

Effect of Natural Aquatic Colloids on the Adsorption of Three Selected Endocrine Disrupting Chemicals by Sediments

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ABSTRACT

The interaction between colloids and three selected endocrine disrupting chemicals (EDCs) (bisphenol A (BPA), 17 β -estradiol (E2), and 17 α -ethynylestradiol (EE2)) and its effects on EDCs adsorption by sediments were investigated using batch experiments. Water and sediment samples were collected from the middle-low reaches of the Yellow River, and aquatic colloids were separated using cross-flow filtration. The results show that the EDCs adsorption by colloids and sediments are well described by linear, Freundlich, and Langmuir isotherms. In a EDCs-colloids system, the values of K_f , K_d and $K_L Q_{max}$ follow the order of BPA > EE2 > E2, indicating inorganic minerals in colloids have great contribution to EDCs adsorption due to the bridging of wetting layer induced by hydrophilic attraction. In a EDCs-colloids-sediments system, aquatic colloids promote the adsorption of EDCs by sediment significantly, and the increased degree of EDCs adsorption onto sediments is mainly related the total organic carbon content of the colloids. Moreover, K_f , K_d and $K_L Q_{max}$ are ordered in E2 > EE2 > BPA. The inorganic components of colloids are prone to associate with the minerals of sediments, so the interaction between EDCs and inorganic minerals of colloids are largely weakened. The present results highlight the importance of aquatic colloids on adsorption of organic pollutants onto sediments in natural rivers.

1. INTRODUCTION

Endocrine disrupting chemicals (EDCs), also known as environmental estrogens, are emerging as a major concern due to their negative effects on endocrine systems of human and wildlife (Watt et al, 2001; Staples 1998; Campbell 2006). EDCs could accumulate in fish, not only in the liver, but also in the muscle (Belfroid 2002). Kashiwada (2002) found that in recent forty years, the species of Japanese medaka declined a lot to almost extinction, largely because of the EDCs. Thereinto, bisphenol A (BPA) is mostly manufactured for the plastic industry and released as an intermediate in the production of polycarbonate plastics and epoxy resins (Sun 2005); 17 α -

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ethynylestradiol (EE2) and 17 β -estradiol (E2) are widely used in oral contraceptives and hormone replacement therapy (Sun 2010). They are commonly detected in natural waters (Barel-Cohen 2006; Hohenblum 2004). Even at concentration of low ng/L range (Harries 1997; Desbrow 1998), these compounds can be extremely potent. For example, less than 1 ng/L of EE2 can stimulate male rainbow trout to produce vitellogenin which was only supposed to be found in sexually mature females (Holthaus 2002). Mature male medaka can produce female specific proteins when exposed for 5 weeks to E2 higher than 5ng/L or BPA higher than 10 μ g/L (Kashiwada 2002).

Once released into surface water, EDCs can be adsorbed by sediments which affect the fate and bioavailability of EDCs (Lai 2000; Holthaus 2002). Adsorption of EDCs and factors affecting their adsorption behaviors have been widely studied (Lioret 2012; Kiran 2012; Brahima 2012; Wang 2012; Kim 2012; Sun 2005, 2007). Dobor (2012) investigated the adsorption of selected acidic drugs on river sediments and found that the adsorption amount was positively correlated with organic matter content (OM) and negatively correlated with pH. Wu (2011) pointed out that for sediments with lower OM (less than 8%), the adsorption amounts of microcystins decreased with increasing OM. Besides OM and pH, BPA adsorption could also be affected by temperature and salinity, and adsorption amount of BPA decreases with temperature and salinity (Xu 2008). Our previous study found that the adsorption amount of EDCs was related to both the dissolved organic carbon and total organic carbon of sediments, and the effects of ions were dependent on the valence of ions (Sun 2005). Among the studies about adsorption of organic pollutants onto sediments, however, the effect of natural aquatic colloids is seldom involved.

Aquatic colloids, generally defined as particles with a size between 1 nm and 1 μ m, are widespread in natural water systems (Khalid 2007; Zhou 2007). Because of their large surface areas and strong adsorption affinity, aquatic colloids are important carriers of organic pollutants (Gustafsson 2001; Liu 2005; Maskaoui 2007; Zhou 2007) and trace metals (Wang 2000; Guo 2002). The interactions between colloids and organic/inorganic pollutants have been widely studied (Avramenko, 2012; Adam 2012; Ohshima, 2004b; Chen 2000; Okamoto 2011; Škvarla, 2012; Hashmi 2012). Bao (2010) found that fine colloids (0.02-0.2 μ m) facilitated the transport of Cu through quartz sand. The adsorption behavior of EDCs to aquatic colloids from different origins varied a lot (Zhou 2007), and the colloidal interaction with pharmaceuticals was stronger than that with EDCs (Maskoui 2007). Generally, the adsorption behavior of colloids could be induced by hydrophilic attraction (Okamoto 2011) or van der Waals attraction (Škvarla, 2012). Moreover, ionization is another important factor to control colloids behavior (Hashmi 2012; Okamoto 2011), colloid surface can either attract or repel water at different degree of ionization (Ohshima, 2004a). Although the interactions between colloids and organic/inorganic pollutants are widely studied, little information on the effects of colloids on the adsorption of organic pollutants by sediments is available.

In this research, the interaction between colloids and three selected common EDCs (BPA, E2 and EE2), and the effect of colloids on the adsorption of EDCs by sediments were investigated. Water and sediment samples were collected from the Yellow River. The natural aquatic colloids were separated and characterized, and the underlying interaction mechanisms between colloids, EDCs and sediments were discussed. This

study is significant to understand and quantify the transport and fate of EDCs in natural waters.

2. MATERIALS AND METHODS

2.1. Materials and reagents

The three EDCs, BPA (98.5%), E2 (98%), and EE2 (99%), were all of analytical grade. BPA were purchased from Augsburg Company (Germany), while E2 and EE2 were from Sigma Company (USA). Stock solutions of the EDCs were prepared in methanol that was HPLC grade from J&K Chemical Company (Belgium). Water was supplied by a Milli-Q water purification system (Millipore, Bedford, MA, USA). Glassware was cleaned by a ultrasonic cleaner for at least 3 times, 20 min at one time, and then rinsed thoroughly with Milli-Q water before being muffled at 550 °C for 5 h.

2.2. Sample collection and storage

Water and sediment samples were collected from Huayuankou Station (Zhengzhou, China, 34°54'24"N 113°40'23"E) and Lijin Station (Dongying, China, 37°30'2"N 118°15'2"E) in the middle-low reaches of the Yellow River. After transported to the laboratory, sediments were mixed, air dried, and sieved to particles smaller than 63 µm (Chen 2000), then sealed in plastic bags and stored at room temperature. Water samples were placed in 25 L plastic buckets and stored at 4 °C in a refrigerator.

Chemical, mineral and organic carbon content of the sediment was detected using ICP (Jarrell-Ash, ICAP-9000, America), X-ray diffractometer (PE983G, America) and Multi 3000 TOC/TN analyzer (Analytik Jena, Germany). The sediment organic carbon content is 1.43 mg/g; The content of mineral components (%) are montmorillonite 1.0, chlorite 2.5, kaolinite 4.0, illite 11.0, quartz 31.5, feldspar 11.0, plagioclase 27.5, calcite 6.0, dolomite 2.0 and Hopfnerite 3.5; The contents of different chemical components (%) are listed as follows, CaO 5.518, MgO 1.494, K₂O 1.999, Na₂O 2.014, SiO₂ 70.580, Al₂O₃ 7.115, MnO 0.164, P₂O₅ 0.103, Fe₂O₃ 3.814.

2.3. Colloids separation and characterization

After sedimentation, the water samples were processed by cross-flow filtration (CFF) whose main part was polysulphone membrane with pore size of 0.003 µm (5 kDa) to isolate the colloids (Guéguen 2002). Filtered through the membrane, the retentate flow was guided back to the feed container, while the permeate flow was directed to a collector. This process would continue until the ratio of the initial feed volume to the retentate volume was about 10.

With this process, two kinds of water samples were obtained, namely: (i) colloidal water (C), the ultima retentate part of the CFF process; (ii) truly dissolved water (D), the permeate part of the CFF process. Both two kinds of water samples were stored at 4 °C for further analysis.

TOC for C and D were measured immediately after ultra-filtration using a TOC 5000A analyzer (Shimadzu, TOC-VCPN). Element concentrations in different fractions were determined by ICP-OES (Prodigy, Leeman, USA) for K, Na, Ca, Mg and Si or ICP-MS (Thermo X2, Thermo Fisher, USA) for Al, Fe, Zn and As. Acid digestions were performed prior to the elements analysis using ultra-pure concentrated nitric acid to

acidify the subsamples of all fractions to pH 2 (Ren 2010), and procedural blanks were included to check for ambient or reagent contamination. All the measurements above were done in duplicate. XPS analysis was performed on a Kratos AXIS Ultra (Kratos Analytical, UK) with a monochromatic Al X-ray source at 150W. To compensate for surface charge effects, binding energies were calibrated using C 1s hydrocarbon peak at 284.80 eV.

Dried under 80 °C, the dry weights of D and C from two stations were measured and the colloids content were calculated as the difference between the dry weights of C and D.

2.4. Adsorption experiments

Batch experiments were conducted in the single solution of BPA, E2 and EE2 to the Yellow River sediment in C and D, respectively. A 0.5 g sediment sample and 50 mL prepared water sample (C or D) were added into a series of Teflon centrifuge tubes, and different amount of BPA, E2, or EE2 was then spiked. The initial concentration was in the range of 0.4-2.4 mg/L for these three EDCs. Duplicate and blank experiments were conducted at the same time. After being shaken for 20 h at 25 °C (Xu 2007a), the slurries were centrifuged for 15 min at 4000 rpm. The EDCs concentration in the supernatants was detected by Liquid Chromatograph-tandem mass spectrometry (LC-MS/MS).

2.5. LC-MS/MS analysis

BPA, E2, and EE2 were quantified by a HP 1100 LC/MSⁿ Trap SL System consisting of a series of 1100 HPLC and an ion trap mass spectrometer equipped with electro-spray interface (ESI). HPLC was performed using a Zorbax Eclipse XDB-C18 (150×2.1mm) reversed-phase column. BPA, E2, and EE2 were eluted with water-methanol mixtures of 3:7, 1:4, 1:3 in periods of 6.50 min, 7.00 min, and 6.00 min, respectively, and the flow rates were 0.18 mL/min, 0.18 mL/min, and 0.20 mL/min, respectively. The analytical condition was tested and adjusted based on our previous studies (Liu 2009; Sun 2007). The detailed ion trap MSD conditions for the BPA, E2 and EE2 were given in Sun (2005, 2007). The correlation coefficients of the calibration curves generated using linear regression analysis were all higher than 0.99. The EDCs concentration in blank samples (processed river water and sediment) was under detection limit.

2.6. Fluorescence Spectrograph

An F-4500 Fluorescence Spectrograph (Varian, the USA) was used to record the fluorescence spectra and quantify the interactions between colloids and the EDCs. A 450-W Xenon lamp was used as the excitation source. Excitation/emission matrix (EEM) were collected every 5 nm over an excitation range of 200-450 nm, with an emission range of 250-600 nm by 5 nm. The spectra were obtained by subtracting Milli-Q water blank spectra, recorded under the same conditions, to eliminate water Raman scatter peaks. The data were processed with SigmaPlot 10.0 software to obtain the fluorescence contour plots of the water samples. The fluorescence intensities of BPA, E2, and EE2 were all determined at Ex/Em= 280 nm/310 nm.

2.7. The EDCs adsorption isotherms

The sorption data were described by the three types of sorption isotherms as follows. The linear adsorption isotherm:

$$Q_{eq}=K_d C_{eq} \quad (1)$$

The Freundlich isotherm:

$$Q_{eq}=K_f C_{eq}^n \quad (2)$$

The Langmuir isotherm:

$$Q_{eq}=K_L Q_{max} C_{eq}/(1+K_L C_{eq}) \quad (3)$$

Where Q_{eq} is the amount of EDCs retained on the sediment ($\mu\text{g g}^{-1}$); C_{eq} is the aqueous equilibrium concentration of the EDCs (mg L^{-1}). K_d (L kg^{-1}) is the distribution coefficient of the linear adsorption isotherm. K_f ($10^{-6} (\text{mg L}^{-1})^{-n}$) is the Freundlich distribution coefficient and n is empirical constant of the Freundlich describing the degree of nonlinearity (Xu 2007a, 2007b; Wu 2011). K_L (L mg^{-1}) is a constant related to the adsorption affinity, and Q_{max} ($\mu\text{g g}^{-1}$) is the maximum sorption amount of EDCs adsorbed onto the sediment.

3. RESULTS AND DISCUSSION

3.1. Properties of water samples

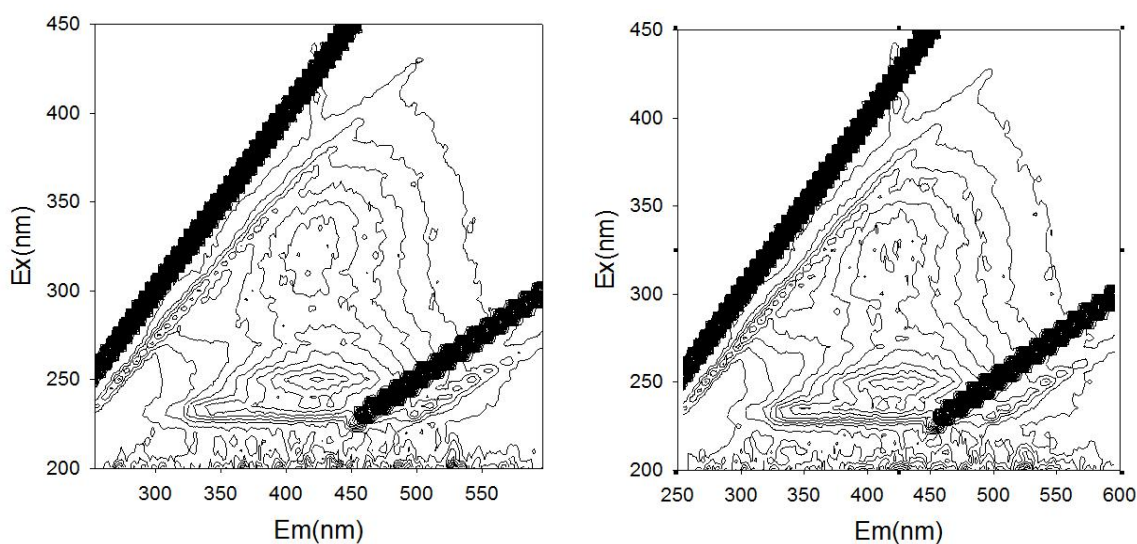
The properties of D and C of the Huayuankou station (HS) and the Lijin station (LS) were shown in Tab.1. In general, the concentrations of TOC, Ca, SiO_2 , Al, and Fe are much higher in C than those in its corresponding D. Guo (2011) also observed big differences in concentrations of Fe, DOC, and Al between 0.45 μm filtered and 5 KDa ultrafiltered samples, suggesting that they mainly exist as colloids. For example, more than 75% of Fe was associated with colloids with grain sizes between 5 KDa to 0.45 μm (Guo 2011). The colloids concentrations of HS and LS are 42.0 mg/L and 103.5 mg/L respectively, suggesting that colloids content in water sample of LS is much higher than that of HS. Calculated from Tab.1, the total colloids organic carbon (TCOC) concentrations in water samples are 0.40 mg/L for HS and 0.51 mg/L for LS, and the colloids organic carbon (COC) contents (per unit dry weight of colloids) are 9.5 mg/g for HS and 4.9 mg/g for LS, respectively. Terrestrial river born dissolved organic matter is dominated by colloidal macromolecules (Guéguen 2002). In the present study, about 87% and 42% of DOC is colloidal organic matters for HS and LS, respectively.

Tab.1 Properties of D and C from the Huayuankou station and the Lijin station of the Yellow River

	Huayuankou Station (HS)		Lijin Station (LS)	
	D	C	D	C
pH	8.24	8.37	8.26	8.35
TOC (mg/L)	0.06	0.46	0.7	1.21
Colloid content (mg/L)		42		103.5
TCOC (mg/L)		0.40		0.51
COC (mg/g)		9.5		4.9
Conductivity ($\mu\text{S/cm}$)	948	974	1080	919

Element concentration				
K (mg/L)	3.94	4.20	3.57	6.18
Na (mg/L)	88.74	104.49	90.65	84.98
Ca (mg/L)	70.86	77.32	74.68	82.98
Mg (mg/L)	30.68	30.03	31.04	33.40
SiO ₂ (mg/L)	2.77	2.89	1.28	1.59
Al (μg/L)	0.82	0.80	0.76	9.53
Fe(μg/L)	0.90	1.08	1.00	6.25
Zn(μg/L)	0.78	0.30	0.26	0.49
As(μg/L)	1.44	3.81	2.26	2.99

To further characterize the properties of different water samples, the fluorescence EEMs for D and C were detected. All the samples presented three main regions of different intensities (Fig. 1). The first peak, centered at Ex/Em = 235 nm/400-420 nm, is attributed to humic-like hydrophobic acid fraction (Hudson 2007; Barker 2009). The fluorophores responsible for the second peak (Ex/Em = 250-255 nm/420-430 nm) and the third peak (Ex/Em = 315-330 nm/400-425 nm) have already been recognized as typical fulvic-like acid (FA) (Baker 2001; Sierra 2005) (Tab. 2). The relatively higher intensities of these two fluorescence peaks indicate that FA is the main organic components in the water samples. The intensities of the three peaks are in the same order of C>D (Tab. 2) for samples from HS and LS. Moreover, the samples from LS (Fig. 1 c and d) demonstrated higher fluorescence intensities than those from HS, which is consistent to their TOC concentrations (Tab. 1).



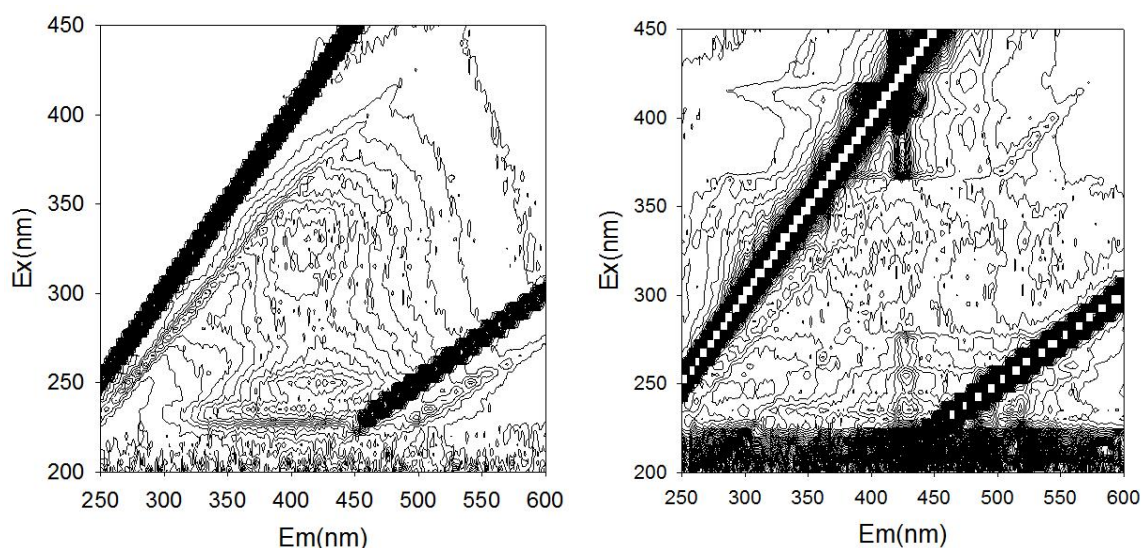


Fig. 1 Fluorescence EEMs of D and C. (a) D and (b) C of the Huayuankou station, (c) D and (d) C of the Lijin station

Tab. 2 Fluorescence intensities of D and C of the Huayuankou station (HS) and the Lijin station (LS) of the Yellow River

Sample		Peak 1		Peak 2		Peak 3	
		Ex/Em(n m/nm)	intens ity	Ex/Em(n m/nm)	intens ity	Ex/Em(n m/nm)	intens ity
HS	D	235/405	26.65	250/425	46.60	320/415	29.13
	C	235/410	43.85	250/430	50.17	315/420	32.56
LS	D	235/420	41.25	250/425	54.71	325/420	41.23
	C	235/430	71.78	255/430	68.53	330/425	41.97

3.2. Interactions between colloids and EDCs

Fig. 2 displays the positive linear correlation of fluorescence intensity with the EDCs initial concentration in different aquatic systems ($R^2 > 0.99$). Obviously, the fitted lines of D and C from HS are close to each other. This indicates the adsorption of EDCs by colloids in the water samples from HS is minute. However, the lines are clearly separated for samples from LS, suggesting great adsorption of EDCs by colloids from LS (Hudson 2007). This may result from its higher colloid content as demonstrated in Tab. 1.

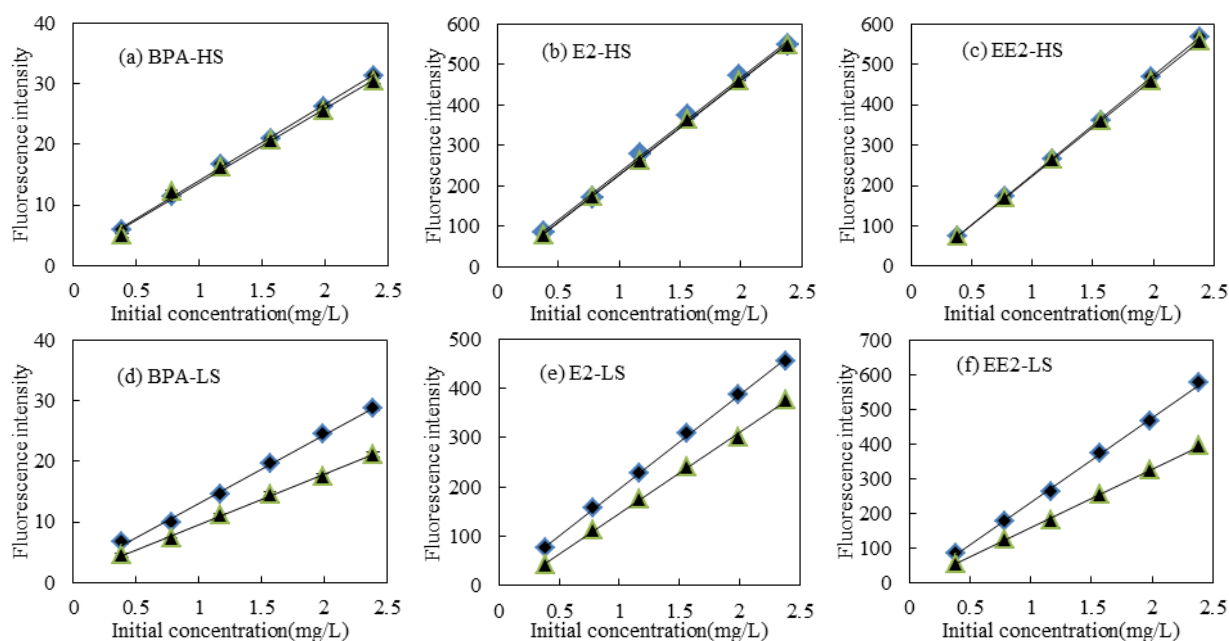


Fig. 2 The fluorescence intensities of EDCs in D (◆) and C (▲) from HS and LS of the Yellow River

The EDCs adsorption amount by colloids was calculated using D curves (the linear correlation between fluorescence intensity and EDCs concentration in D) as the corresponding standard curves (Fig. 3). It is evident that the adsorption amounts of EDCs by colloids from LS are much higher than those from HS. The sorption parameters, calculated from the three proposed models (equation (1)-(3)), are provided in Tab. 3. The results show that the experimental data could be well described by these three models with $R^2 > 0.95$. The Freundlich constant parameter n ranged from 0.78 to 1.01 for C of HS and from 0.87 to 1.17 for C of LS, suggesting that the nonlinearity of the sorption isotherms is not very strong (Wu 2011).

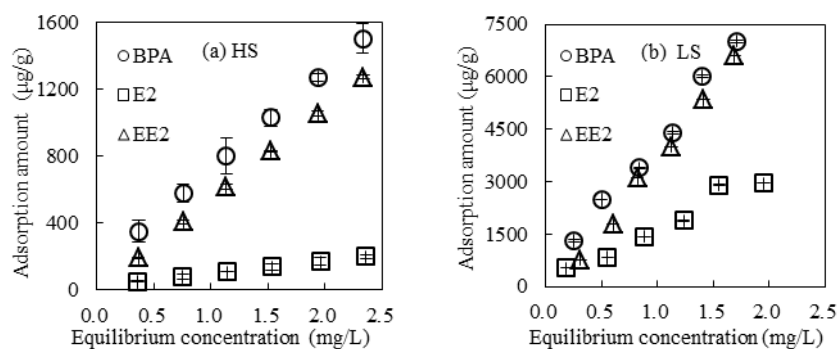


Fig. 3 Adsorption isotherms of BPA, EE2 and E2 by colloids from (a) HS and (b) LS of the Yellow River

The values of the distribution coefficients (K_d and K_f) and sorption coefficients ($K_L Q_{max}$) (Tab.3) are one magnitude higher for LS than those for HS. As shown in Tab.

1, minor difference in TCOC between HS and LS was observed (0.40 mg/L and 0.51 mg/L), so the TCOC may not be the key factor for the great differences in K_d , K_f , and $K_L Q_{\max}$. This indicates that besides the organic components, the inorganic minerals of the colloids may also have great contribution to the EDCs adsorption by colloids. Emmerik (2003), in the study of adsorption of E2 by clay minerals, found that the adsorption capacity of minerals could be significant especially montmorillonite, and the bond is tight because of E2 adsorbed into interlayer regions, stacks or particle aggregates (Morrissey 1999). Wu (2011) found that minerals could be the dominant factor controlling the adsorption of microcystins in the case of low organic matter content (i.e., less than 8%), with the mechanisms of cation bridging, hydrogen-bonding and surface electrostatic interactions (Silva 2009; Yuan 2001). Especially, polyvalent cations of minerals can act as a bridge (Sun 2005; Silva 2009; Sharma 2010; Yuan 2001) between selected EDCs and organic matters. In the absence of divalent and trivalent cations (such as Fe, Ca, Mg, Al), the adsorption capacity of colloids/sediments could be reduced significantly (Sharma 2010; Sun 2009; Lai 2000; Yuan 2001). In addition, mineral surface hydroxyl groups (e.g. Si-OH and Al-OH) play relatively major roles to interact with carboxyl or phenol groups of EDCs (Wu 2011; Tipping 2002; Guo 2011).

Tab. 3 Sorption parameters for EDCs onto colloids from HS and LS of the Yellow River

Sample		Linear		Freundlich			Langmuir	
		K _d (L kg ⁻¹)	R ²	K _f × 10 ⁶ ((mg L ⁻¹) ⁻ⁿ)	n	R ²	K _L Q _{max} × 10 ⁶ (L mg ⁻¹)	R ²
HS	BPA	668.88	0.977	736.13	0.83	0.998	830.70	0.995
	EE2	545.29	1.000	540.79	1.01	1.000	483.15	1.000
	E2	88.75	0.954	101.02	0.78	0.997	120.19	0.990
LS	BPA	4054.70	0.961	4199.02	0.87	0.971	4693.26	0.967
	EE2	4013.60	0.974	3829.50	1.17	0.987	3640.46	0.973
	E2	1627.30	0.950	1670.64	0.93	0.952	1766.92	0.952

The values of the distribution coefficients (K_d and K_f) and sorption coefficients ($K_L Q_{\max}$) all follow the same order of BPA > EE2 > E2, which is contrary to the order of octanol-water partition coefficient K_{ow} , BPA < EE2 < E2 (Lai 2000; Machatha 2005). This also suggests that different binding mechanisms other than nonspecific hydrophobic interaction play an important role in EDCs adsorption by colloids (Liu 2005; Maskouei 2007; Gong 2011). Hydrophilic matters could induce a completely wetting layer, the bridging of which could amplify the interactions between colloids and organic pollutants (Okamoto 2011). Because the polarity order of the EDCs is in order of BPA > EE2 > E2, there would be more specific binding (e.g., hydrogen bonding) sites for BPA than EE2 and E2.

3.3. Effects of the colloids on the EDCs adsorption by sediments

The adsorption isotherms of EDCs by sediments are shown in Fig. 4. Obviously, the aquatic colloids enhance the EDCs adsorption by sediments. The adsorption data could

be well described by the three proposed models with $R^2 > 0.91$ (parameters shown in Tab. 4). The values of n are generally larger than those in Tab. 3, indicating stronger and more consistent nonlinearity (Wu 2011).

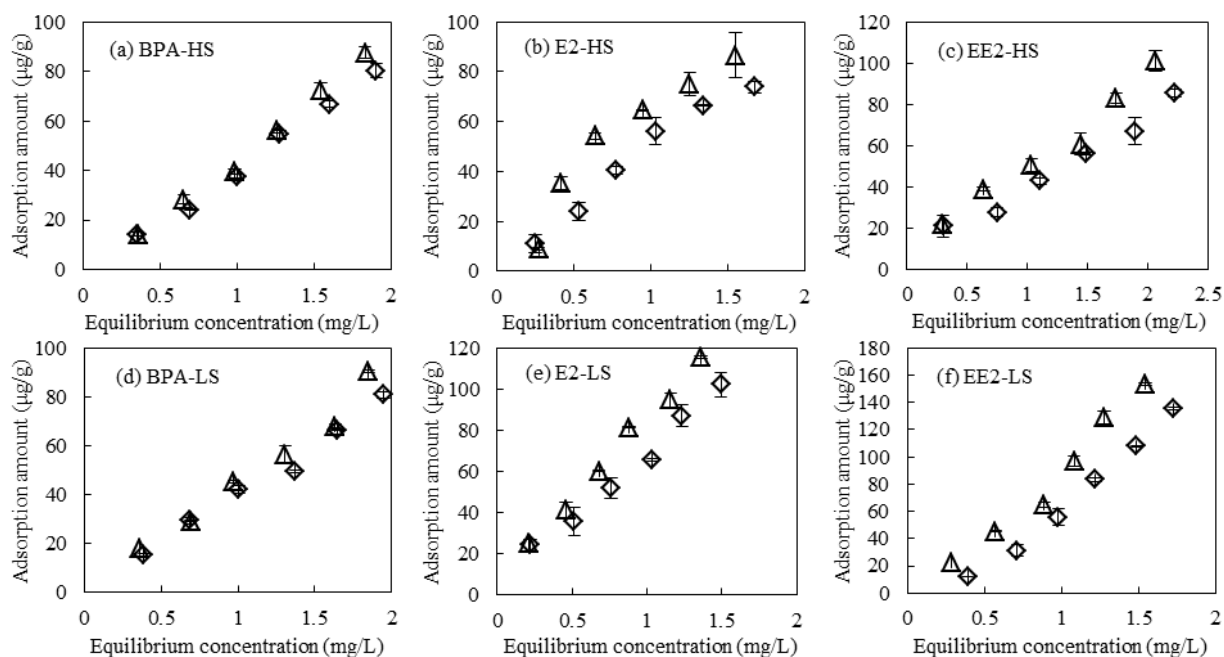


Fig. 4 Adsorption isotherms of BPA, E2 and EE2 to sediments in D (◇) and C (Δ) of HS and LS of the Yellow River

Tab. 4 Adsorption parameters for EDCs onto sediments in D and C of HS and LS of the Yellow River

Samples			Linear		Freundlich			Langmuir	
			K_d ($L\ kg^{-1}$)	R^2	$K_f \times 10^6$ ($(mg\ L^{-1})^{-n}$)	N	R^2	$K_L\ Q_{max} \times 10^6$ ($L\ mg^{-1}$)	R^2
D	HS	BPA	39.93	0.983	39.41	1.12	0.994	34.61	0.987
		EE2	38.67	0.966	39.80	0.89	0.969	40.34	0.964
		E2	48.00	0.965	49.14	0.90	0.972	57.62	0.978
	LS	BPA	40.32	0.984	40.11	1.01	0.984	43.83	0.984
		EE2	69.50	0.912	57.96	1.57	0.997	57.69	0.912
		E2	68.42	0.973	69.22	0.92	0.976	71.69	0.974
C	HS	BPA	45.68	0.985	43.08	1.16	0.996	46.16	0.984
		EE2	47.79	0.954	50.77	0.87	0.964	53.03	0.957
		E2	61.85	0.876	63.99	0.78	0.921	91.89	0.937
	LS	BPA	45.30	0.972	44.42	1.05	0.974	49.26	0.972
		EE2	90.11	0.934	86.54	1.53	0.973	93.42	0.952
		E2	91.85	0.9779	86.77	0.87	0.991	101.50	0.989

The ratios of $K_d(C)/K_d(D)$, $K_f(C)/K_f(D)$, and $K_L Q_{\max}(C)/K_L Q_{\max}(D)$ were used to assess the increased degree of EDCs adsorption induced by colloids in the present study. The $K_d(C)/K_d(D)$ values range from 1.14 to 1.29 for HS and vary from 1.12 to 1.34 for LS. This indicates that no evident differences in the effect of colloids between LS and HS were observed. Similar conclusion can be drawn from the $K_f(C)/K_f(D)$ and $K_L Q_{\max}(C)/K_L Q_{\max}(D)$ values. However, as shown in Fig. 3 and Tab 3, great differences in EDCs adsorption by colloids between LS and HS were observed. Such a deviation may indicate that the sorption mechanism of EDCs adsorption by sediments may differ from that by colloids.

Fig. 4 and Tab. 4 also display that the adsorption amount of EDCs in D of LS are observably greater than those in D of HS. This may result from its higher ionic strength (the conductivity of D-HS and D-LS are 948 and 1080 $\mu\text{S}/\text{cm}$, respectively). Ocwieja (2011) demonstrated that the maximum coverage of particle monolayer on PAH modified mica exceeded 0.39 for higher ionic strengths ($I = 3 \times 10^{-2} \text{ M}$). Urena-Amate's (2005) study showed that the Freundlich parameter K_f ranged from $2.31 \times 10^3 \text{ mg kg}^{-1}$ in pure water solution to $3.31 \times 10^3 \text{ mg kg}^{-1}$ in 0.1M KCl solution. The salt ions could attract the polarizable water molecules around themselves, making the solution more polar and the amount of water molecules available less, leading to a decrease of the solubility of organic pollutants. This is characterized as a "salting out" effect (Hurle 1972; Urena-Nmate 2005).

It is interesting to find that all values of K_d , K_f , and $K_L Q_{\max}$ for the three EDCs follow the same order of $\text{E2} > \text{EE2} > \text{BPA}$, which is inverse with the order of K_d , K_f , and $K_L Q_{\max}$ for EDCs adsorption by colloids (Tab. 3) both in D and C. The results also suggest that the adsorption mechanisms of EDCs by sediments are different from those by colloids. This order is consistent with that found in previous studies (Sun 2010b; Karnjanapiboonwong 2010). Because the inorganic component of colloids is combined with sediments, SOM and COM (colloids organic matters) become the major factors to control EDCs' adsorption behavior (Gong 2011; Sun 2010b; Chin 1992). The $\log K_{\text{OW}}$ values of BPA, EE2, and E2 are 3.32 (Lai 2000), 3.67, and 3.86 (Machatha 2005), respectively. EDCs with higher $\log K_{\text{OW}}$ (higher hydrophobicity) can associate with SOM and COM stronger (Gong 2011; Sun 2010b) through nonspecific hydrophobic interaction or/and hydrogen bridge mechanisms.

3.4. Interaction mechanisms between EDCs, colloids, and sediments

Based on the above results, the proposed interaction mechanisms between EDCs, colloids, and sediments were given in Fig. 5. In a EDCs-colloids system (Fig. 5 a), the interactions between EDCs and colloids may include two aspects: (1) Electrostatic interactions (because of the charged surface of inorganic minerals), cation bridge, and hydrogen bonds between EDCs and inorganic minerals in colloids (Wu 2011). The main polyvalent cations responsible for the binding of EDCs to clay mineral are Ca^{2+} , Fe^{3+} , and Al^{3+} . The H-bonding may form between the phenolic group of EDCs and mineral surface hydroxyl groups (e.g. Si-OH and Al-OH) (Zhou 2007; Liu 2005; Holbrook 2004). (2) The nonspecific hydrophobic interaction and hydrogen bonds (Sun 2007) between EDCs and colloidal organic matters. Carboxylic and phenolic-type groups are considered as two major classes of functional groups (Benedetti 1995) in colloidal organic matters. They can form hydrogen bonds with phenolic groups in EDCs'

molecular structure. Liu (2005) also found the EDCs interact with colloids through many different mechanisms including ion exchange, chemical bonding, and nonspecific forces such as hydrophobic partitions. The results obtained here are consistent with previous reports by Yamamoto (2003) and Holbrook (2004), who also revealed the contribution of different binding mechanism other than nonspecific hydrophobic interaction. Therefore, When EDCs are adsorbed by colloids alone, both organic and inorganic components of colloids have great contribution to EDCs' adsorption (Fig.5 a).

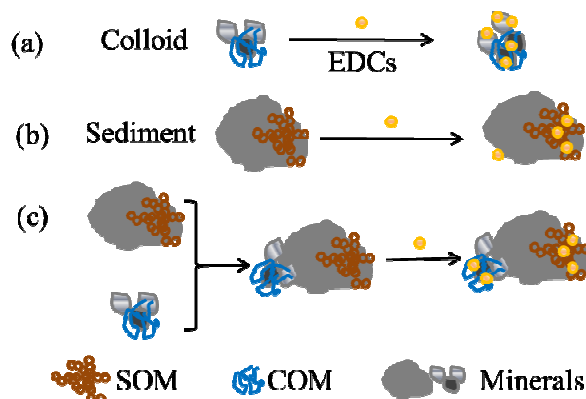


Fig. 5 Schematic illustration of suggested interaction mechanisms between EDCs, colloids, and sediments (SOM, sediment organic matter; COM, colloidal organic matter)

Different from aquatic colloids, SOM rather than inorganic minerals of sediments (due to their larger particle size) plays dominant role in EDCs' adsorption (Sun 2010b; Sun 2012) (Fig. 5 b). In a EDCs-colloids-sediment system, the inorganic component of colloids (e.g., Al, Fe, SiO_2), which played principal role in the adsorption of EDCs onto colloids (Fig. 5 a), tends to be attached to the surfaces of minerals in sediments (Wu 2011) mainly through cation bridge and bond by hydrous oxides on interlamellar spaces of clay minerals (Fig.5 c). Thus, the interaction between EDCs and inorganic component of colloids are largely weakened, and the adsorption of EDCs is dominated by SOM and COM. It is widely recognized that the SOM is the principal factor controlling sorption of organic compounds by sediments (Sun 2007; Cunha 2012). SOM and COM possess large quantities of oxygenated functional groups, in the form of phenolic hydroxyls and different types of carboxylic groups (Rosa 2005; Wang 2011). So the EDCs can bind with SOM and COM through hydrogen bridge mechanisms besides hydrophobic interaction. Cunha (2012) studied the adsorption of BPA, E2, EE2, and E1 onto two kinds of sediments (S_1 with 13% m/m SOM and S_2 with 25% m/m SOM), and found that the K_f values increased significantly from 1.7×10^{-3} - 3.1×10^{-3} for S_1 to 4.2 - 7.4×10^{-2} for S_2 .

4. CONCLUSION

Aquatic colloids (C) were separated from natural water collected from Huayuankou station and Lijin station of the Yellow River. The concentrations of TOC, Ca, SiO_2 , Al,

and Fe are much higher in colloidal water (C) than those in its corresponding truly dissolved water (D). However, the total colloids organic carbon (TCOC) of LS (0.51mg/L) is a little higher than that of HS (0.40mg/L). The sorption of EDCs by colloids and sediments were well described by linear, Freundlich, and Langmuir isotherms. The values of the distribution coefficients (K_d and K_f) and sorption coefficients ($K_L Q_{max}$) of EDCs by colloids are one magnitude higher for LS than those for HS, and the K_d , K_f , and $K_L Q_{max}$ for different EDCs follow the same order of BPA > EE2 > E2. The results indicate both organic matters and inorganic minerals in colloids play critical roles in EDCs adsorption by colloids through different binding mechanisms other than nonspecific hydrophobic interaction. In EDCs-colloids-sediments system, the EDCs adsorption by sediments is enhanced significantly by aquatic colloids. Moreover, the K_d , K_f , and $K_L Q_{max}$ values are in the order of E2 > EE2 > BPA. This suggests that the adsorption of EDCs is dominated by sediment organic matters (SOM) and colloids organic matters (COM), since the inorganic components of colloids is attached to the minerals of sediments. This study reveals that aquatic colloids could promote the EDCs adsorption by sediments, but the adsorption mechanisms change due to the interaction between colloids and sediments.

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