Partitioning of water soluble organic carbon in three sediment size fractions: Effect of the humic substances

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Abstract

Water soluble organic carbon (WSOC) in sediments plays an important role in transference and transformation of aquatic pollutants. This article investigated the inherent mechanisms of how sediemnt grain size affect the partitioning coeffcient (k) of WSOC. Influences of NaOH extracted humic substances were particularly focused on. Sediments were sampled from two cross-sections of the middle Yellow River and sieved into three size fractions (< 63 μm, 63–100 μm, and 100–300 μm). The total concentration of WSOC in sediments (C_{WSOC}) and k were estimated using multiple water-sediment ratio experiments. Results showed that C_{WSOC} ranged from 0.012 to 0.022 mg/g, while k ranged from 0.8 to 3.9 L/kg. Correlations between the spectrum characteristics of NaOH extracted humic substances and k were analyzed. Strong positive correlations are determined between k and the aromaticity indicators of NaOH extracted humic substances in different sediment size fractions. Comparing with finer fractions (< 63 μm), k is higher in larger size fractions (63–100 μm and 100–300 μm) related to higher aromaticity degree of NaOH extracted humic substances mostly. While negative relationship between k and the area ratio of fourier transform infrared spectroscopy (FT-IR) at 3400 and 1430 cm^{-1} implied that the lowest k was related to the highest concentration of acidic humic groups in particles < 63 μm. WSOC in finer fractions (< 63 μm) is likely to enter into pore water, which may further accelerate the transportation of aquatic contaminants from sediment to water.

Key words: humic substances; water soluble organic carbon; partitioning; sediment

Introduction

The total organic carbon in sediments includes both water soluble organic carbon (WSOC) and water insoluble organic carbon (WIOC) (Hishi *et al*., 2004; Akkanen *et al*., 2005). The interaction of hydrophobic contaminants and trace metals with WSOC in pore water may reduce the sorption of hydrophobic contaminants and trace metals to the sediments, e.g., third-phase effects (Fauser and Thomsen, 2002) and solution-phase complexing (Kim *et al*., 1999), resulting in increasing contaminant mobility (Cho *et al*., 2002) and decreasing contaminant bioavailability (Akkanen and Kukkonen, 2001). Moreover, for rivers with a high content of sediments in China, WSOC could also affect the COD monitoring and result in an exaggerated COD value (Ni *et al*., 2007). Therefore, characterizing the partitioning of WSOC between sediment and water phases is essential to well understand water quality and the environmental fate of aquatic pollutants (Kögel-Knabner and Totsche, 1998; Tao and Lin, 2000).

Many previous publications have investigated the partitioning characteristics of WSOC using a variety of sorbents including clay, quartz, metal oxides and so on (Kalbitz *et al*., 2000b; Kaiser *et al*., 2000). Few of them have focused

on the effects of sediment size fractions. However, grain size is important for the deposition process of sediments (Chang *et al*., 2007). Some researchers (Stone and Droppo, 1996; Wang *et al*., 2001; Rockne *et al*., 2002) have revealed that the concentration of sediment organic carbon in different sediment size fractions varied greatly, which could further affect the distribution and partitioning of the hydrophobic organic pollutants. Ni *et al*. (2007) also reported that the partitioning coefficients of WSOC varied in different sediment size fractions.

To fully understand the behaviors of aquatic persistent organic pollutants, studies on the inherent mechanisms of how sediment grain size affect the partitioning of WSOC are required. Among sediment organic compositions, NaOH extracted humic substances (including fulvic acids and humic acids) are main sources of WSOC and have important influences on the water solubility of sediment organic matter (Maie *et al*., 2004; Shirshova *et al*., 2006). Therefore, this research also focused on the effects of the NaOH extracted humic structures on the partitioning coefficients of WSOC in three size fractions (< 63 μm, 63–100 μm, and 100–300 μm) of sediments collected from the Yellow River.

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1 Materials and methods

1.1 Sediment samples and characteristics

Surface sediments (0–20 cm) were sampled from two cross-sections, Tongguan (TG, 34°56′67″N, 110°25′00″E) and Sanmenxia (SMX, 34°50′00″N, 111°21′21″E), in the Middle Yellow River in high flow period (August, 2004). Four sampling sites were set for each crosssection. The collections at the same crosssection were mixed and air dried to obtain representative samples. Most (> 99%) size fractions of the collected sediments were ⩽ 300 μm. Physico-chemical properties of coarse fractions (⩾ 100 μm), eroded into the Middle Yellow River in flood season, are quite differnt with silt fractions (Yan *et al.*, 2007). Silt and clay fractions (< 63 μm) could be suspended and are usually used to investigate transportantion of aquatic contaminants (Chen *et al.*, 2000). Therefore, collected sediemnts were sieved into three size fractions (100–300 μm, 63–100 μm, and < 63 μm). A total of six types of sediment samples were obtained, including TG1 (100–300 μm), TG2 (63–100 μm), TG3 (< 63 μm), SMX1 (100–300 μm), SMX2 (63–100 μm), and SMX3 (< 63 μm). The mineral composition of the sediment was analyzed using Dmax 2400 X-Ray diffractometer (Rigaku, Japan). The concentration of the total organic carbon (TOC) in sediment was analyzed by a CHN analyzer (Elementar Vario EL, Germany) using dried and homogenized sediments, which were first acidified using 10% HCl overnight to remove carbonate and then dried at 60°C.

1.2 Multiple water sediment ratio experiments

Deionized water was used for the multiple water sediment ratio experiments in laboratory. Batch equilibrium experiments were conducted in 150 mL bottles with 0.01 mol/L NaNO$_3$ controlling the ionic strength of the solution and pH was adjusted to 8.0, which is similar to average natural environmental parameters of the Middle Yellow River. Water sediment ratio ranged from 2.5:1 to 50:1 calculated according to their mass weight at fixed water volume of 100 mL. The prepared samples were shaken at room temperature (25 ± 1°C) for 4 h and maintained for 20 h. After equilibration, supernatant was separated using a 0.45-μm glass fibre membrane. The equilibrium concentration of WSOC in supernatant was determined using Multi 3000 TOC/TN analyzer (Analytik Jena, Germany).

1.3 Humic substances extraction

The humic substances in sediments were extracted using 0.1 mol/L NaOH (containing humic acid (HA) and fulvic acid (FA)) as recommended by International Humic Substances Society (IHSS) (Schnitzer, 1982). The NaOH extracted humic substances are mixtures of HA and FA solutions, which are not further separated from each other. The NaOH extracted humic solutions were stored in refrigerator at 4°C and part of the extractions were freezedried to solids and stored in refrigerator also. The concentration of the NaOH extracted humic substances in terms of organic carbon (OC) in solutions were determined using Multi 3000 TOC/TN analyzer. The contents of the NaOH extracted humic substances (as carbon content per unit mass of sediment, $C_{H\text{-}Na}$) and the proportions of the NaOH extracted humic substances to the total organic carbon ($C_{H\text{-}Na}/C_T$) in different sediment samples were also estimated.

1.4 Humic substances characterization

UV-Vis spectra of the NaOH extracted humic substances were carried out using UV-Visible spectrophotometer (SPECORD 200, Analytik Jena, Germany) in a 1-cm quartz cell. The specific UV absorptivity at 285 nm (ABS$_{285}$) was calculated to estimate the aromaticity of the extracted humic substances (Kalbitz *et al.*, 2000a).

The FT-IR spectra of the freeze dried NaOH extracted humic substances were recorded using KBr pellets with a VECTOR22 FT-IR spectrometer (Bruker, Germany) scanning over the frequency range from 4000 to 400 cm^{-1}. The KBr pellets were obtained by pressing 8000 kg/cm^2 during 1 min with a mixture of 1 mg extracted humic substances and 100 mg KBr (spectroscopy grade).

Excitation emission matrix fluorescence spectroscopy (EEM) of the NaOH extracted humic substances were carried out using a Hitachi F-4500 Fluorescence Spectrometer (Japan). Solutions were irradiated in a 1-cm path length fused silica cell at 20 ± 1°C. EEM was collected when excitation wavelengths ranged from 200 to 500 nm and emission wavelengths from 210 to 700 nm with increment of 5 nm. The spectra were obtained by subtracting Milli-Q water (Millipore) blank spectra, recorded under the same conditions, to eliminate water Raman scatter peaks. The original organic carbon concentrations of the extrations from different samples are 0.68, 0.50, 0.38, 5.60, 2.40, and 2.00 mg/L for TG1, TG2, TG3, SMX1, SMX2, and SMX3, respectively. To eliminate concentration effects on the resultant EEM, the concentrations of NaOH extracted humic solutions for all samples were diluted to 0.30 mg/L, and pH was controlled to 13.5.

1.5 Calculation of the total concentration and partitioning coefficient of WSOC

According to the definition of WSOC, the total concentration of WSOC includes those sorbed on particles and those dissolved in interstitial pore water when sorption desorption equilibrium is reached (Cao *et al.*, 1999; Tao and Lin, 2000).

$$C_{WSOC} = q_e + C_e \times R \qquad (1)$$

where, C_{WSOC} (mg/g) is total concentration of the entire pool of WSOC in sediments; q_e (mg/g) and C_e (mg/L) are the equilibrium WSOC concentration in sediment and in water, respectively; R (L/g) is water sediment ratio.

The partitioning mechanism is dominated by the non-specific hydrophobic sorption and described by the linear type isotherm (Tao and Lin, 2000; Ni *et al.*, 2007), which

can be expressed as Eq. (2).

$$q_e = k \times C_e \qquad (2)$$

where, k (L/kg) is the partitioning coefficient of WSOC. Combining Eq. (1) and Eq. (2), we obtain Eq. (3).

$$C_e = \frac{C_{WSOC}}{k + R} \qquad (3)$$

Statistic 6.0 (StatSoft, USA) was used to estimate the parameters of C_{WSOC} and k with 95% confidence level according to Eq. (3) (Ni *et al.*, 2007).

2 Results and discussion

2.1 Sediment characteristics

The physico-chemical properties of the collected sediments are summarized in Table 1. For sediments from both TG and SMX, TOC contents range from 1.06 to 4.13 mg/g by dry weight. The proportions of the NaOH extracted humic substances to TOC ($C_{H\text{-}Na}/C_T$) range from 0.6% to 3.2% and 2.4% to 16.8% for TG and SMX sediments, respectively. $C_{H\text{-}Na}/C_T$ decreases with decreasing sediment grain size, following the order: TG1 > TG2 > TG3 and SMX1 > SMX2 > SMX3. It implies that the total concentration of the soluble humic substances is decreasing with decrease of the sediment size fractions, which is mainly attributed to the increasing interaction of clay mineral and the sediment organic matter in finer fractions (Wang *et al.*, 2001; Guggenberger and Kaiser, 2003).

2.2 Concentration and partitioning variations of WSOC

As shown in Table 2, the C_{WSOC} for TG and SMX range from 0.012 to 0.022 mg/g, accounting for 0.3%–2.0% of the TOC in sediments (C_{WSOC}/C_T). C_{WSOC} is less enriched in silt and clay fractions (< 63 μm) than larger size fractions (63–100 μm and 100–300 μm). The similar order of the C_{WSOC}/C_T and $C_{H\text{-}Na}/C_T$ in different sediment size fractions may suggest the contribution of the NaOH extracted humic substances to WSOC. On the other hand, fractions (< 63 μm) have higher WIOC than other fractions, which may result in higher aquatic contaminants sorbed onto the fractions.

The partitioning coefficient (k) of WSOC range from 2.4 to 3.9 L/kg for TG sediments and from 0.8 to 1.5 L/kg for SMX sediments, as the order: TG1 > TG2 > TG3 > SMX1 > SMX2 > SMX3. WSOC in finer fractions (< 63 μm) has the lowest k value.

In flood season, large amounts of sediemnts are eroded into the Middle Yellow River, and most of contaminants are sorbed onto sediemnts (Zhao *et al.*, 1998). Secondary pollution would happen when envrionmental conditions change (Segura *et al.*, 2006). WSOC in finer fractions (< 63 μm) enters into pore water, which may further accelerate the transportation of aquatic contaminants from sediment to water. Meanwhile, finer sediment fractions (< 63 μm) could be transported to lower reaches of the Yellow River and thus become potential pollution sources.

2.3 UV absorptivity of the humic substances

Generally, ABS_{285} increases with the increase of the aromatic composition in humic substances and becomes the indicator of the aromaticity of the humic substances (Kalbitz *et al.*, 2000a; Veeken *et al.*, 2000). As shown in Fig. 1, ABS_{285} of the NaOH extracted humic substances is in the order of TG1 > TG2 > TG3 > SMX1 > SMX2 > SMX3, which implies the higher aromaticity of the NaOH extracted humic substances in the larger size fractions of the collected sediment samples.

The k value of the WSOC in Fig. 2 shows a relatively strong positive correlation ($R^2 = 0.899$) with ABS_{285} (the UV absorptivity at 285 nm) of the NaOH extracted humic substances in different sediment samples. It suggests that the abundance of aromatic rings in the humic substances is of great importance to the reservation of the WSOC on sediment.

Table 2 Concentration and partitioning variations of water soluble organic carbon

Sample	C_{WSOC} (mg/g)	k (L/kg)	C_{WSOC}/C_T (%)	R^2
TG1	0.021	3.9	2.0	0.980
TG2	0.022	3.2	1.6	0.992
TG3	0.018	2.4	0.6	0.988
SMX1	0.014	1.5	0.8	0.995
SMX2	0.015	1.1	0.7	0.994
SMX3	0.012	0.8	0.3	0.990

C_{WSOC}: the total concentration of the whole pool of water soluble organic carbon in sediments; k: the partitioning coefficient of water soluble organic carbon between sediment and water phases; C_{WSOC}/C_T: the proportions of C_{WSOC} to the total organic carbon (TOC) in sediments.

Table 1 Physico-chemical properties of the collected sediments

Sample	Size fraction (μm)	TOC (mg/g)	$C_{H\text{-}Na}$ (mg/g)	$C_{H\text{-}Na}/C_T$ (%)	Mineral composition (%)									
					Montmor-illonite	Illite	Amphi-bole	Kaoli-nite	Chlo-rite	Quartz	Feld-spar	Plagio-clase	Cal-cite	Ddolo-mite
TG1	100–300	1.06	0.034	3.2	0.0	0.0	0.0	1.0	0.0	42.0	29.0	20.0	6.0	2.0
TG2	63–100	1.35	0.025	1.9	1.0	5.0	1.0	1.0	1.0	44.0	12.0	30.0	4.0	1.0
TG3	<63	3.15	0.019	0.6	2.0	9.0	2.0	3.0	1.0	33.0	17.0	26.0	5.0	2.0
SMX1	100–300	1.67	0.28	16.8	1.0	4.0	1.0	1.0	1.0	47.0	18.0	21.0	5.0	1.0
SMX2	63–100	2.27	0.12	5.3	1.0	9.0	2.0	3.0	1.0	44.0	13.0	22.0	4.0	1.0
SMX3	<63	4.13	0.10	2.4	2.0	11.0	1.0	2.0	1.0	39.0	12.0	27.0	4.0	1.0

$C_{H\text{-}Na}$: the concentration of the NaOH extracted humic substances in sediments; $C_{H\text{-}Na}/C_T$: the proportions of the NaOH extracted humic substances to the total organic carbon (TOC) in sediments.
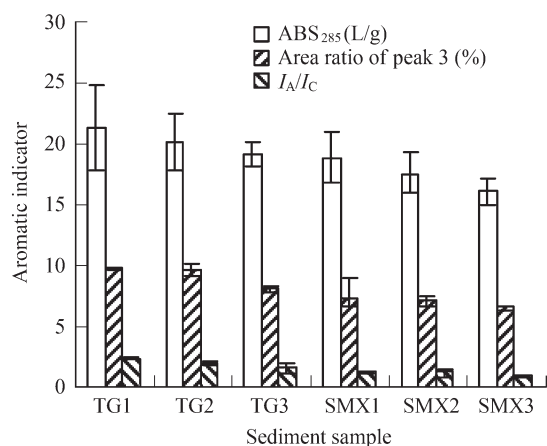
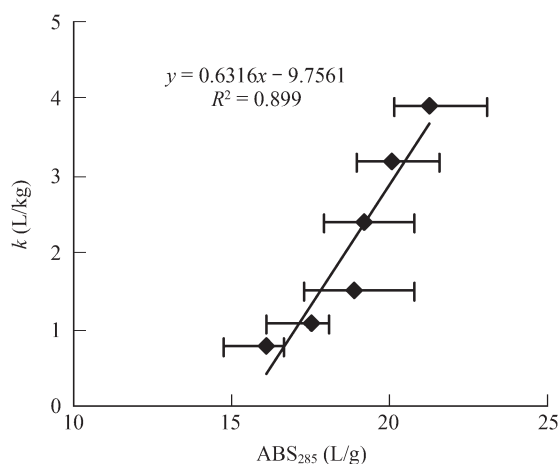**Fig. 1** Aromatic indicators of the NaOH extracted humic substances in the collected sediment samples.

Fig. 2 Partitioning coefficient (k) of water soluble organic carbon as a function of UV absorptivity at 285 nm (ABS285).

2.4 FT-IR characteristics of the NaOH extracted humic substances

The FT-IR spectra of the humic substances in different sediment samples show typical broad transmittance bands: (1) strong band around 3400 cm^{-1} (peak 1, from 3000 to 3700 cm^{-1}) corresponded to O–H stretching of hydroxyl groups from phenol and alcohol and/or carboxylic groups; (2) weak couple peaks at 2920 cm^{-1} and 2850 cm^{-1} (peak 2, from 2700 to 3000 cm^{-1}) caused by aliphatic C–H bonds; (3) medium band around 1620 cm^{-1} (peak 3, from 1550 to 1850 cm^{-1}) attributed to the C=C vibrations of aromatic structures and antisymmetrical stretching of COO$^-$; (4) strong band around 1430 cm^{-1} (peak 4, from 1200 to 1550 cm^{-1}) attributed to C–H stretching of aliphatic or O–H stretching of phenolic and carboxylic groups; and (5) shoulder bands around 1050 cm^{-1} (peak 5, from 900 to 1200 cm^{-1}), attributed to C–O stretching polysaccharides or Si–O vibrations of clay impurities (Rivero *et al.*, 1998; Shin *et al.*, 1999; Ghita *et al.*, 2004; Li *et al.*, 2005).

The area ratio of FT-IR peak *i* (the integral area of peak *i*/the sum of five peak areas, *i* = 1, 2, 3, 4 or 5) was employed to characterize the functional groups of the NaOH extracted humic substances (Sun *et al.*, 2007a). The sum area ratio of peak 1 and peak 4 is associated with the contents of acidic functional group, such as carboxylic and phenolic group. The area ratio of peak 2 is associated with the contents of aliphatic group. The area ratio of peak 3 is associated with the contents of aromatic group. The area ratio of peak 5 is associated with the contents of clay impurities or polysaccharides. As illustrated in Fig. 3, the contents of aliphatic group (area ratio of FT-IR peak 2) and aromatic group (area ratio of FT-IR peak 3) are in the order of TG1 > TG2 > TG3 > SMX1 > SMX2 > SMX3, while contents of the acidic functional group (the sum of area ratio of FT-IR peak 1 and peak 4) follows the order: TG1 < TG2 < TG3 < SMX1 < SMX2 < SMX3.

The partitioning coefficient (k) of WSOC shows a strong positive linear correlation with the area ratio of peak 2
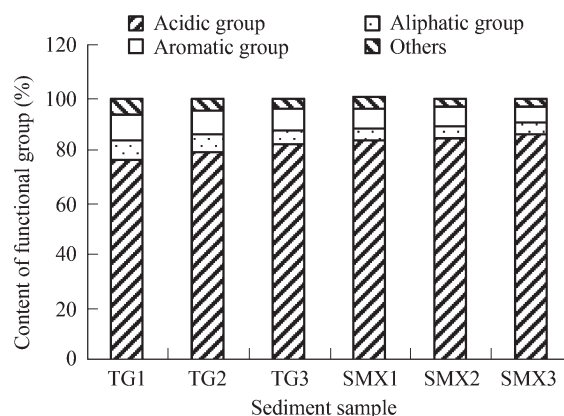

Fig. 3 Contents of functional groups calculated from FT-IR peaks of the NaOH extracted humic substances in the collected sediment samples.
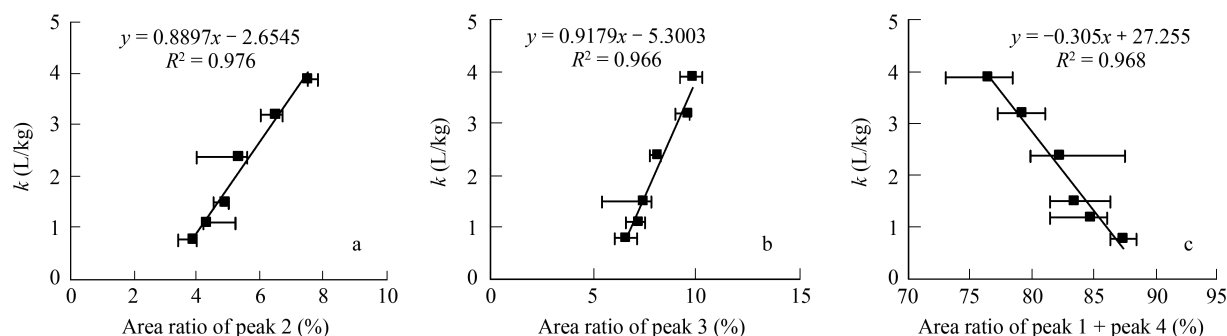

Fig. 4 Partitioning coefficient (k) of water soluble organic carbon as a function of area ratio of FT-IR peak.

(R^2 = 0.976, Fig. 4a), peak 3 (R^2 = 0.966; Fig. 4b) and a negative linear correlation with the sum of area ratio of peak 1 and peak 4 (R^2 = 0.968; Fig. 4c) of the NaOH extracted humic substances in the collected sediment samples.

The increase of the area ratio of peak 2 and peak 3 indicate the rising contents of the hydrophobic groups (aliphatic and aromatic groups) in the NaOH extracted humic substances (Benke et al., 1999). The positive linear relationships show in Figs. 4a and 4b suggest that hydrophobic humic groups with high molecular mass may lessen the release of WSOC from sediment to water phases, which agrees well with Fig. 1 and the work by Kögel-Knabner and Totsche (1998).

Chi and Amy (2004) have indicated that humic subatances with lower molecular weight fractions and higher acidic functional group density could have higher water solubility. The negative relationship of the acidic group (Fig. 4c) and the partitioning coefficient (k) of WSOC is resulted from the higher contents of the acidic functional group in the NaOH extracted humic substances in finer size fractions of the collected sediment samples.

2.5 EEM characteristics of the humic substances

EEM plots of the NaOH extracted humic substances in the collected sediment samples show two maxima fluorescent intensity related to peak A (UV humic compounds, centered at E_x 235–245 nm, E_m 420 nm) and peak C (visible humic compounds, centered at E_x 305–310 nm, E_m 400 nm) (Sun et al., 2007a). The fluorescent intensity ratio is associated with the molar mass distributions and structure features of the humic substances (Sun et al., 2007b; Parlanti et al., 2000; Patel-Sorrentino et al., 2002). As illustrated in Fig. 1, the relative fluorescent intensity of peak A and peak C (I_A/I_C) of the NaOH extracted humic substances, following the order: TG1 > TG2 > TG3 > SMX1 > SMX2 > SMX3.

As illustrated in Fig. 5, the partitioning coefficient (k) of WSOC shows a strongly positive linear correlation with I_A/I_C of the NaOH extracted humic substances (R^2

= 0.985). The higher I_A/I_C values may indicate higher molecular mass and higher aromatic degree of the humic substances (Sierra et al., 2005). The positive relationship suggests that soluble humic fractions with higher molecular weight and higher aromaticity exhibit higher affinities to the sediment organic matter, which is consistent with the conclusion of Chi and Amy (2004).

In general, Figs. 2, 4, and 5 agree well with each other. ABS_{285}, area ratio of FT-IR peak at 1620 cm^{-1} and I_A/I_C could be used to indicate the aromatic degree of the NaOH extracted humic substances. All these aromaticity indicators follow the same order (TG1 > TG2 > TG3 > SMX1 > SMX2 > SMX3) (Fig. 1) and are positively related with the partitioning coefficient (k) of WSOC (Figs. 2, 4b, and 5) in different size fractions of the collected sediment samples. The results suggest that lower water solubility (higher k values) of WSOC is associated with higher aromaticity of the NaOH extracted humic substances in larger size fractions of the collected sediment samples. Comparing Fig. 4 a, b, and c, it could be concluded that the finer sediment size fraction with higher concentration of small acidic functional group may be particularly prone to releasing WSOC to pore water under the certain condition.

The sediment size fractions varied in the process of sediment transport in the middle Yellow River, especially in changing from dry season to rainy season (Zhao et al., 1998). The results in this research could be used to further understand the redistribution of aquatic pollutions from different sediment size fractions in the Middle Yellow River. Finer sediment size fractions could release aquatic pollutants sorbed on WSOC easily, and thus the increase of their mobility is due to the acidic functional groups of the humic substances.

3 Conclusions

Three sedimnt size fractions (< 63 μm, 63–100 μm, and 100–300 μm) were used to investigate the influences of sediment grain size on the concentrations and partitioning coefficients (k) of water soluble organic carbon in sediments of the Middle Yellow River. Total water soluble organic carbon is less enriched in the silt and clay fractions (< 63 μm) than in the larger size fractions (63–100 μm and 100–300 μm) of the collected sediment samples, which is mainly attributed to the increasing interaction of clay mineral and sediment organic matter with the decrease of particle size. The partitioning coefficient (k) of water soluble organic carbon is highly affected by the chemical structures of the NaOH extracted humic substances in different sediment size fractions. Strong positive relationships between k and the aromaticity indicators of the NaOH extracted humic substances suggest that lower water solubility of the sediment organic carbon is associated with the higher aromatic groups in the larger size fractions (63–100 μm and 100–300 μm). The highest concentration of samll acidic groups of the NaOH extracted humic substances may result in the lowest k of water soluble organic carbon in silt and clay fractions (< 63 μm), which is prone to releasing WSOC to pore water under the certain condition.
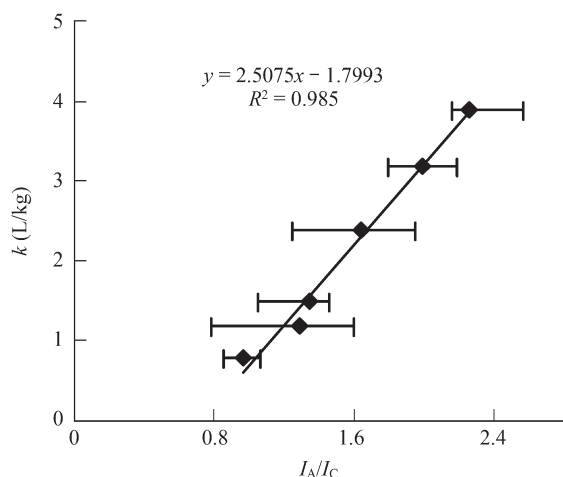

$$y = 2.5075x - 1.7993$$
$$R^2 = 0.985$$

Fig. 5 Partitioning coefficient (k) of water soluble organic carbon as a function of relative fluorescent intensity (I_A/I_C) of the NaOH extracted humic substances.

These results may help for further understanding of the mobility and bioavailability of the aqueous contaminants in sediments with different size fractions.

Acknowledgments

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