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Selected emerging organic contaminants in the Yangtze Estuary, China: A comprehensive treatment of their association with aquatic colloids

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HIGHLIGHTS

- Multiphase distribution of selected EOCs were studied.
- Colloids can act as a sink for EOCs with high sorption capacities.
- Correlations between colloidal properties and EOCs were found.
- Salinity is a vital factor controlling the colloidal properties and EOCs behavior.

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ABSTRACT

Contaminants that are becoming detected in the environment but are not yet generally regulated or monitored are known collectively as emerging contaminants. In the present study, the occurrence and distribution of 42 emerging organic compounds (EOCs) were investigated in the Yangtze River Estuary and adjacent East China Sea coastal areas. Study compounds were mainly pharmaceuticals, including antibiotics, hormones and sterols, and also included two industrial endocrine disruptors. Samples were analyzed using cross-flow ultrafiltration (CFUF) and ultra-performance liquid chromatograph–tandem mass spectrometry (UPLC–MS/MS). Results revealed that chloramphenicols, sulfonamides and non-steroidal anti-inflammatory drugs were the dominant compounds in filtered samples with relatively high concentrations and detection frequencies. EOC levels varied with location, with the highest concentrations being observed around rivers discharging into the estuary, and near sewage outfalls. Colloids that were separated by CFUF tended to be a sink for EOCs with up to 60% being colloid-associated in the water phase. In addition, colloidal properties, including hydrodynamic size, zeta-potential and organic carbon composition, were found to be the main factors controlling the association of EOCs with aquatic colloids. Moreover, these colloidal properties were all significantly related to salinity, indicating the critical role played by increasing salinity in EOCs–colloids interaction in an estuarine system.

1. Introduction

Pharmaceuticals, organic components of personal care products, food additives, hormones and sterols, etc., are biologically active but still unregulated or not commonly regulated contaminants. These are collectively classified as emerging organic contaminants (EOCs) [1,2]. Many of them have exhibited toxicity at trace level (ng/L) for aquatic flora, fauna and/or human beings [3–5]. Moreover, EOC concentrations may persist or pseudo-persist in aquatic environments because their transformation/removal rates are balanced or overcome by their continuous introduction into the environment [6]. This has prompted several studies on the occurrence and behavior of EOCs in wastewater [7–9], surface water [10,11], ground water [12,13], and even drinking water [14,15].

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Up until now, a paucity of studies has focused on the occurrence and behavior of EOCs in estuarine aquatic systems. Perhaps this is because, in part, estuaries act as an aquatic buffer between continents and oceans, and therefore exhibit physically and chemically complex hydrodynamic conditions. On the other hand, estuaries are most often heavily impacted by human activities due both to the rapid contaminant transport down river hydrologic gradients from highly populated drainage basins, as well as the common occurrence of major population centers proximal to estuaries themselves. In addition, with regard to the type of study conducted, most look at the occurrence and distribution of EOCs in aquatic systems focusing on the so-called "dissolved" phase, which actually is arbitrarily, but conveniently anything that passes through a membrane filter with openings usually from 0.22 μm to 0.70 μm. Typically in these studies, permeates are operationally defined as the soluble fraction. However, it is well known that the smallest colloids, which are ubiquitous in natural aquatic environments, pass through these filters and are therefore often neglected for their role in contaminant distribution and behavior. They have received more and more attention because of their high contaminant reactivity and mobility implications [16–18]. For example, in landfill leachates and stormwaters, polycyclic aromatic hydrocarbons (PAHs) were found to predominantly attach to smaller colloids rather than larger particulate matter [19]. Hofmann and von der Kammer [20] estimated that the engineered carbonaceous nanoparticles (ECN) could enhance contaminant transport that was dependent on the ECN size, sorption kinetics and ECN residence time. Moreover, previous studies, although limited, suggest that colloids can act as a significant sink for selected pharmaceuticals [21,22]. Colloids are particles with a wide variety of chemical compositions and atomic structures, as well as origins and physicochemical properties [23], but the specific relationships between EOCs and colloids are still largely unknown. What parameters are most important in the interaction between colloids and EOCs, and how are these parameters influenced by environmental factors such as salinity gradients within estuaries? To our knowledge, this has not been addressed previously.

The present study investigates the occurrence and phase distribution of 42 EOCs in the Yangtze Estuary, China. This vitally important estuary is at the mouth of the Yangtze River as it flows into the East China Sea past the city of Shanghai, the largest city proper in the world (nearly 18 million, with several million more in neighboring suburbs). Further, the Yangtze River Delta is home to over 100 million people. Overall, the Yangtze River drains approximately 20% of the People's Republic of China (PRC) and its river basin contains one third of China's population, roughly 450 million people in 2012 [24]. Colloids, isolated from the surface water, were further characterized using multiple technologies. The goal of the study was to elucidate the role of colloids in the distribution of EOCs in the study area. A specific objective was to establish correlations between colloidal geochemical properties, estuary salinity, and EOCs, and thus provide significant data for understanding the interaction between EOCs and colloids in this highly complex estuarine aquatic environment.

2. Materials and methods

2.1. Chemicals and standards

Forty-two EOCs were measured in the Yangtze Estuary, China as a part of this study. Their physicochemical properties are shown in Table 1, grouped according to their therapeutic class or purpose. These contaminants were selected due to their high prescription rates or volumes, high consumption and the availability of reliable analytical methods, as well as their frequent detection in aquatic environments. Internal standards used in this study were CAP-d_5, SMX-d_4, NFD-d_5, demeclocycline and RTM-d_7, BPA-d_{16}, E2-d_2, DCF-d_4, SVT-d_6, CMZ-d_{10}, CMT-d_3, and NFD-d_6. All compounds including internal standards were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany (http://www.analytical-standards.com/). A 10 mg/L standard mixture containing each compound was prepared by diluting the stock solution (1000 mg/L) with methanol. Methanol and hexane (CNW, Germany) were of HPLC grade and supplied from ANPEL (Shanghai, China). All standard solutions were stored at 20 °C.

2.2. Sample collection

Seven sampling sites were selected along the Yangtze Estuary shown in Fig. 1: Xupu (XP), Daxingang (DXG), Yinyang (YY), Bailonggang (BLG, the largest WWTP in Asia), Luchao (LC), Wusongkou (WSK, the junction of the Huangpu River and the Yangtze River), and Liuhekou (LHK, the junction of the Liu River and the Yangtze River). The sampling campaign was conducted in October 2011. Surface water samples were collected in 50 L stainless steel barrels that had been sequentially cleaned by acetone, deionized water and Milli-Q water. Once transported to the laboratory, 50 L of water samples were filtered immediately through 1 μm glass fiber filters (PAUL, USA) held in a 293 mm stainless steel sanitary filter holder (Handwheel Wrench 316 Holder, Millipore). All water samples were coarsely filtered within 2 days and then immediately filtered further using cross flow ultra-filtration (CFUF).

Colloids in this study were defined as particles ranging from 1 kDa (the finest filter used in this study, roughly equivalent to 1 nm in size if particles are spherical) to 1 μm (the initial filtration). Specifically, the colloid sample was operationally isolated by the pore size of separating devices, i.e. filtered water samples (filtrates) were separated into permeates (<1 kDa, soluble phase) and retentates (1 kDa–1 μm, concentrated colloidal phase) by CFUF (Pellicon System, Millipore) using a Millipore 1 kDa regenerated cellulose Pellicon 2 PLAC ultrafiltration membrane [21]. Over time, the retentate became concentrated and retentate flow was directed back to the feed container; while the permeate flow was collected separately. A concentration factor (*cf*) (ratio of the volume of the initial sample to the retentate volume) of 25 was used in the present study. The ultrafiltration system was initially cleaned with 0.1 M NaOH solution for 1 h. Before loading the sample, the system was thoroughly rinsed with 10 L Milli-Q water and 2 L filtered sample. The feed pressure was kept at 20 psi.

2.3. Sample treatment and analyses

Aliquots of aqueous samples in triplicate (retentates: 0.2 L; filtrates/permeates: 2 L) were extracted by solid phase extraction (SPE) using Oasis HLB cartridges (200 mg, Waters), which had been pre-conditioned by 6 mL methanol and 10 mL ultrapure water at a flow rate of 5–10 mL/min. Prior to the SPE, internal standards (20 ng each) were added into the aqueous samples. Once extracted, the analytes were eluted using 10 mL methanol, and then concentrated to 0.5 mL by evaporation under N_2. Finally, about 0.5 mL pure water was added to each vial to reach the final volume of 1.0 mL for the instrumental analysis.

The selected target EOCs were analyzed by ultra-performance liquid chromatograph–tandem mass spectrometry (UPLC–MS/MS, Waters Acquity^{TM}), and separated on a Waters BEH C_{18} column (2.1 mm × 100 mm, 1.7 μm) in multiple reactions monitoring (MRM) mode. The column temperature was set at 40 °C and the injection volume was 4 μL. The mobile phase was as follows: ultrapure water containing 0.1% formic acid (eluent A1) and acetonitrile containing 0.1% formic acid (eluent B1) were used in the positive ionization mode; ultrapure water (eluent A2) and acetonitrile

Table 1
Emerging organic contaminants (EOCs) measured in this study.

Group	CAS number	Compound	Acronym	Molecular mass	Molecular formula	Log K_{ow}[a]
Chloramphenicols (CPs, antibiotics)	56-75-7	Chloramphenicol	CAP	323.1	$C_{11}H_{12}Cl_2N_2O_5$	1.14
	15318-45-3	Thiamphenicol	TAP	356.2	$C_{12}H_{15}Cl_2NO_5S$	−0.33[b]
	76639-94-6	Florfenicol	FF	358.2	$C_{12}H_{14}Cl_2FNO_4S$	0.37
Sulfonamides (SAs, antibiotics)	68-35-9	Sulfadiazine	SD	250.3	$C_{10}H_{10}N_4O_2S$	−0.09
	144-83-2	Sulfapyridine	SP	249.3	$C_{11}H_{11}N_3O_2S$	0.35
	723-46-6	Sulfamethoxazole	SMX	253.3	$C_{10}H_{11}N_3O_3S$	0.89
	72-14-0	Sulfathiazole	ST	255.3	$C_9H_9N_3O_2S_2$	0.05
	127-79-7	Sulfamerazine	SM	264.3	$C_{11}H_{12}N_4O_2S$	0.44
	57-68-1	Sulfamethazine	SMT	278.3	$C_{12}H_{14}N_4O_2S$	0.14
	59-40-5	Sulfaquinoxaline	SQ	300.3	$C_{14}H_{12}N_4O_2S$	1.68
Fluoroquinolones (FQs, antibiotics)	70458-96-7	Norfloxacin	NFC	319.3	$C_{16}H_{18}FN_3O_3$	−0.46
	85721-33-1	Ciprofloxacin	CFC	331.3	$C_{17}H_{18}FN_3O_3$	0.28
	93106-60-6	Enrofloxacin	EFC	359.4	$C_{19}H_{22}FN_3O_3$	0.70[b]
	82419-36-1	Ofloxacin	OFC	331.3	$C_{18}H_{20}FN_3O_4$	−0.02
Tetracyclines (TCs, antibiotics)	60-54-8	Tetracycline	TC	444.4	$C_{22}H_{24}N_2O_8.HCl$	−1.37
	2058-46-0	Oxytetracycline	OTC	496.9	$C_{22}H_{24}N_2O_9.HCl$	−0.90
	24390-14-5	Doxycycline hyclate	DXC	545.0	$C_{24}H_{32}N_2O_{10}.HCl$	−1.36[b]
	64-72-2	Chlortetracycline	CTC	515.3	$C_{22}H_{23}ClN_2O_8.HCl$	−0.62
Macrolides (MLs, antibiotics)	59319-72-1	Erythromycin	ETM	732.0	$C_{38}H_{69}NO_{12}$	3.06
	80214-83-1	Roxithromycin	RTM	837.1	$C_{41}H_{76}N_2O_{15}$	2.75
Estrogens	53-16-7	Estrone	E1	270.4	$C_{18}H_{22}O_2$	3.13
	50-28-2	17β-estradiol	E2	272.4	$C_{18}H_{24}O_2$	4.01
	50-27-1	Estriol	E3	288.4	$C_{18}H_{24}O_3$	2.45
	57-63-6	17α-Ethinylestradiol	EE2	296.4	$C_{20}H_{24}O_2$	3.67
	140-66-9	4-tert-octyphenol	OP	206.4	$C_{14}H_{22}O$	5.00
	1980/5/7	Bisphenol A	BPA	228.3	$C_{15}H_{16}O_2$	3.32
Lipid regulators (LRs)	79902-63-9	Simvastatin	SVT	418.6	$C_{25}H_{38}O_5$	4.68
	25812-30-0	Gemfibrozil	GFB	250.3	$C_{15}H_{22}O_3$	4.77
	49562-28-9	Fenofibrate	FNB	360.8	$C_{20}H_{21}ClO_4$	5.19
Non-steroidal anti-inflammatory drugs (NSAIDs)	53-86-1	Indomethacin	IDM	357.8	$C_{19}H_{16}ClNO_4$	4.27
	103-90-2	Paracetamol	PRCT	151.2	$C_8H_9NO_2$	0.46
	15307-79-6	Diclofenac	DCF	296.2	$C_{14}H_{18}C_{12}N_2O$	4.51
	15687-27-1	Ibuprofen	BRF	206.3	$C_{13}H_{18}O_2$	3.97
Antihistaminics (AHTs, gastric acid secretion inhibitor)	73590-58-6	Omeprazole	OMR	345.4	$C_{17}H_{19}N_3O_3S$	2.23
	51481-61-9	Cimetidine	CMT	252.3	$C_{10}H_{16}N_6S$	0.40
Antihypertensive (AHPs)	66085-59-4	Nimodipine	NMD	418.4	$C_{21}H_{26}N_2O_7$	3.13[b]
	21829-25-4	Nifedipine	NFD	346.3	$C_{17}H_{18}N_2O_6$	2.20
Anticonvulsants (ACs)	298-46-4	Carbamazepine	CMZ	236.3	$C_{15}H_{12}N_2O$	2.45
	439-14-5	Diazepam	DZP	284.8	$C_{16}H_{13}ClN_2O$	2.82
Antineoplastic (ANs)	10540-29-1	Tamoxifen	TMX	371.5	$C_{26}H_{29}NO$	6.30
	114977-28-5	Docetaxel	DCT	807.9	$C_{43}H_{53}NO_{14}$	2.83[b]
	33069-62-4	Paclitaxel	PCT	853.9	$C_{47}H_{51}NO_{14}$	3.31[b]

[a] Values obtained from U.S. National Library of Medicine: http://toxnet.nlm.nih.gov/.
[b] Values calculated by EPI Suite (USEPA).

(eluent B2) were used in the anion detection mode. At the flow rate of 0.4 mL/min, the gradient for both positive and negative ion mode was started with 5% B (i.e. B1 and B2, respectively), and increased to 100% B within 10 min and held for 2 min, and then reset to initial conditions of 5% B for 2 min. Other information of mass spectrometer parameters is available in our previous study [25].

The quality control procedures were taken as described previously [25]. The recoveries of the selected compounds were between 62.96% and 126.77% (considered acceptable due to exceptionally low concentrations and the complexity of simultaneously analyzing for 42 compounds) and the average standard deviation (SD) was lower than 5.5%. The limit of detection (LOD) and limit of quantification (LOQ) ranged from 0.01 ng/L to 1.18 ng/L and from 0.03 ng/L to 1.97 ng/L, respectively. Analysis of reagent blanks ($n = 3$) demonstrated that the analytical system and glassware were free of contamination.

2.4. Mass balance of EOCs under static and CFUF conditions

A mass balance experiment was processed under static conditions following Maskaoui et al. [26] to assess whether EOCs were adsorbed to the membrane material or degraded during the CFUF operation. Briefly, batch experiments were conducted in a brown glass bottle, which contained the same small pieces of ultrafiltration membrane material (Ultracel Ultrafiltration Disk: Millipore, PLAC 15005, regenerated cellulose, 1 kDa, 177 cm^2) and 1 L Milli-Q water spiked with 5 μg/L of the target EOC compounds. Sodium azide (200 mg/L) was added to the system as the bacterial inhibitor. Triplicate aliquots were taken at regular intervals, synchronously spiked with 20 μg/L internal standards. Prior to UPLC–MS/MS analysis, methanol (V_{water}:$V_{methanol}$ = 1:1) was added into each sample. The control experiments without the ultrafiltration membrane were performed identically to ascertain the effect of hydrolysis or adsorption to the glass.

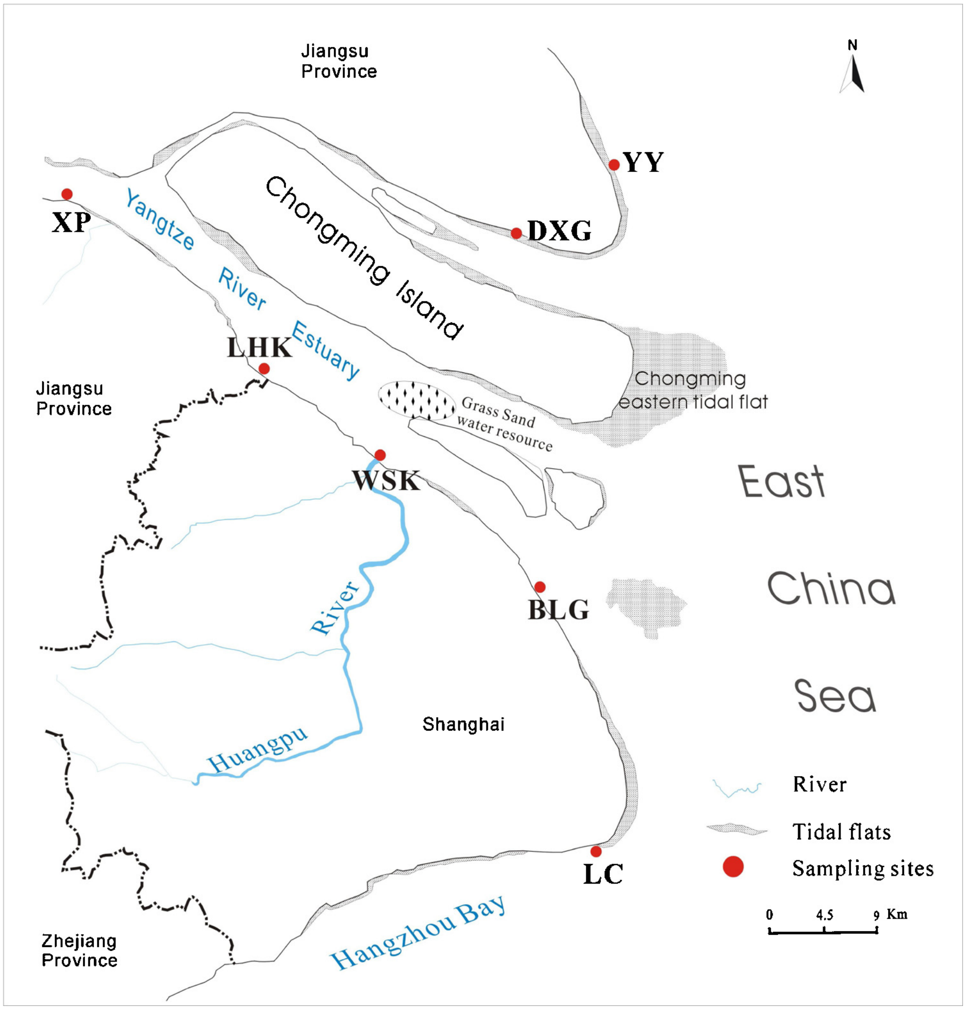

Fig. 1. Sampling sites along the Yangtze River Estuary and its coastal area.

A "dynamic" experiment (referred to below) was conducted with the CFUF in recirculation mode aiming to check the losses of EOCs during the CFUF operation. Both permeate and retentate flows were directed back to the feed container (5 L Milli-Q water with 100 ng/L target compounds). Six hours later, 1 L water samples in triplicate were processed by SPE UPLC–MS/MS as described above.

2.5. Colloid characterization

Before analysis, all samples were ultrasonicated for 30 min and desalted in a 1 kDa-dialysis bag (Baomanbio). Dissolved organic carbon (DOC) contents in filtrates, retentates and permeates were analyzed using liquiTOC II (Elementar, Germany).

A scanning electron microscope (SEM, S-4800, Hitachi) was used to obtain the size and morphologies of particles in the colloid sample. The colloid size and zeta potential were also characterized by dynamic light scattering (DLS) using a Zetasizer Nano-ZS (Malvern Instruments, UK).

A Hitachi F-4500 fluorescence spectrophotometer was used to analyze the fluorophore compositions in both retentates and permeates. Spectrophotometer PMT voltage was adjusted to 700 V. A wide range of wavelengths were selected from 200 nm to 400 nm and from 250 nm to 500 nm for excitation and emission respectively, with stepwise increments of 5 nm for both excitation and emission. Once the fluorophores were detected and identified, the peak intensity for each fluorophore was located within an area covering the range of known fluorescence for each fluorophore [27].

3. Results and discussion

3.1. Mass balance of EOCs to the membrane material and under CFUF operation conditions

The recoveries of 34 EOCs at different times in the batch system with and without membrane materials were conducted. Eight FQs and TCs in the study area were not considered further in this study due to the low detection frequency and concentrations (see details in the following discussions). In the control system without membrane materials, most of the target compounds remained within an acceptable range of the initial concentrations over 35 h (Fig. S1). According to the sorption experimental data, 28 EOCs showed no significant sorption to the control system with the recoveries from 62.33% to 119.33% (Fig. S1). However the recoveries of OP, SVT, FNB, TMX, DCT and PCT were all below 50% after 35 h. The loss of these compounds may be caused by adsorption to glass walls, hydrolysis, as well as their relatively high octanol–water partition coefficient ($\log K_{ow}$) values. In contrast, macrolide concentrations decreased dramatically in the batch experiment with membrane materials present. The recovery of RTM was below 40% within 30 min, showing the strong sorption of these compounds to the ultrafiltration

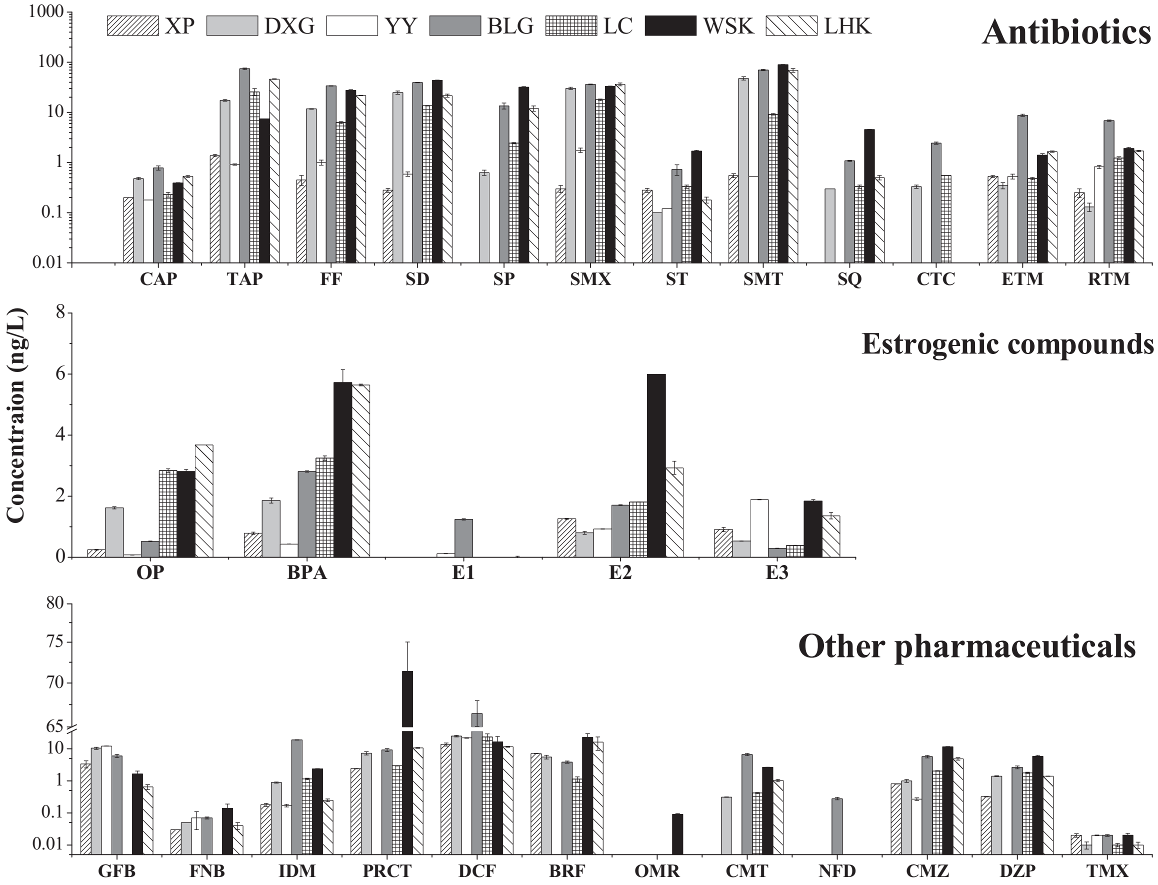

Fig. 2. The twenty-nine detected EOC concentrations in the filtrated water (through 1 μm filter).

membranes. Therefore, 27 EOCs (excluding RTM) were selected as the target compounds in the colloid phase and soluble phase analysis.

A "dynamic" experiment (defined in Section 2.4 above) was conducted in order to further assess the mass balance of the selected 27 EOCs through the CFUF system. The results showed that the losses could be neglected during the sampling mode with satisfactory recoveries ranging from 64.24% to 117.82% (RSD < 5.38%) (Table S1). Therefore, the CFUF system was proven to be a suitable tool to study these 27 EOCs in colloidal and true dissolved phases. It is worth to note that in the present study, the colloidal isolation from water was done using CFUF. In fact, the colloidal dispersion/aggregation behavior can be influenced by environmental factors, such pH, salinity and DOC, and further affect the colloidal compositions. Therefore, further studies are needed to elucidate the impact of the environmental factors on the natural colloids isolation.

3.2. Occurrence of EOCs in the filtered water

All 42 EOCs were investigated in filtered water samples that have been traditionally classified as a "dissolved phase" (through 1 μm filters). Among them, 13 compounds, including 3 CPs (CAP, TAP and FF), 4 SAs (SD, SMX, ST and SMT), 2 MLs (ETM and RTM), 4 estrogens (OP, BPA, E2 and E3), 2 NSAIDs (IDM and DCF), 1 ACs (CMZ) and 1 ANs (TMX), were the most frequently detected compounds with a detection frequency of 100% in all the samples. 13 compounds, including 1 SAs (SM), 4 FQs (NFC, CFC, EFC and OFC) and 3 TCs (TC, OTC and DXC), 1 estrogen (EE2), 1 LRs (SVT), 1 AHPs (NMD) and 2 ANs (DCT and PCT), were not detected in any of the water samples. Out of the 42 EOCs, seven contaminants namely TAP, FF, SD, SMX, SMT, DCF and PRCT, were the dominant EOCs with the average concentration above 10 ng/L. Twenty-two EOC compounds were detected at least once with the average concentration lower than 10 ng/L as shown in Fig. 2.

Antibiotics are one of the dominant classes among EOCs and are usually represented by a variety of substances, such as CPs, SAs, TCs, FQs and MLs. In this study, SAs were the dominant antibiotics in the Yangtze Estuary, followed by CPs. In contrast, none of the FQs were found at any of the sampling sites. Among SAs, SD, SP, SMX and SMT were the dominant antibiotics, contributing 80.36–99.61% to the total SAs concentrations. For CPs, the concentrations of TAP and FF were much higher than those of CAP. For TCs, CTC was the only detected compound with the highest concentration of 2.43 ng/L. For MLs, ETM and RTM were detected at all sampling sites with the concentration ranging from 0.35 to 8.75 ng/L and 0.13–6.85 ng/L, respectively. The concentration of antibiotics in this study was comparable to those in Ebro River basin [28] and Huangpu River [29], and much lower than those reported in Pearl River, Yellow River, USA and Australia [30–33].

The concentrations of estrogens were between <LOQ and 5.99 ng/L in Yangtze Estuary water, which were relatively low in comparison to the groups of CPs, SAs, LRs and NSAIDs. However, potential risk may still exist because permanent and irreversible alteration of organisms could occur when exposed to estrogens even at trace levels [34,35]. The concentrations of estrogens in this study are within the range of data reported in Taihu Lake (<34.4 ng/L) [36] and Yundang Lagoon (<31.4 ng/L) [37]. In this study, BPA showed high detection frequency (100%) and concentration (average concentration: 2.93 ng/L), followed by E2 (100%

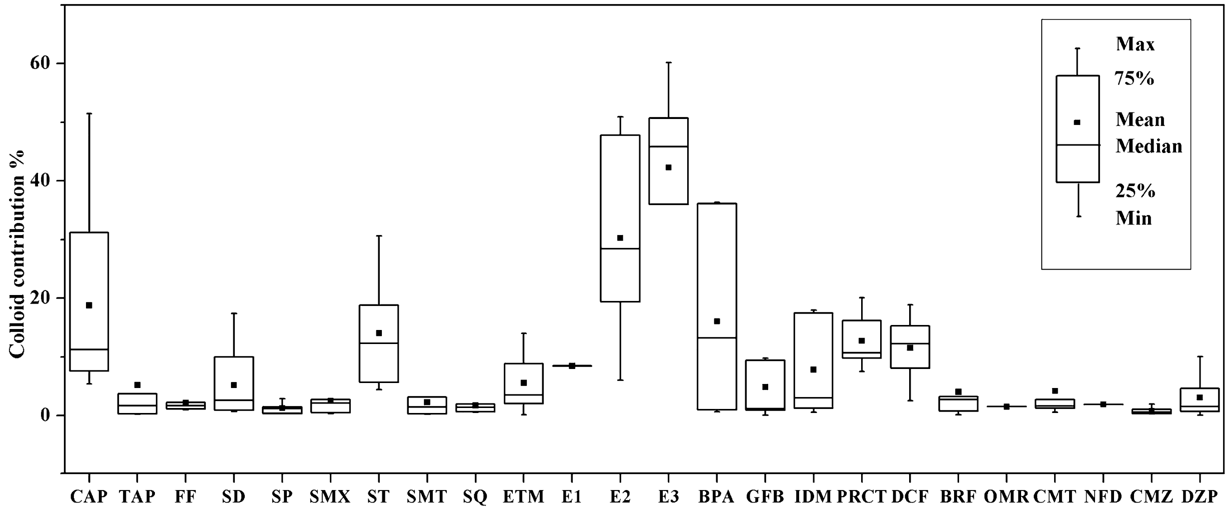

Fig. 3. Contribution of the colloids to the total EOCs concentrations in the Yangtze Estuary (%).

frequency; average concentration: 2.21 ng/L), while EE2 was not found in any of the sampling sites. A recent study in the Huangpu River, Shanghai (an important tributary of the Yangtze River) also found that EE2 were at a very low level with low detection frequency [38].

In the class of NSAIDs, DCF was the most dominant with concentrations between 14.52% and 99.24% of the total NSAID concentrations. As a refractory contaminant, DCF was found to be the dominant contaminant in the sewage influents and effluents, which resulted in its high abundance and detection frequencies in the aquatic environment [39–41]. PRCT contributed from 0% to 63.15% relative to the total NSAID concentrations. Up to hundreds of ng/L PRCT detected in the effluent of conventional secondary WWTPs suggested that WWTPs are a potential source of PRCT in the aquatic environment [42,43]. LRs were the other dominant pharmaceuticals in the Yangtze Estuary due to the high concentrations of GFB (<LOQ–12.16 ng/L) with its contribution over 90% to the total LRs concentration. GFB is reported to be a persistent compound with a half-life more than 70 days and hardly biodegraded [44], which might result in the persistence of GFB in the aquatic environment. Other groups of pharmaceuticals including AHTs, AHPs, ACs and ANs revealed a small contribution ranging from 0.83% to 15.58% to the total EOCs. However, it was notable that CMZ was detected at all sampling sites with the highest concentration of 11.62 ng/L. Similar to DCF, CMZ was hardly eliminated and degraded in WWTP [45].

The spatial distribution of the total EOC concentrations at the sampling sites generally decreased as follows: BLG > WSK > LHK > DXG > LC > YY > XP. Total EOC concentrations at WSK and BLG were 8.9–11.7 times higher than those at the YY and XP sites. For the dominant classes of EOCs (SAs, CPs and NSAIDs), their highest concentrations were mainly observed at the sampling sites influenced by the confluence of rivers (WSK and LHK) and WWTPs effluent (BLG).

It had been reported that DOC shows significant correlation to antibiotics in aquatic systems [25]. In this study, this positive correlation was also investigated between the DOC and the total EOC concentrations ($R = 0.77$, $p = 0.042$), and a similar relationship was found between DOC and SAs concentrations ($R = 0.83$, $p = 0.022$). For the individual compound, significant positive correlations were only found for CAP, FF, SD, SMX, SMT and DZP, which contributed up to about 60% to the total EOCs in filtered samples (Fig. S2). These all indicated that DOC might play a vital role in controlling the occurrence and distribution of these compounds in the Yangtze Estuarine area.

3.3. Colloidal contribution to the selected EOCs in water

3.3.1. EOCs concentrations in colloidal phases

It has been suggested that colloids are important sorbents that affect the fate of contaminants, such as phenanthrene, norfloxacin and phenols in aquatic environments [19,46,47]. To get more information on the EOC-associated colloids, the filtrates were further separated into retentates (the concentrated colloidal solution) and permeate samples (the true soluble phase) through ultrafiltration with 1 kDa membrane. Concentrations of the selected 27 EOCs in retentate and permeate samples are summarized in Fig. S3. The results illustrated that CPs, SAs and NSAIDs were the dominant EOCs both in permeate and retentate samples. Moreover, all of the EOC concentrations in the retentates were higher than those in the corresponding soluble phase (permeates).

EOCs concentrations in colloids (C_c) are estimated according to the equation: $C_c = (C_r - C_p)/cf$ (where C_r and C_p are the EOC concentrations in retentate and permeate, respectively). The average highest C_c was observed for DCF (3.41 ng/L), followed by PRCT (2.28 ng/L), which resulted in the much higher average C_c of NSAIDs among all EOC groups (Fig. S4). Although the estrogen concentrations were much lower than SAs and CPs in retentates, the colloidal concentrations of estrogen were higher than those of SAs and CPs. Similar to the filtrates, WSK and BLG also showed relatively high total EOC concentrations in colloids among all sampling sites, and this level was 3–4 times higher than those at XP and YY sites.

3.3.2. Mass balance of EOCs in water

To further evaluate the contribution of colloidal EOCs in the Yangtze estuarine area, the mass balance of EOCs was calculated by including the colloidal and soluble phases. The EOCs contribution of colloids is shown in Fig. 3. The average level of the selected EOCs associated with colloids ranged from 0.73% to 42.29% with the highest value of 60.16% in E3 at the YY site, indicating that colloids can act as a significant sink for EOCs in the aquatic system and further regulate the transportation and transformation of contaminants in the environment [16,18]. Moreover, it is found that the contributions of estrogens and NSAIDs in colloidal phases are higher compared to other EOCs (Fig. 3), and in the CPs group, CAP shows a higher tendency to associate with colloids compared to TAP and FF, which might be attributed to the high octanol–water partition coefficient ($\log K_{ow}$) of these compounds (Table 1). However, no significant correlation was found between the contributions of colloids and the $\log K_{ow}$ values of EOCs.

Table 2
Organic carbon normalized partition coefficients between colloids and permeates ($\log K_{coc}$) as well as the relevant values from the literatures ($\log K_{coc}^{lit}$).

Compound	$\log K_{coc}$	$\log K_{coc}^{lit}$	Compound	$\log K_{coc}$	$\log K_{coc}^{lit}$
CAP	7.15 ± 0.25		E2	7.58 ± 0.53	
TAP	6.20 ± 0.38		E3	7.80 ± 0.29	
FF	6.26 ± 0.37		BPA	6.94 ± 0.75	4.50[d]
SD	6.37 ± 0.34		GFB	6.23 ± 0.79	
SP	5.99 ± 0.26		IDM	6.60 ± 0.52	5.50[b], 7.65 ± 0.30[b], 7.06[b]
SMX	6.08 ± 0.26	4.95[b], 6.50 ± 0.12[b], 7.17[b]	PRCT	7.09 ± 0.36	
ST	7.01 ± 0.43		DCF	6.99 ± 0.44	5.29[a], 6.70 ± 0.16[b], 6.89[c]
SMT	5.98 ± 0.37		BRF	6.29 ± 0.70	2.35–3.06[e]
SQ	6.22 ± 0.54		CMT	6.46 ± 0.56	
ETM	6.47 ± 0.61		CMZ	5.75 ± 0.51	4.74[a], 6.66[c]
E1	7.09 ± 0.10		DZP	6.15 ± 0.55	

[a] Ref. [26].
[b] Ref. [22].
[c] Ref. [21].
[d] Ref. [19].
[e] Ref. [41].

3.3.3. *The colloidal/dissolved partition coefficient*

To evaluate the colloidal binding of EOCs, the colloidal/dissolved partition coefficient (K_{coc}, mL/g) for each compound was calculated using the equation: $C_r/C_p = 1 + K_{coc}$ [COC] ([COC] is the total colloidal organic carbon concentration) [21]. The average $\log K_{coc}$ values ranged from 5.75 to 7.80 (Table 2). The results for SMX, CMZ, IDM and DCF were generally in agreement with those found by Yang et al. [22] and Maskaoui and Zhou [21], and were 1–2 orders of magnitude higher than those investigated in the laboratory suggesting that the natural colloids act as a strong sorbent for EOCs in the aquatic environment [26]. The $\log K_{coc}$ values for BPA and BRF in this study were higher than those found by Kalmykova et al. [19] and Duan et al. [41]. In addition, a straight line was produced by plotting C_r/C_p against [COC] and the slope represents the K_{coc} value. Among all the selected EOCs, the linear correlations between C_r/C_p and COC contents were only found for CAP, TAP, SD, SMX and DZP with relatively high R^2 values (Fig. S5). It was consistent with the positive correlations between the concentrations of these compounds and DOC contents (discussed above), which indicated that organic carbon could

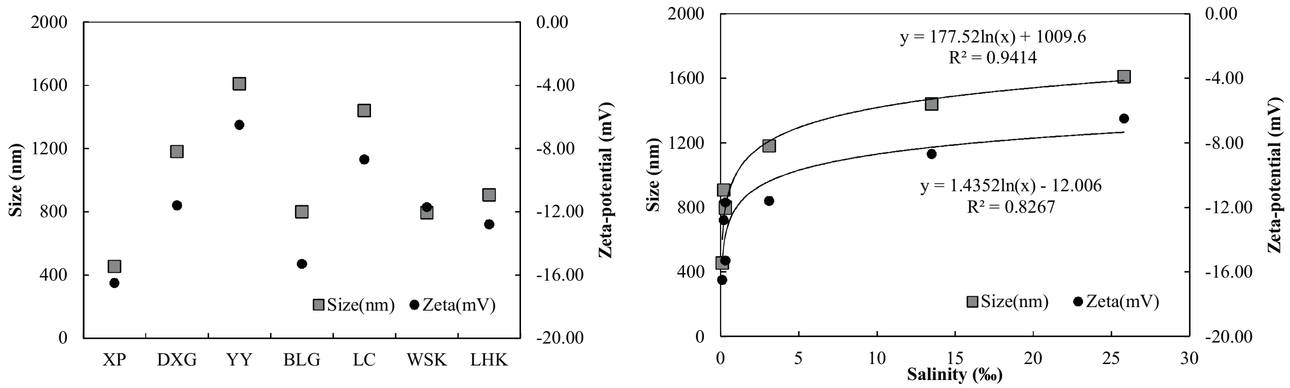

Fig. 4. Intercorrelations among the size, zeta-potential and salinity.

Table 3
The correlation between EOC concentration and fluorescence intensity of TYLIS, TPYLIS and HULIS fluorophores in colloidal phase.

Compounds	TYLIS		TPYLIS		HULIS		United TYLIS, TPYLIS and HULIS		
	R	*P*	*R*	*P*	*R*	*P*	Regression equation[b]	R^2	*P*
Salinity[a]	0.33	0.941	–0.42	0.273	–0.53	0.100	$y = 0.048042x_1 - 0.00405x_2 - 0.05659x_3 + 2.897156$	0.99	<0.001**
SD	0.06	0.891	0.70	0.078	0.79	0.033*	$y = -0.06609x_1 + 0.005614x_1 + 0.133896x_3 + 21.33264$	0.90	0.049*
SP	0.28	0.543	0.77	0.042*	0.89	0.007**	$y = -0.01621x_1 - 0.00802x_2 + 0.085604x_3 - 0.02497$	0.91	0.045*
ST	0.71	0.074	0.99	<0.001**	0.93	0.002**	$y = 0.000368x_1 + 0.002038x_2 - 0.00042x_3 + 0.378521$	0.99	0.001**
SMT	0.04	0.925	0.63	0.127	0.79	0.036*	$y = -0.12229x_1 - 0.05036x_2 + 0.428465x_3 + 25.52183$	0.94	0.027*
SQ	0.57	0.18	0.97	<0.001**	0.90	0.006**	$y = -0.00122x_1 + 0.004948x_2 - 0.0021x_3 - 0.22066$	0.95	0.020*
PRCT	0.59	0.164	0.96	0.001**	0.90	0.006**	$y = -0.05331x_1 + 0.295259x_2 - 0.07553x_3 - 31.9136$	0.92	0.037*
BRF	0.16	0.739	0.75	0.052	0.86	0.014*	$y = -0.01989x_1 - 0.00146x_2 + 0.057634x_3 + 6.243062$	0.94	0.023*
CMZ	0.44	0.325	0.93	0.020*	0.97	<0.001**	$y = -0.00525x_1 + 0.003361x_2 + 0.017522x_3 + 0.315787$	0.98	0.005**
DZP	0.25	0.593	0.85	0.016*	0.88	<0.001**	$y = -0.0035x_1 + 0.001938x_2 + 0.004694x_3 + 1.428918$	0.93	0.029*
Total EOCs	0.28	0.549	0.78	0.037*	0.87	0.012*	$y = -0.44148x_1 - 0.00126x_2 + 1.581742x_3 + 235.1824$	0.84	0.099

[a] R^2 values are the result of power function excluding XP site.
[b] y is the concentration of each EOC and salinity, x_1, x_2, x_3 are the fluorescence intensity of TYLIS, TPYLIS and HULIS respectively.
* Significant correlation ($P < 0.05$).
** Very significant correlation ($P < 0.01$).

be a significant factor controlling these compounds not only in the colloidal phase but also in the filtrated water in the study area.

3.3.4. The correlation between colloidal properties and EOC concentrations

Colloids are often a heterogeneous mixture of particles with different sizes, shapes, coatings and surface chemistry, crystalline and amorphous structures, as well as chemical composition [48]. The morphology and size of colloids at the seven sampling sites were characterized by SEM, examples of which are shown in Fig. S6. Heterogeneous particles with different aggregate shapes were visible, including anomalous spherical, lens-shaped or fibrous objects and cellular structures (presumably debris of biological cells and their exudates and inorganic aggregates). The results showed that the sizes and zeta-potential values of colloids ranged from 454 nm to 1610 nm and from −6.5 mV to −16.5 mV, respectively (Fig. 4). A strong positive correlation was found between the size and zeta-potential of the colloids ($R = 0.94$, $P = 0.001$). These could be explained within the extended Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. When the absolute value of zeta-potential was higher, the van der Waals forces around particles are lower than that of repulsion, resulting in dispersion stability and small size particles.

The transport of contaminants, such as pesticides [49], PAHs and metallic elements [50] can be facilitated by decreasing sizes of colloids, suggesting that smaller colloids may have higher sorption capacities. In the present study, no significant correlation was found between colloid hydrodynamic sizes and EOC concentrations in colloidal phases at all sites (Fig. 4). However, when the XP site was excluded, a significant negative correlation was found between colloid sizes and the concentrations of dominant EOCs, such as FF, SD, SP, SMX, SMT, BRF, CMZ, DZP, as well as the total EOCs concentration (Table S2), which revealed that colloidal hydrodynamic size could be an important factor controlling the EOCs sorption to aquatic colloids. Moreover, a less significant negative correlation between zeta potentials and these EOC concentrations in colloids was also observed (Table S2). This might be attributed to the positive correlation between size and zeta potential.

It is known that a portion of DOC was fluorescent and could be used to characterize DOC composition [51]. According to Muller et al. [27], three fluorophores were identified: tyrosine-like substances (TYLIS), tryptophan-like substances (TPYLIS) and humic-like substances (HULIS). In this study, the average fluorescence intensity of the retentates (colloidal phase) was 427.8 ± 165.9 a.u., 486.7 ± 330.8 a.u. and 234.9 ± 134.5 a.u. for TYLIS, TPYLIS and HULIS, respectively (Table S3), which was generally 2–4 times higher than those in the permeate (true soluble phase). The correlations between EOC concentrations and fluorescence intensities of TYLIS, TPYLIS and HULIS in colloidal phase were analyzed and shown in Table 3. A significant correlation between EOC concentrations and all three fluorophore intensities was found only for ST. Compared to TYLIS and TPYLIS, HULIS in retentates showed more significant correlation to the EOC concentrations ($R > 0.79$, $P < 0.05$), and nearly half of the selected compounds were strongly correlated with HULIS. In contrast, such correlation was not found between HULIS and EOC concentrations in the permeate samples (see details in the Supporting Information). Therefore, as an important composition of colloids, HULIS could regulate these EOCs in the colloidal phase. In addition, when TYLIS, TPYLIS and HULIS were considered simultaneously, significant nonlinear correlations between EOC concentrations and fluorophore intensities were established with higher R^2 values than those of individual fluorophores (Table 3), which confirmed the united influence

Table 4
Regression fitting between salinity and dominant EOCs in filtrate/retentate samples.

Compounds	Filtrate			Retentate			Colloids			Colloid contribution (%)		
	Equation	R^2	P	Equation	R^2	P	Equation	R^2	P	Equation	R^2	P
CAP	$y = 0.5335e^{-0.047x}$[a]	0.80	0.017*	–	0.01	–	–	0.06	–	$y = 0.8225x + 7.4355$	0.87	0.007**
TAP	$y = 33.986e^{-0.116x}$	0.59	0.075	$y = 35.936e^{-0.119x}$	0.71	0.034*	$y = 0.1733x^{-0.695}$	0.81	0.015*	–	0.04	–
FF	$y = 25.949e^{-0.123x}$	0.96	0.001**	$y = 25.156e^{-0.086x}$	0.90	0.004**	$y = 0.2384x^{-0.338}$	0.68	0.044*	$y = 0.1514x + 1.21$	0.75	0.026*
SD	$y = 39.726e^{-0.145x}$	0.58	0.004**	$y = 48.423e^{-0.113x}$	0.92	0.003**	$y = 0.3508x^{-0.491}$	0.87	0.007**	$y = 0.2556x + 1.3194$	0.56	0.087
SMX	$y = 40.564e^{-0.108x}$	0.92	0.003**	$y = 45.552e^{-0.092x}$	0.93	0.002**	$y = 0.2626x^{-0.537}$	0.89	0.005**	–	0.01	–
SMT	$y = 84.196e^{-0.19x}$	0.99	<0.0001**	$y = 92.508e^{-0.148x}$	0.97	<0.0001**	$y = 0.4526x^{-0.562}$	0.78	0.022*	$y = 0.2581x + 0.747$	0.89	0.005**
BPA	$y = 4.3197e^{-0.077x}$	0.70	0.037*	–	0.22	–	–	0.09	–	$y = 0.8517x + 6.5815$	0.41	0.174
CMZ	$y = 5.219e^{-0.11x}$	0.71	0.037*	$y = 5.3755e^{-0.113x}$	0.71	0.036*	$y = 0.0202x^{-0.662}$	0.84	0.010**	–	0.09	–
Total	$y = 331.41e^{-0.078x}$	0.94	0.002**	$y = 550.55e^{-0.039x}$	0.63	0.061	$y = 10.254x^{-0.218}$	0.72	0.032*	$y = 0.2613x + 3.5049$	0.80	0.017*

[a] x is the salinity and y is the EOCs concentration of each phase or colloidal contribution.

of TYLIS, TPYLIS and HULIS to the EOCs occurred in the aquatic colloids.

3.4. The role of salinity

In estuarine areas, salinity is an important parameter as it plays a very important role in colloidal properties, and therefore it likely plays an important role in the behavior of contaminants. In the Yangtze Estuary, the salinity increases sharply from 0.1‰ at the XP site to 25.8‰ at the YY site. A negative linear relationship is found between salinity and DOC concentrations (Fig. S2). Furthermore, a negative trend is observed between salinity and HULIS fluorophores (Table 3). This is consistent with the literature which shows that a negative relationship between salinity and terrestrial HULIS fluorophore is prevalent [52,53]. When the XP site is excluded, a multi-regression fitting equation with a good R^2 value is established between salinity and the combined TYLIS, TPYLIS and HULIS fluorophores (Table 3). Moreover, significant logarithmic correlation was found between salinity and colloidal size ($R^2 = 0.94$) (Fig. 4). A similar trend was also observed between salinity and the zeta-potential values ($R^2 = 0.83$). It is well known that estuarine systems exhibit not only sharp increases in salinity, but also rapid aggregation due to decreased particle repulsion [54]. This is likely the reason for the sharp apparent increase in colloidal size in this study from freshwater (XP, LHK and WSK sites) to seawater (LC and YY sites).

Simultaneously, when XP is excluded, some EOCs concentrations in the filtrate are found to decrease as an exponential function when salinity increases, including for CAP, FF, SD, SMX, SMT, BPA, CMZ and the total EOCs concentration (Table 4). This could be attributed to the decreased DOC concentrations with increasing salinity. Moreover, these EOC concentrations in colloids decrease as a power function with increasing salinity, while a significant linear correlation was observed between salinity and the colloidal contributions of these EOCs (Table 4). Consequently, salinity is a significant factor controlling water physicochemical and colloidal properties, thus further controlling the EOCs behavior in the estuarine system.

4. Conclusions

The occurrence and multi-phases distribution of 42 selected EOCs were conducted within the Yangtze Estuary, China and its neighboring coastal area. Of the 42 EOCs, seven compounds were the dominant EOCs. The highest concentrations were mainly observed at the sampling sites influenced by the confluence of rivers (WSK and LHK) and WWTPs effluent (BLG). Furthermore, a significant positive correlation between DOC contents and the total EOCs concentration suggest that DOC may play a significant role in the behavior of the EOCs in the estuarine system. The results of the selected EOCs in the soluble and colloidal fractions show that the colloids in the Yangtze estuary ecosystem are a significant sorbent for EOCs ($5.75 < \log K_{coc} < 7.80$). This is confirmed by mass balance calculations. In addition, the correlation analysis suggests that colloidal size, zeta-potential, and HULIS may be the dominant properties that control the EOC-colloid association. In the present study, salinity is also shown to be an important factor controlling the colloidal properties in aquatic environments, and to have further impact on the EOC behavior. However, colloids are heterogeneous particles with varying and complex geochemical properties. Consequently, much more information on the interaction between EOCs and colloids in the aquatic environment will be sought in future studies. Moreover, dispersion/aggregation behavior of nanoparticles can be affected by environmental factors, such as salinity, pH, temperature and organic carbon, and further regulate the colloidal compositions and their interaction with EOCs in the aquatic system. Therefore, further studies are needed to elucidate the impact of the environmental factors on the behavior of colloids in the aquatic system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.09.011.

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