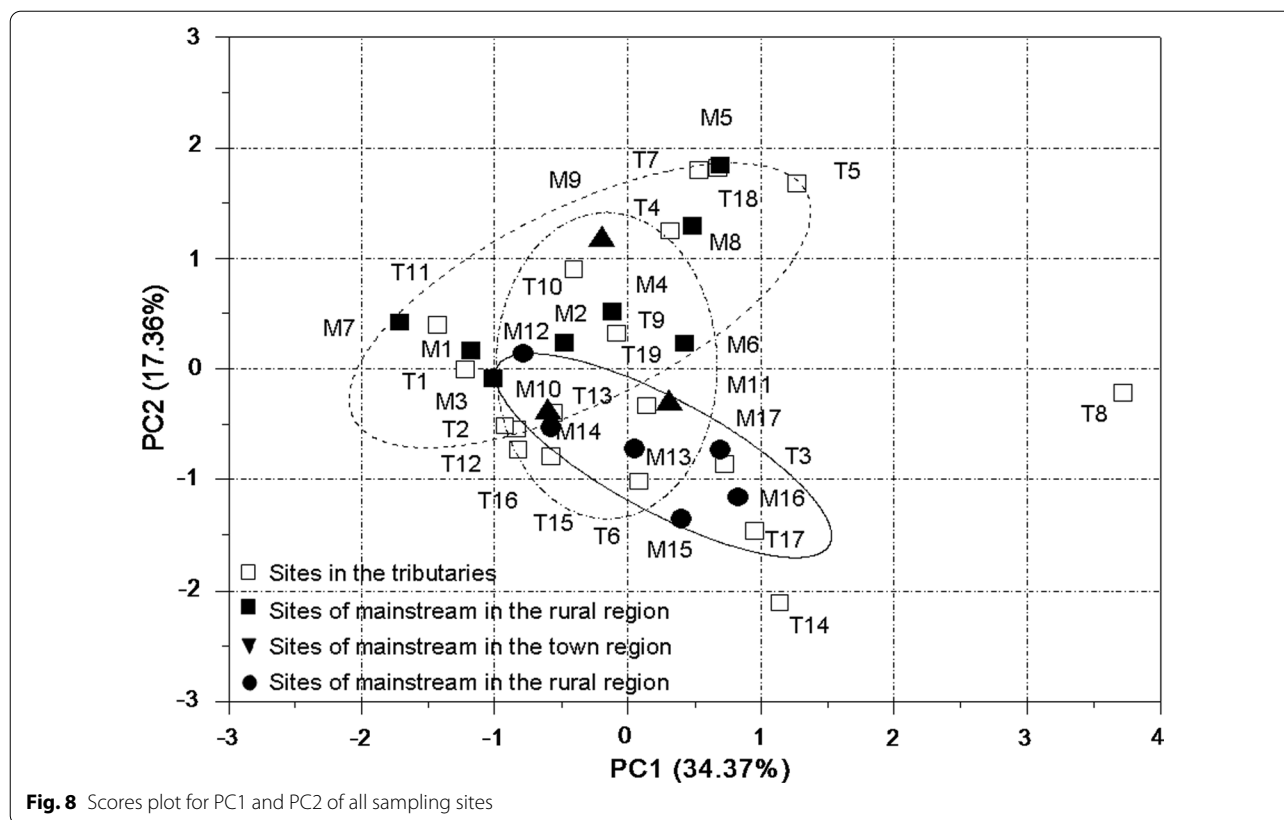
Primary productions were dominated by phytoplankton in the Baitapuhe River, which lacked substantial marshes that could supply the autochthonous organic matter [29]. Principal component analysis (PCA) was conducted on the peak areas of the components and water quality parameter data across the river, and produced four PCs for the 36 water samples. The relationship between the components and water quality parameters was explored using the clustering of loadings plots for the four PCs, where the variable with the absolute value of more than 0.6 could be much highlighted.

The PC1 accounting for 34.37% of the total variance had the strong positive loadings on the TP, NH<sub>3</sub>-N and DOM (Fig. 7a), indirectly explained that the DOM could be partially originated from the domestic sewage, apart from partially autochthonous production decomposition, sorption/desorption reactions, and/or adverse release from surface sediment pore water. The DOM components (except for the C4d) had strong negative loadings and contributed roughly equally to the PC1, elaborating that these components were becoming prominent during river transport. Moreover the C1p2 and C4p2 had the positive loadings on the PC1, and they also had the correlations with the TP ( $r > 0.36$ ,  $p < 0.05$ ,  $N = 36$ ). This suggested that C1p2 or C4p2 should be used as a surrogate for the TP concentration. Site T8 had a higher positive score on the PC1 (Fig. 8), indicating its relatively higher NH<sub>3</sub>-N and TP concentrations compared to other sites in the river. This was attributed to the wastewater from a feed mill at site T8 which might discharge directly into the tributary. The

site M1 in the source of the river had the lower negative score on the PC1, proving its relatively lower NH<sub>3</sub>-N and TP concentrations.

The PC2 (17.36% of the total variance) exhibited strong positive loadings on the C3p2, C2p2 and DO, whereas the negative loadings on the POM2 and COD<sub>Cr</sub> (Fig. 7a). Moreover, the DO had negative correlations with the COD<sub>Cr</sub>, TN, NH<sub>3</sub>-N and TP ( $r > 0.511$ ,  $p < 0.01$ ,  $n = 36$ ), suggesting that these pollutants should be degraded under the aerobic condition. The PC3 (12.47% of the total variance) exhibited the strong positive loading on the EC and the strong negative loading on the C3p1, and the PC4 (11.21% of the total variance) had the strong positive loading on the C1p1 and the strong negative loading on the POM1 (Fig. 7b). Moreover, only the C1p1 among the POM–DOM fractions had the negative correlations with the POM1 and DO ( $r < -0.39$ ,  $p < 0.05$ ,  $N = 36$ ), and positive correlations with the NH<sub>3</sub>-N and Chl-a ( $r > 0.35$ ,  $p < 0.05$ ,  $N = 36$ ). This indicated that the POM–DOM fractions in the river system showed the strong mixing of the autochthonous sources with the allochthonous/terrestrial sources during the low discharge, for the river system was ubiquitous sensitive to the nutrients [34, 41].

All the sampling sites were projected onto the plane PC1 × PC2 scores (Fig. 8). The points of the sites T1 to T19 showed a larger dispersion than those of sites M1 to M17 in the plane, especially the sites T8 and T14 being far away from other sample sites. This indicated that the variations of the POM–DOM and water quality in the tributaries were much larger than those in the mainstream, which resulted from one or several types of wastewater flown into a given tributary, apart from rainfall. Three expected clusters were presented in the scores



**Fig. 8** Scores plot for PC1 and PC2 of all sampling sites

plot of the mainstream sampling sites with the 70% confidence level for each confidence ellipse, which corresponded to the rural (M1 to M8), town (M9 to M11) and urban (M12 to M17) regions. The decreasing order of the water quality was rural region > town region > urban region, which the trend of the humification degree of the POM–DOM fraction was opposite to the water quality. The ellipse of the town region was located between the ellipses of the rural and urban, indirectly suggesting that the town region was the transitional zone of the rural and town regions. Moreover, the sites T1 to T12 (except for the sites T3, T6 and T8) were located in the rural ellipses, and the sites T13 to T17 (except for the sites T14 and T17) were located in the town ellipses. This indirectly proved that the tributaries had an important impact on the POM–DOM and water quality of the mainstream.

**Conclusions**

The DOM was dominated in the organic carbon pool, which could be mainly derived from the allochthonous and terrestrial sources, especially the domestic sewage. The trophic level of the river water decreased in the order of urban region > town region > rural region, while the trend of the molecular sizes of the DOM was opposite to the trophic level. The phenolic and carboxylic groups

were dominant for the POM–DOM fractions. The percentage contents of the primary humified materials stayed relatively stable in the POM–DOM, while the percentage contents of the deeply humified organic matter varied extensively. Moreover, the average relative content of the strongly humified materials in the tributaries was much more than that in the mainstream. The humification degree of the POM pool was higher than that of the DOM pool. The peak area of the phenolic groups could be utilized to estimate the contributions of the TP to the river system. Base-extraction of the UV–visible POM is a rapid method to simultaneously evaluate DOM–POM fractions and water quality in rivers and could be transferred to other water environments. The principal component analysis provided a classification of the variations of DOM fractions, which might aid in designing a monitoring plan of DOM–POM with an adjustment of the sampling sites. Derivative UV–visible spectroscopy could be an effective approach for insight into the structural components of the POM–DOM fractions exhibited in urban rivers, which could present support to quality improvement and management measures for urbanized rivers.

**Acknowledgements**

Not applicable.



### Authors' contributions

WX and HY: conceptualization, methodology, software, formal analysis, investigation, data curation, writing original draft, writing—review and editing; FY: conceptualization, formal analysis, investigation, supervision, project administration, funding acquisition; HG and YS: methodology, formal analysis, supervision, writing—review and editing; DL and KL: investigation, data curation, review; FY: investigation, data curation. All authors read and approved the final manuscript.

### Funding

This research was jointly supported by the National key research and development program (2020YFC1806302) and the National Natural Science Foundation of China (41907338).

### Availability of data and materials

The datasets supporting the conclusions of this article are included within the article.

### Declarations

#### Ethics approval and consent to participate

Not applicable.

#### Consent for publication

Not applicable.

#### Competing interests

The authors declare no competing interests.

### Author details

<sup>1</sup>College of Water Sciences, Beijing Normal University, Beijing 100875, China. <sup>2</sup>State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China. <sup>3</sup>Basin Research Center for Water Pollution Control, Chinese Research Academy of Environmental Sciences, Beijing 100012, China.

Received: 7 January 2022 Accepted: 11 March 2022

Published online: 24 March 2022

### References

- Albrecht R, Le Petit J, Terrom G, Périssol C (2011) Comparison between UV spectroscopy and nirs to assess humification process during sewage sludge and green wastes co-composting. *Bioresour Technol* 102:4495–4500
- Aftab B, Hur J (2017) Fast tracking the molecular weight changes of humic substances in coagulation/flocculation processes via fluorescence EEM-PARAFAC. *Chemosphere* 178:317–324
- Benner R, Kaiser K (2003) Abundance of amino sugars and peptidoglycan in marine particulate and dissolved organic matter. *Limnol Oceanogr* 48(1):118–128
- Borisover M, Laor Y, Parparov A, Bukhanovsky N, Lado M (2009) Spatial and seasonal patterns of fluorescent organic matter in Lake Kinneret (Sea of Galilee) and its catchment basin. *Water Res* 43:3104–3116
- Cao J, Sun Q, Zhao D, Xue M, Shen Q, Wang D, Wang Y, Ding S (2020) A critical review of the appearance of black-odorous waterbodies in China and treatment methods. *J Hazard Mater* 385:121511
- Capuano E, Ruth S (2016) Infrared spectroscopy: applications. *Encyclopedia of food and health*. Elsevier, Amsterdam, pp 424–431
- Chin YP, Aiken G, O'Loughlin E (1994) Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environ Sci Technol* 28:1853–1858
- Dave HN, Mashru RC, Thakkar AR (2007) Simultaneous determination of salbutamol sulphate, bromhexine hydrochloride and etofylline in pharmaceutical formulations with the use of four rapid derivative spectrophotometric methods. *Anal Chim Acta* 597:113–120
- Deflandre B, Gagné JP (2001) Estimation of dissolved organic carbon (DOC) concentrations in nanoliter samples using UV spectroscopy. *Water Res* 35:3057–3062
- Derrien M, Brogi SR, Gonalves-Araujo R (2019) Characterization of aquatic organic matter: assessment, perspectives and research priorities. *Water Res* 163:114908
- Ding S, Xu D, Bai X, Yao S, Fan C, Zhang C (2013) Speciation of organic phosphorus in a sediment profile of Lake Taihu II. Molecular species and their depth attenuation. *J Environ Sci* 25:925–932
- Dodds WK (2006) Eutrophication and trophic state in rivers and streams. *Limnol Oceanogr* 51(1):671–680
- Domeizel M, Khalil A, Prudent P (2004) UV spectroscopy: a tool for monitoring humification and for proposing an index of the maturity of compost. *Bioresour Technol* 94:177–184
- Dryer DJ, Korshin GV, Fabbicino M (2008) In situ examination of the protonation behavior of fulvic acids using differential absorbance spectroscopy. *Environ Sci Technol* 42:6644–6649
- Evans CD, Monteith DT, Cooper DM (2005) Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environ Pollut* 137(1):55–71
- Ferree MA, Shannon RD (2001) Evaluation of a second derivative UV/visible spectroscopy technique for nitrate and total nitrogen analysis of wastewater samples. *Water Res* 35(1):327–332
- Giegunzyska E, Kocmit A, Golebiovska D (1998) Studies on humic acids in eroded soils of western Pomerania. 1. Differentiation of some chemical as well as optical properties of humic acids along the eroded slope. In: Zaujec A, Gonet SS, Bielek P (eds) *Humic substances in ecosystems*. VUPOP, Bratislava, pp 35–41
- Goldman JH, Rounds SA, Needoba JA (2012) Applications of fluorescence spectroscopy for predicting percent wastewater in an urban stream. *Environ Sci Technol* 46:4374–4381
- Grace BL, Bianchi TS (2010) Sorption and desorption dynamics of bulk dissolved organic matter and amino acids in the Mississippi River plume—a microcosm study. *Mar Freshw Res* 61(9):1067–1081
- Hassouna M, Massiani C, Dudal Y, Pech N, Theraulaz F (2010) Changes in water extractable organic matter (WEOM) in a calcareous soil under field conditions with time and soil depth. *Geoderma* 155:75–85
- He C, Jiang B, Shi Q, Hsu CS (2018) Comment on "laser desorption/ionization coupled to FTICR mass spectrometry for studies of natural organic matter". *Anal Chem* 90(9):5965–5967
- Helms JR, Stubbins A, Ritchie JD, Minor EC, Kieber DJ, Mopper K (2008) Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnol Oceanogr* 53(3):955–969
- Huo S, Ma C, Xi B, Su J, Zan F, Ji D, He Z (2013) Establishing eutrophication assessment standards for four lake regions, China. *J Environ Sci* 25:2014–2022
- Ishii SK, Boyer TH (2012) Behavior of reoccurring PARAFAC components in fluorescent dissolved organic matter in natural and engineered systems: a critical review. *Environ Sci Technol* 46(4):2006–2017
- Korshin G, Li CW, Benjamin MM (1997) Monitoring the properties of natural organic matter through UV spectroscopy: a consistent theory. *Water Res* 31:1787–1795
- Kuballa T, Brunner TS, Thongpanchang T, Walch SG, Lachenmeier DW (2018) Application of NMR for authentication of honey, beer and spices. *Curr Opin Food Sci* 19:57–62
- Kueltzo LA, Ersoy B, Ralston JP, Middaugh CR (2003) Derivative absorbance spectroscopy and protein phase diagrams as tools for comprehensive protein characterization: a bGCSF case study. *J Pharm Sci* 92:1805–1820
- Liang Z, Siegert M, Fang W, Sun Y, Jiang F, Lu H, Chen G, Wang S (2017) Blackening and odorization of urban rivers: a bio-geochemical process. *FEMS Microbiol Ecol* 94(3):fix180
- Liu D, Gao H, Cui B et al (2021) Fluorescence spectra and multivariate statistical model characterization of DOM composition structure of Baitapu river sediment. *J Environ Eng Technol* 11(2):249257
- Lucas LH, Ersoy B, Kueltzo LA, Joshi SB, Brandau DT, Thyagarajapuram N, Peek LJ, Middaugh CR (2006) Probing protein structure and dynamics by second-derivative ultraviolet absorption analysis of cation- $\pi$  interactions. *Protein Sci* 15(10):2228–2243
- McCallister SL, Bauer JE, Ducklow HW, Canuel EA (2006) Sources of estuarine dissolved and particulate organic matter: a multitracer approach. *Org Geochem* 37(4):454–468

32. Madden HH (1978) Comments on the Savitzky–Golay convolution method for least-squares-fit smoothing and differentiation of digital data. *Anal Chem* 50(9):1383–1386
33. Mantele W, Deniz E (2017) UV–VIS absorption spectroscopy: Lambert–Beer reloaded. *Spectrochim Acta A* 173:965–968
34. Matson EA, Brinson MM (1990) Stable carbon isotopes and the CN ratio in the estuaries of the Pamlico and Neuse Rivers, North Carolina. *Limnol Oceanogr* 35(6):1290–1300
35. Miller EM (2013) Local- and landscape-level controls on coarse particulate organic matter retention in urban and forested small streams of central Massachusetts. *Freshw Sci* 32(2):576–585
36. Morales L, Toral MI, Álvarez MJ (2007) A new Cu(II)-5-(4-sulphophenylazo)-8-aminoquinoline complex used for copper determination in presence of gold and silver in water and mineral samples. *Talanta* 74:110–118
37. Müller A, Österlund H, Marsalek J, Viklander M (2019) The pollution conveyed by urban runoff: a review of sources. *Sci Total Environ* 709:136125
38. Noori R, Berndtsson R, Hosseinzadeh M, Adamowski J, Abyaneh MR (2019) A critical review on the application of the national sanitation foundation water quality index. *Environ Pollut* 244:575–587
39. Ogura N, Hanya T (1966) Nature of ultraviolet absorption of seawater. *Nature* 212:758
40. Ojeda CB, Rojas FS (2004) Recent developments in derivative ultraviolet/visible absorption spectrophotometry. *Anal Chim Acta* 518:1–24
41. Osburn CL, Handsel LT, Mikan MP, Paerl HP (2012) Fluorescence tracking of dissolved and particulate organic matter quality in a river-dominated estuary. *Environ Sci Technol* 42:6644–6649
42. Ouyang T, Zhu Z, Kuang Y (2006) Assessing impact of urbanization on river water quality in the Pearl River Delta Economic Zone, China. *Environ Monit Assess* 120(1–3):313–325
43. Raymond PA, Bauer JE (2001) Use of C-14 and C-13 natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis. *Org Geochem* 32(4):469–485
44. Rodenas V, Garcia MS, Sánchez-Pedreño C, Albero MI (2000) Simultaneous determination of propacetamol and paracetamol by derivative spectrophotometry. *Talanta* 30(3):517–523
45. Rojas FS, Ojeda CB (2009) Recent development in derivative ultraviolet/visible absorption spectrophotometry: 2004–2008: a review. *Anal Chim Acta* 635:22–44
46. Rosa LN, Coqueiro A, Marco PH, Valderrama P (2019) Thermal rice oil degradation evaluated by UV–Vis–NIR and PARAFAC. *Food Chem* 273:52–56
47. Sengupta S, Nawaz T, Beaudry J (2015) Nitrogen and phosphorus recovery from wastewater. *Curr Pollut Rep* 1(3):155–166
48. Simsek H, Kasi M, Wadhawan T, Bye C, Blonigen M, Khan E (2012) Fate of dissolved organic nitrogen in two stage trickling filter process. *Water Res* 46(16):5115–5226
49. State Environment Protection Administration of China (SEPA) (2002) *Methods for water and wastewater monitoring and analysis in China*, 4th edn. China Environmental Science Press, Beijing
50. Stedmon CA, Markager S (2005) Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis. *Limnol Oceanogr* 50(5):1415–1426
51. Sun W, Xia C, Xu M, Guo J, Sun G (2016) Application of modified water quality indices as indicators to assess the spatial and temporal trends of water quality in the Dongjiang River. *Ecol Indic* 66:306–312
52. Toral MI, Richter P, Cavieres M, González W (1999) Simultaneous determination of O- and P-nitrophenol by first derivative spectrophotometry. *Environ Monit Assess* 54:191–203
53. Tremblay L, Gagne JP (2009) Organic matter distribution and reactivity in the waters of a large estuarine system. *Mar Chem* 116(1–4):1–12
54. Wang L, Yu L, Xiong Y, Li Z, Geng J (2021) Study on the governance of black-odor water in Chinese cities. *J Clean Prod* 709:136125
55. Williams CJ, Yamashita Y, Wilson HF, Jaffé R, Xenopoulos MA (2010) Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. *Limnol Oceanogr* 55(3):1159–1171
56. Yan M, Dryer D, Korshin GV, Benedetti MF (2012) In situ study of binding of copper by fulvic acid: comparison of differential absorbance data and model predictions. *Water Res* 47:588–596
57. Yu H, Song Y, Tu X, Du E, Liu R, Peng J (2013) Assessing removal efficiency of dissolved organic matter in wastewater treatment using fluorescence excitation emission matrices with parallel factor analysis and second derivative synchronous fluorescence. *Bioresour Technol* 144:595–601
58. Yu H, Song Y, Du E, Yang N, Peng J, Liu R (2016) Comparison of PARAFAC components of fluorescent dissolved and particular organic matter from two urbanized rivers. *Environ Sci Pollut Res* 23(11):10644–10655
59. Yu HB, Song YH, Qian F, Yang N, Liu R, Gao H (2015) Multivariate data analysis of water quality and source identification in an urbanized river. *Fresen Environ Bull* 24(24):4847–4854
60. Zhang H, Zhang Y, Wang XC et al (2021) Characterization and biogeochemical implications of dissolved organic matter in aquatic environments. *J Environ Manag* 294:113041
61. Zheng Y, Niu J, Zhou Q, Xie C, Ke Z, Li D, Gao Y (2018) Effects of resource availability and hydrological regime on autochthonous and allochthonous carbon in the food web of a large cross-border river (China). *Sci Total Environ* 612:501–512
62. Zbytyniewski R, Buszewski B (2005) Characterization of natural organic matter (NOM) derived from sewage sludge compost. Part 1: chemical and spectroscopic properties. *Bioresour Technol* 96:471–478
63. Zhu Z, Wu Y, Liu S, Wenger F, Hu J, Zhang J, Zhang R (2016) Organic carbon flux and particulate organic matter composition in Arctic valley glaciers: examples from the Bayelva River and adjacent Kongsfjorden. *Biogeosciences* 13(4):975–987
64. Yang, J, Gao J, Chang J (2012) Characterization of the change in DOM during municipal secondary effluent treatment with magnetic ion exchange resin by 3D EEM. *Environ Sci.* 33(6):1878–1883
65. Johnson MS, Couto EG, Abdo M, Lehmann J (2012) Fluorescence index as an indicator of dissolved organic carbon quality in hydrologic flowpaths of forested tropical watersheds. *Biogeochemistry*. 105:149–157
66. Pan H, Yu H, Wang Y, Liu R, Lei H (2018) Investigating variations of fluorescent dissolved organic matter in wastewater treatment using synchronous fluorescence spectroscopy combined with principal component analysis and twodimensional correlation. *Environ Technol*. 39:2495–2502

## Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Submit your manuscript to a SpringerOpen® journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► [springeropen.com](https://www.springeropen.com)