Influence of the natural colloids on the multi-phase distributions of antibiotics in the surface water from the largest lake in North China

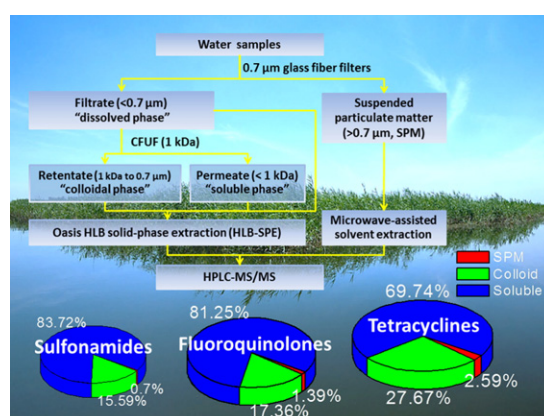Dengmiao Cheng [a,b], Xinhui Liu [a,*], Shengnan Zhao [a], Baoshan Cui [a], Junhong Bai [a], Zhaojun Li [b]

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HIGHLIGHTS

- Occurrence and multi-phase distribution of antibiotics were monitored seasonally.
- Colloids can play an important role to remove antibiotics from aquatic environments.
- Partition coefficient log $K_{col.}$ was mainly negatively correlated with binding Ca and Mg.
- Competitive adsorption was insignificant in the colloidal sorption behaviors of antibiotics.
- Colloid-bounding is important in the environmental behaviors of organic pollutants.

GRAPHICAL ABSTRACT

ABSTRACT

Understanding antibiotic adsorption on natural colloids is crucial for prediction of the behavior, bioavailability and toxicity of antibiotics in natural waters. In the present study, the filtered water (dissolved phase, <0.7 μm) was further separated into colloidal phase (1 kDa-0.7 μm) and soluble phase (<1 kDa) by cross-flow ultrafiltration (CFUF), and the spatial-temporal variation and distribution of six antibiotics in multi-phases were investigated in Baiyangdian Lake. Results indicated that antibiotic concentrations differed significantly with sampling location and time. The mean concentrations of antibiotics ranged between 13.65 and 320.44 ng L^{-1} in the dissolved phase, and the colloidal phase accounted for 4.7–49.8% of all antibiotics, suggesting that natural colloids play an important role as carriers of antibiotics in aquatic environments. Because of the influence of colloids, the partition coefficients of antibiotics between suspended particulate matter (SPM) and soluble phase (intrinsic partition coefficients, K_p^{int}) were found to be 6.18–109.60% higher than corresponding observed partition coefficients (K_p^{obs}, between SPM and dissolved phase). The mean partition coefficients between colloidal and soluble phase (K_{col}) ranged between 6218 and 117,374 L kg^{-1}, which were 1–2 orders of magnitude greater than K_p^{int} values. In order to explore the adsorption mechanism of antibiotics on colloids, Pearson's correlations were performed. The results showed that log $K_{col.}$ were negatively correlated with cations in natural colloids; especially with Mg (r, −0.643, $P < 0.01$) for oxytetracycline (OTC), and with both Ca (−0.595, $P < 0.01$) and Mg (−0.593, $P < 0.01$) in the case of ofloxacin (OFL). This result revealed that the competitive effect between cations

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and antibiotics was the main factor influencing the adsorption behavior of antibiotics on natural colloids in the lake.

1. Introduction

Since the discovery of penicillin, humans have developed thousands of strong bactericidal antibiotics that have been widely applied in the treatment of microbial infections (Kümmerer 2003; Kümmerer 2009a), and in the livestock and aquaculture industries (Gibs et al. 2013), which has resulted in a large amounts of these compounds and their metabolites being introducing into the aquatic environment (Cheng et al. 2014a; Yan et al. 2013). Antibiotic residues can cause the development of antibiotic-resistant bacteria in the aquatic ecosystems (Jo et al. 2011), and also accelerate the generation of antibiotic resistance genes (ARGs) (Kümmerer 2009b). Such genes may eventually enter the human body through horizontal gene transfer and produce unpredictable negative effects on human health (Peng et al. 2008). Therefore, antibiotics and their environmental effects have become a focus for research on environmental pollutants in the aquatic environment (Zhang et al. 2012).

In recent years, there has been much research focused on distribution, transport and effect factors on antibiotics in environmental waters (Kümmerer 2009a, 2009b). Studies have found that the transportation and transformation behavior of pollutants is dependent on their adsorption characteristics in the aquatic environment (Gustafsson and Gschwend 1997). For example, the photodegradation rate of amoxicillin showed an obvious positive correlation with its sorption on dissolved organic matter (DOM) (Xu et al. 2011). However, most studies to date have been limited to the "pure state" or "truly dissolved state" of antibiotics. Less is understood about the real state of antibiotics in the natural waters where they may be in a "particulate state" formed by the sorption of antibiotics on inorganic or organic particles.

When organic contaminants are introduced into the aquatic environment, their adsorption on suspended particulate matter (SPM) undoubtedly becomes one of the most important factors determining their transport and fate. The adsorption abilities are usually designated based on their distribution between two phases according to the particle size, i.e.,"dissolved phase" that passes through the filters of pore size between 0.22 μm to 0.70 μm, and "SPMs" that are retained on the 0.70 μm filters (Baker et al. 2012; Duan et al. 2013). The conventional dissolved phase can be further divided into a spectrum of colloidal particles plus a further filtrate that was termed the "soluble phase" (Lead and Wilkinson 2006). Colloids are ubiquitous components in the size range between 1 nm and 1 μm of aquatic environments such as freshwater, seawater and groundwater, and may reach a maximum of 10^8 particles per liter (Gustafsson and Gschwend 1997; Kim 1994). It has been shown that colloidal organic carbon (COC) makes up a significant fraction (up to 76%) of total organic carbon (TOC) in aquatic environments (Benner and Hedges 1993; Dai and Benitez-Nelson 2001).

Colloids can act as potential adsorption sites for organic pollutants, such as pharmaceuticals and estrogen compounds, in the aquatic environment, and thus their colloidal adsorptions should influence their mobility, reactivity and bioavailability (Yan et al. 2015b; Yang et al. 2011). Therefore, it is important to understand the adsorption mechanism of organic pollutants on natural colloids. Up to now, most studies of the interactions between natural colloid and organic contaminants have been applied on humic substances that are produced commercially and which are isolated chemically from total colloid matter in natural aquatic environments (Xu et al. 2011). It is generally known that humic substances may not replace natural colloids in their geochemical properties and environmental behavior. In addition, recent studies of adsorption of organic pollutants on natural colloids have focused on hydrophobic and moderately hydrophobic organic compounds (Means

and Wijayaratne 1982; Nie et al. 2014; Yang et al. 2011) and neglected ionic organic compounds such as antibiotics.

The adsorption behavior of antibiotics in the environment depends not only on the structures of antibiotics, but it also strongly depends on their physicochemical properties (Gong et al. 2012; Tolls 2001; Wegst-Uhrich et al. 2014; Yan et al. 2015b). Because most antibiotics are amphoteric molecules that exist in complex speciation behaviors with varying pH, their interactions with soil or sediment are likely to be highly pH dependent (Chu et al. 2013; Wegst-Uhrich et al. 2014). Although factors affecting adsorption of antibiotics to environmental substrates such as soil and sediment have been studied (Li and Zhang 2016; Pan and Chu 2016), few studies have examined interactions between antibiotics and natural colloids.

In the present study we hypothesized that natural colloids would have strong interactions with antibiotics, and that colloids with different physicochemical properties should lead to different partitioning behaviors of antibiotics. Therefore, the major objectives of this study were (1) to investigate the spatio-temporal variation of antibiotics in the SPM, the colloidal phase and the soluble phase, (2) to evaluate the influence of colloids in the partitioning among different phases and (3) to determine the factors that could possibly influence the colloid partition of antibiotics. We selected three types of typical antibiotics, including tetracyclines (TCs), sulfonamides (SAs) and fluoroquinolones (FQs), as a primary focus for our study because of their wide use and variable sorption properties (Table S1) (Cheng et al. 2014a; Gong et al. 2012). Considering the conformity with the previous studies, 0.70 μm of particle size as upper limit of colloids was selected in this study, that was slightly smaller than the upper limit of colloidal definition (1 μm), which facilitated the comparisons of the current results with those from the previous studies.

2. Experimental section

2.1. Reagents and chemicals

Oxytetracycline (OTC), tetracycline (TC), sulfadiazine (SDZ), sulfamethazine (SMZ), norfloxacin (NOR) and ofloxacin (OFL) (Table S1) were acquired from Dr. Ehrenstorfer (Augsburg, Germany). $^{13}C_3$-Caffeine as internal standard was purchased from Cambridge Isotope Laboratories, USA. Separate standard stock solutions (500 mg L^{-1}) of individual antibiotics and $^{13}C_3$-Caffeine were prepared by dissolving in methanol. One 50 mg L^{-1} mixture of working standards containing each compound was prepared by diluting each standard stock solution with methanol. All standard solutions were stored at −20 °C. Methanol and acetonitrile (HPLC grade) were acquired from Fisher Science Co. The other chemicals used in the study were of analytical grade.

2.2. Sampling sites

Baiyangdian Lake is the largest natural freshwater lake in the North China Plain (Fig. 1), which covers >366 km² with an average depth of approximately 2–4 m. It consists of >100 small and shallow lakes linked by thousands of ditches. Currently, there are >243,000 people living in 39 villages scattered in it. Two sampling events were conducted in October 2013 and June 2014 at ten sampling sites (Site 1–10) representing slightly polluted, urban, and agriculturally influenced areas in the Baiyangdian Lake (Fig. 1 and Table S5). All water samples were collected in pre-cleaned high-density polyethylene (HDPE) fluorinated plastic barrels (30 L). Sodium azide (2 mol L^{-1}, 5 mL L^{-1} of sample) was added to water samples for effective preservation so as to
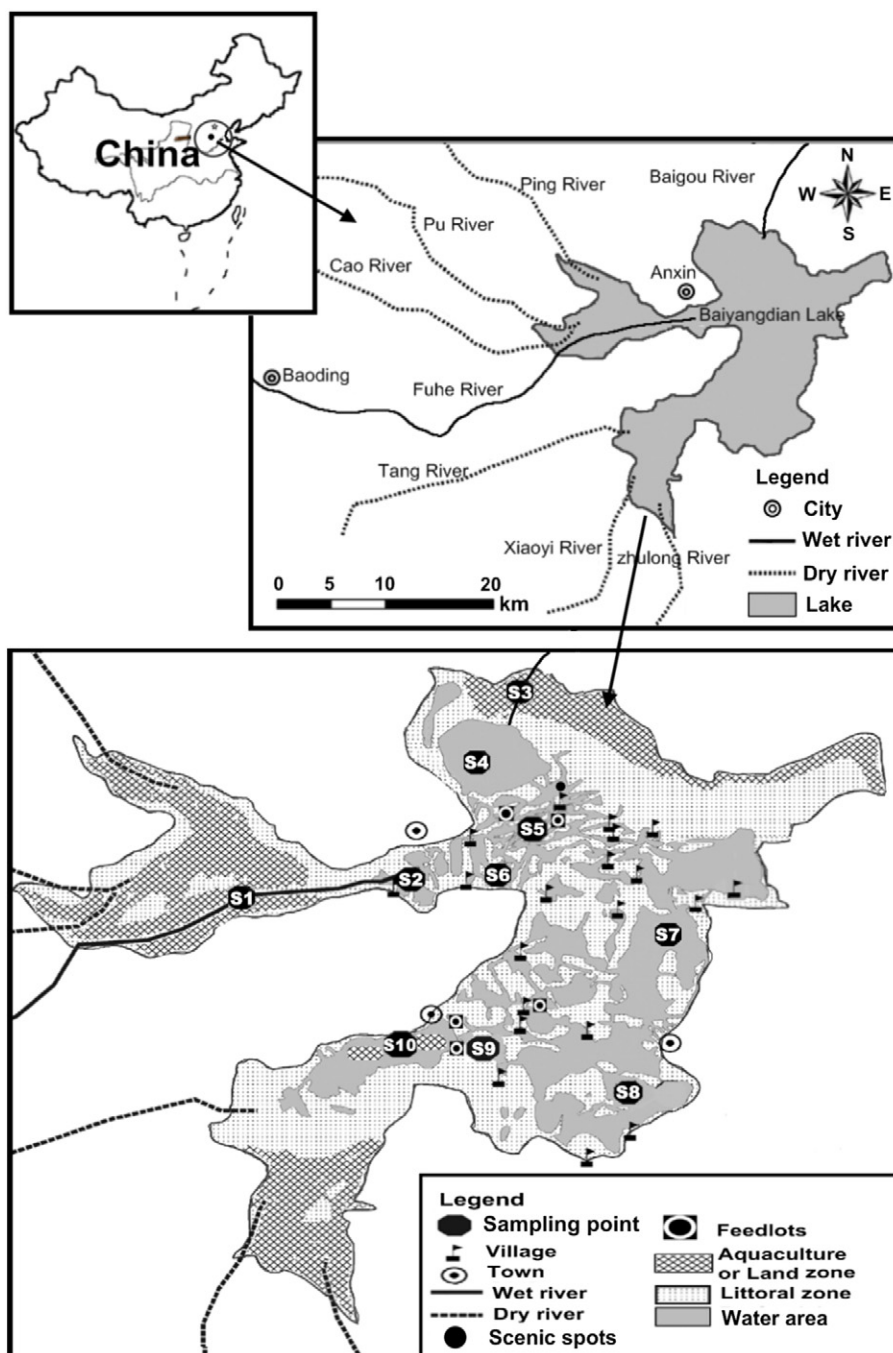
Fig. 1. Sampling sites (S1–S10) in the Baiyangdian Lake and its geographical location.

minimize any degradation of the target antibiotics. Once transported to the laboratory, the water samples were filtered immediately through 0.7 μm glass fiber membranes (GF/F, Whatman) to obtain filtrates (dissolved phases) (Fig. 2) (Maskaoui and Zhou 2010). The glass fiber membranes were previously combusted at 450 °C for 5 h in muffle to remove any organic matter and get constant weigh. The collected SPM on the glass fiber membranes were determined after being freeze dried and stored in an airtight container until extraction.

2.3. Natural colloid isolation

As showed in Fig. 2, the filtered water samples were further proc-essed by cross-flow ultrafiltration (CFUF) (1 kDa-PLAC, Millipore

Pellicon 2) to obtain colloidal and soluble phases, and an optimum con-centration factor (cf) of 10 was adopted due to the minimized targeted antibiotics sorptive losses during the CFUF (Maskaoui et al. 2007; Wilding et al. 2005). When the isolation was over, all aqueous samples (dissolved, colloidal and soluble phases) were refrigerated at 4 °C and analyzed within two weeks of sampling. In addition, the dry weight of the colloidal fraction was determined after freeze drying (Sigleo and Macko 2002). All aqueous samples were analyzed for organic carbon with a TOC analyzer (Shimadzu TOC-VCPH/CPN, Japan) (Maskaoui and Zhou 2010). All aqueous samples were acidified to 1% HNO_3 and stored in acid-cleaned polypropylene bottles at 4 °C until inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Arcos, Germany) analysis for major element (Mg, Ca, Na, K, Fe) contents (Hill and Aplin 2001).
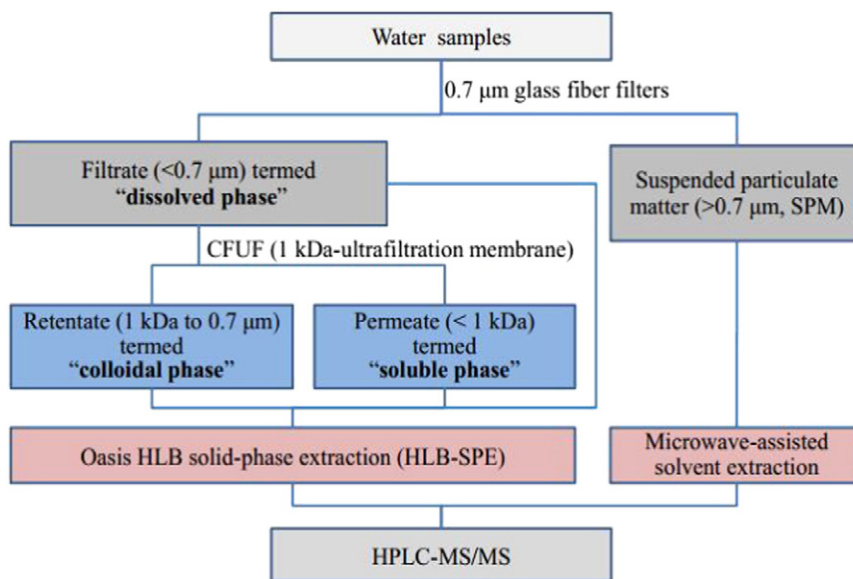
Fig. 2. Procedure used for multi-phases (SPM, dissolved, colloidal and soluble phase) separation and corresponding extraction methods of antibiotics.

2.4. Extraction and analysis

The methods of extraction and analysis of antibiotics are shown in Fig. 2. All aqueous samples (dissolved, soluble and colloidal phases) were extracted by solid phase extraction (SPE) using Oasis HLB cartridges (500 mg, Waters) (Cheng et al. 2014a). Before extraction, all aqueous samples were spiked with $^{13}C_3$-Caffeine (100 ng). Once extracted by SPE, the antibiotics and internal standard were eluted using 10 mL methanol, and then concentrated to 0.5 mL by evaporation under N_2. The SPM samples were extracted by microwave-assisted solvent extraction (MASE) (MARS-6, CEM Microwave Technology, North Carolina, USA) (Cheng et al. 2014a; Maskaoui and Zhou 2010). Prior to the MASE by the addition of solvents (methanol), SPM samples were spiked with $^{13}C_3$-Caffeine (100 ng) and allowed to mix for 4 h.

All the extracted antibiotics were analyzed by high performance liquid chromatography- electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS), using the multiple reaction monitoring (MRM) mode (Cheng et al. 2014a). The LC separation was performed using Ultimate 3000 HPLC separations module (Dionex, USA), equipped with a Sunfire C18 column (150 mm × 4.6 mm, 3.5 μm, Waters, USA). The mobile phase was composed of A (0.1% formic acid in ultrapure water), and eluent B (acetonitrile). At the flow-rate of 0.8 mL min^{-1}, 10 μL sample extracts were injected and the gradient elution runs as follows: 0–1 min, 15% B; 1–7 min a linear gradient to 95% B; 7–9 min, 95% B. The column temperature was maintained at 40 °C. The tandem MS analyses were carried out on a API 3200 triple-quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source that was operated in positive (ESI+) mode (Applied Biosystems/MDS Sciex, USA). The ion spray voltage and source temperature were set at 5500 V and 600 °C, respectively. Following the selection of precursor ions by the first quadrupole mass analyzer, nitrogen as curtain gas, ion source gas 1 and ion source gas 2 was set at 25, 60, and 70, respectively. The multiple reactions monitoring (MRM) experiment were listed in Fig. S1 and Table S2. The detailed processes of extraction and analysis are summarized in the Supporting Information.

2.5. Quality assurance and statistical analysis

To assess the adsorption of antibiotics on the ultrafiltration membranes during the CFUF operation, the static and CFUF equilibrium adsorption tests were performed (Liu et al. 2005). The detailed testing processes are summarized in the Supporting Information. To quantify the six targeted antibiotics, stable isotope-labeled internal standards ($^{13}C_3$-Caffeine) were selected on the basis of the relative response factor (RRF) (Zhang and Zhou 2007).

$$RRF = \frac{A_{is}}{A_{ant}} \times \frac{C_{ant}}{C_{is}} \qquad (1)$$

where A_{ant} is peak area of the antibiotic in the standard; C_{ant} is concentration of the antibiotic in the standard; A_{is} is peak area of internal standard; and C_{is} is concentration of the internal standard. The recoveries of the selected target compounds were determined using the standards addition method. Limits of detection (LOD) and limits of quantification (LOQ) were determined as the minimum detectable amount of an analyte with a signal-to-noise (S/N) of 3 and 10, respectively. The detailed testing processes are summarized in the Supporting Information. All samples were analyzed in triplicate, and the relative standard deviation was <25%.

Pearson's correlation (SPSS software, Windows version 16.0, SPSS Inc.) was performed in order to determine relationships between colloidal adsorption characteristics of antibiotics and the physicochemical properties of the colloidal phase.

3. Results and discussion

3.1. Quality assurance

The six antibiotics showed little adsorption onto the glass container's walls and membrane materials in the three types of waters during the static experiments, and the recovery varied between 78% and 122% (Fig. S2). In addition, the CFUF equilibrium adsorption tests were shown good recoveries for target compounds, ranging from 85.7% to 120%, 58.9% to 107% and 64.4% to 128% in pure, river, and sea water, respectively (Table S3).

The RRF of all antibiotics was stable throughout the duration of 96 h. The variability of RRF values for 6 antibiotics (represented by RSD) within 96 h is between 1 and 10% (Fig. S3). Thus the selected internal standards combined with their RRF value provide a suitable and affordable means for quantifying the antibiotics in environmental samples in this study. The recovery ranged from 68 to 102% and 65–92% for lake water and SPM, respectively (Table S4). The high recoveries in the lake waters and SPMs suggested that the matrix effects of the lake

waters and SPMs were relatively minor. The LOQ ranges of the six antibiotics in the lake water and SPM samples were between 1.3 and 3.7 ng L^{-1} and 1.2–3.6 ng g^{-1}, respectively (Table S4).

3.2. Occurrence of antibiotics in Baiyangdian Lake

3.2.1. Occurrence of antibiotics in the dissolved phase

The concentrations of antibiotics in the dissolved phase are summarized in Table 1. Concentrations of TCs, SAs and FQs ranged from 2.08 (OTC) to 220.16 (TC) ng L^{-1}, <LOQ (SDZ) to 1198.12 (SMZ) ng L^{-1} and 2.86 (NOR) to 3107.68 (OFL) ng L^{-1}, respectively.

The concentrations of SAs and TCs in the Baiyangdian Lake are of similar levels to some other regions such as the fishponds around Tai Lake in China (Song et al. 2016) with 176.50 ng L^{-1} of SAs and 23.89 ng L^{-1} of TCs on their average concentrations. Concentrations of SAs and FQs were greater than what was previously found in Baiyangdian Lake, especially for both SMZ and NOR. Both of these antibiotics have increased more than tenfold within the previous three to five years (Cheng et al. 2014a; Li et al. 2012). The increased concentrations might be attributed to their heavy use in both livestock and aquaculture industries expanded in this area due to economic development (Fabinyi and Liu 2014; Yang 2013). However, for TCs, the mean concentrations (OTC, 29.67 ng L^{-1}; TC, 17.46 ng L^{-1}) were similar or slightly reduced compared with our earlier study in Baiyangdian Lake (OTC, 27.17 ng L^{-1}; TC, 25.95 ng L^{-1}) (Cheng et al. 2014a), likely due to the gradual replacement of TCs by other more effective antibiotic compounds that have been extensively used as both human and livestock medicine in China in the past (Zou et al. 2011).

In the dissolved phase, there were significant differences ($P < 0.05$) in antibiotic concentrations between sampling sites within the two sampling periods (Fig. 3a). Site 10 was the most polluted with the highest total average concentration (TAC, $TAC = \sum \overline{C}_i$, where $\overline{C}_i$ is the average concentration of every antibiotic in every sampling site) of the six antibiotics (2961.23 ng L^{-1}). Site 10 was located in a region with aquaculture and livestock feeding (Fig. 1), and the highest levels were the result of discharge of aquaculture and livestock wastewater in the lake without treatment. There was a trend of decreasing antibiotic concentration levels with increasing distance from Site 10 (TAC, decreased from 2961.23 ng L^{-1} at Site 10 to 980.25 ng L^{-1} and 396.60 ng L^{-1} at site 9 and Site 8, respectively), Site 10 lies within an aquaculture area, in contrast to Sites 8 and 9, indicating that aquaculture may be a possible source of the antibiotics in Baiyangdian Lake (Cheng et al. 2014b; Shi et al. 2012). The second highest TACs of antibiotics in the dissolved phase were 1367.11 ng L^{-1} and 874.47 ng L^{-1} at Site 1 and Site 3, respectively. Site 1 and Site 3 were located in Fuhe River and Baigou River, respectively, that were two rivers receiving wastewaters from Baoding City and nearby villages (Fig. 1), especially Fuhe River that runs through the Baoding city receives a huge amount of domestic wastewater from the city (Cheng et al. 2014a), thus Site 1 and Site 3 had higher antibiotics than those in Baiyangdian Lake Site 2 and Site 4–8 (TAC, 313.36–764.98 ng L^{-1}). Therefore, wastewater discharge from city and villages is the main source of antibiotics in Baiyangdian Lake (Li et al. 2012). The higher concentration of antibiotics was also found at Site 6 (TAC, 764.98 ng L^{-1}), which was located in a well-known tourism location, which had a more dense population than other regions. In general, antibiotics levels varied with locations in Baiyangdian Lake, with high concentrations being contributed around rivers' wastewater discharging into the lake and agricultural activities nearby residents, such as aquaculture.

With the exception of TCs, overall antibiotic levels in June were higher than those in October (Fig. 3a). The total contents of SAs at each sampling site were about 2–112 times greater in June than in October. The average concentration of SMZ in June was 34 times higher than in October, which was the highest ratio among all of the antibiotics. Total concentrations of FQs were about 2–6 times higher in June than in

Table 1
Concentrations of antibiotics in dissolved, SPM, colloidal particle and soluble phases collected from Baiyangdian Lake.

Antibiotic group	Antibiotic	Dissolved phase (ng L^{-1})				SPM (ng g^{-1}, dry wt)				Colloidal particle phase (ng g^{-1}, dry wt)				Soluble phase (ng L^{-1})			
		Mean	Max[a]	Min[b]	Med[c]	Mean	Max	Min	Med	Mean	Max	Min	Med	Mean	Max	Min	Med
Tetracyclines (TCs)	Oxytetracycline (OTC)	17.43	85.92	2.08	9.83	17.35	67.11	<LOQ[d]	10.42	296.60	1011.45	58.33	206.37	12.53	69.45	<LOQ	6.08
	Tetracycline (TC)	29.67	220.16	4.39	14.37	10.67	37.25	<LOQ	7.64	841.64	5476.93	53.79	634.99	19.10	178.75	1.61	6.48
Sulfonamides (SAs)	Sulfamethazine (SMZ)	292.80	1198.12	4.32	242.59	15.41	143.66	<LOQ	5.09	3072.75	27,414.48	18.70	984.50	214.88	606.53	3.93	181.74
	Sulfadiazine (SDZ)	108.08	621.45	<LOQ	43.11	19.13	75.01	<LOQ	13.99	805.75	3662.91	10.23	112.74	86.54	541.37	<LOQ	21.97
Fluoroquinolones (FQs)	Norfloxacin (NOR)	57.04	376.80	2.86	19.34	23.62	51.39	7.41	23.79	366.82	2092.18	13.22	236.63	45.81	313.47	1.75	16.14
	Ofloxacin (OFL)	376.39	3107.68	12.60	189.48	50.32	180.08	7.41	39.92	2901.17	22,036.32	22.53	659.85	231.36	1640.6	5.99	142.37

[a] Maximum.
[b] Minimum.
[c] Median.
[d] Limit of quantification.

October. This result was not surprising because SAs and FQs is typically used in human and veterinary medicine to treat and prevent infectious diseases, especially fish diseases, that occur more frequently due to the high ambient temperature in June (during the early and intermediate aquaculture season) (Shah et al. 2014; Song et al. 2016). For TCs, their total concentrations at each sampling site in October (6.57–220.16 ng L^{-1}) were 1–16 times higher than in June (2.08–23.04 ng L^{-1}). The concentrations of TCs were significantly high in
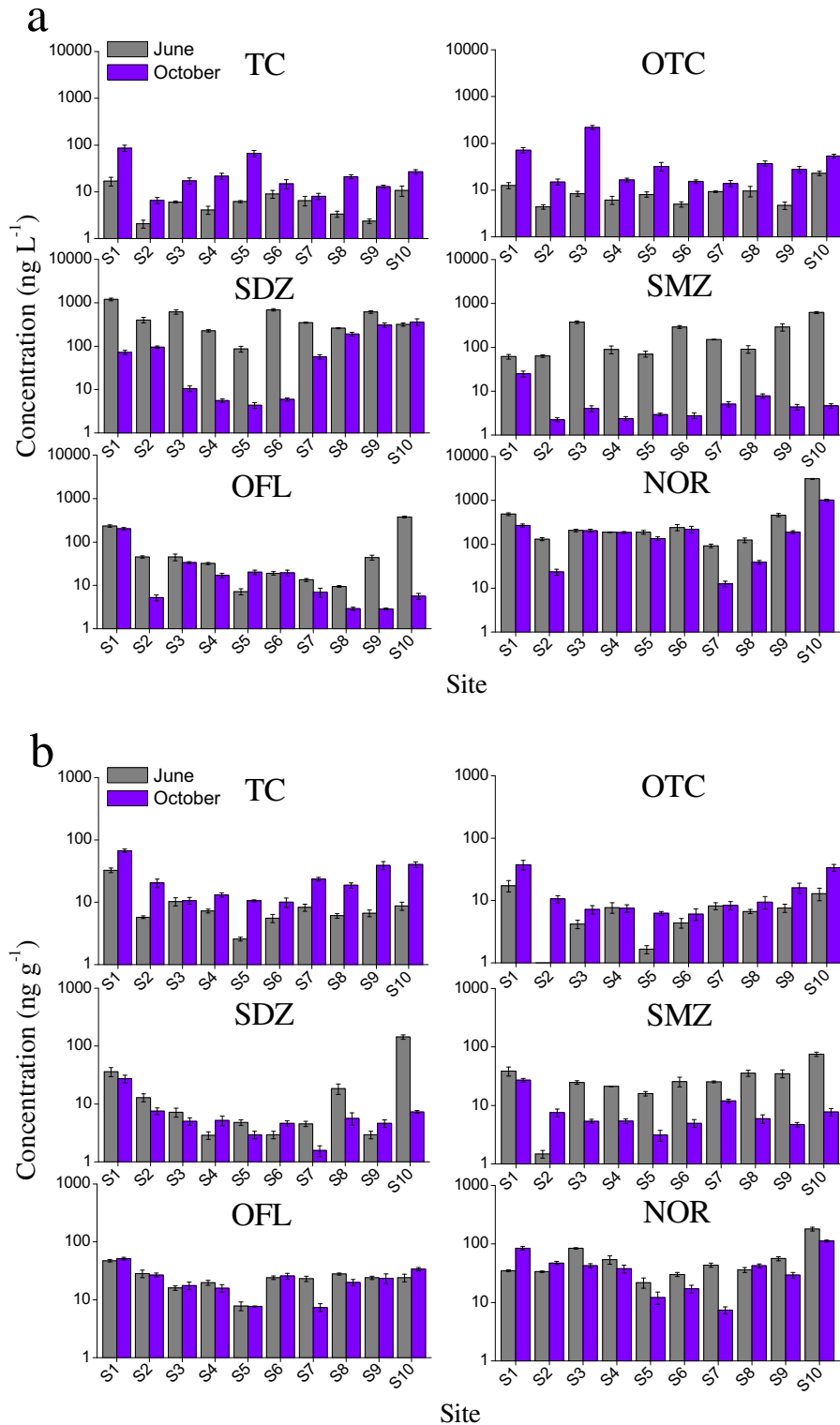

Fig. 3. Concentrations of the selected antibiotics at each sampling site of the Baiyangdian Lake in June 2013 and October 2014 in the four different phases: (a) dissolved phase, (b) SPM (c) colloidal and (d) soluble phase (error bars represent standard deviations).
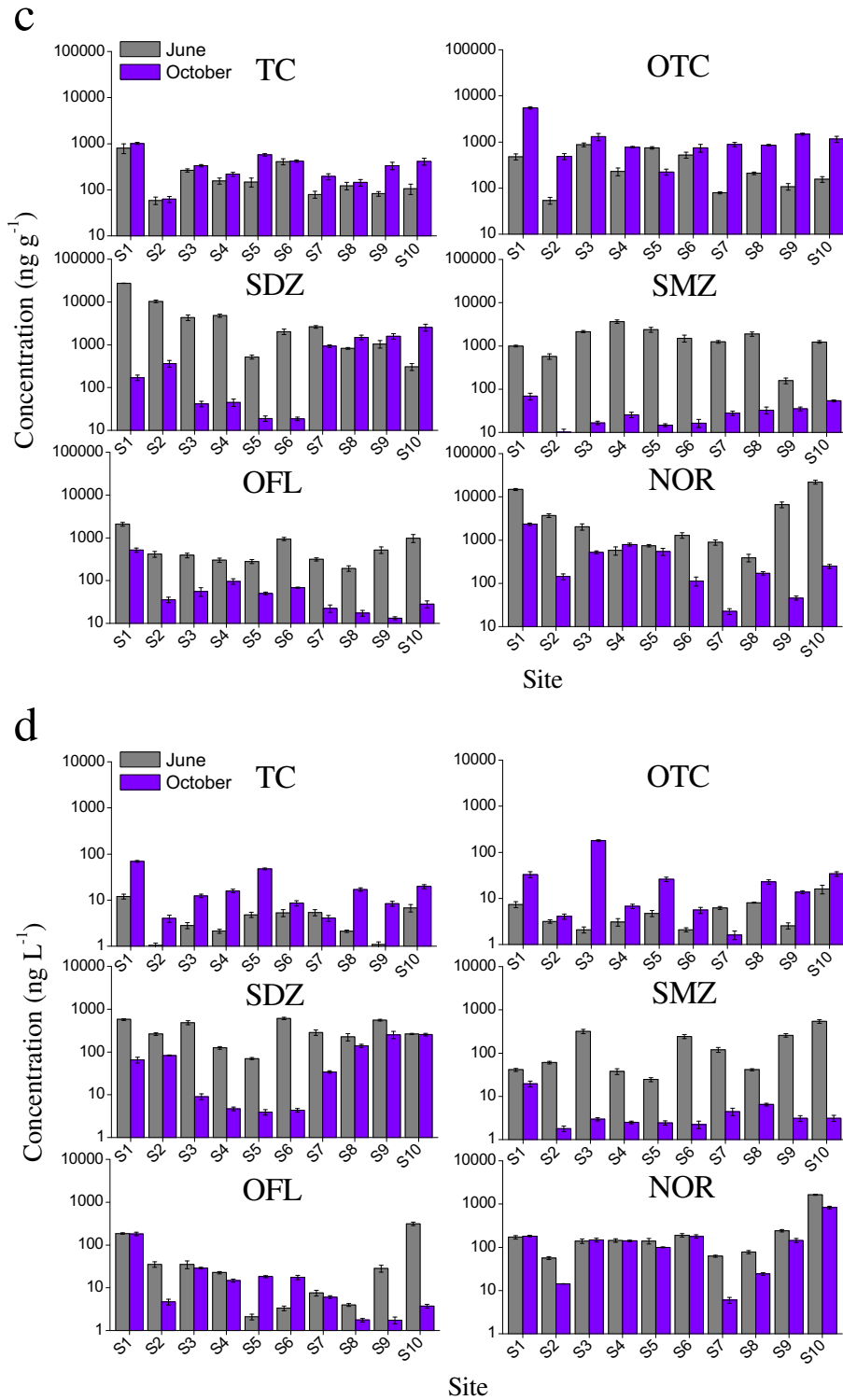
Fig. 3. (continued).

October, possibly due to therapeutic strategies to prevent and treat most respiratory infection in north China (Matsuia and Ozub 2008). Due to the lower temperature, less effective of photo- and bio-degradation rates would also contribute to the higher concentrations of TCs in October (Doll and Frimmel 2003; Loftin et al. 2008). In addition, traditional planting of winter wheat using manure application and flood irrigation can lead to the release of TCs from manure into surface water via overflow and drain flow (Cheng et al. 2014a).

3.2.2. Occurrence of antibiotics in SPM

The concentrations of TCs, SAs and FQs in SPM were summarized in Table 1 and ranged from <LOQ (OTC and TC) to 67.11 (OTC in October at Site 1), <LOQ (SMZ and SDZ) to 143.66 (SMZ in June at Site 10) and 7.41 (NOR and OFL) to 180.08 (OFL in June at Site 10) ng g^{-1}, respectively. Similar levels of antibiotics in SPM were reported by Stein et al. (2008).

As shown in Fig. 3b, the highest TAC of 339.81 ng g^{-1} was found at Site 10. The highest mean concentration was found for NOR

(146.19 ng g^{-1}) in SPM. Heavy use of antibiotics in high-intensity aquaculture areas may be contributed to this result. Antibiotics from Site 1 displayed the second highest concentrations (TAC, 250.88 ng g^{-1}) in SPM. Distribution of antibiotics were relatively uniform, and it ranged from 23.84 (NOR) to 10.87 (OTC) % to the total average concentration. This phenomenon reinforced the importance of municipal sewage water as a source of antibiotics to natural aquatic environments (Maskaoui and Zhou 2010; Nie et al. 2014). The lowest TAC of 48.65 ng g^{-1} was found at Site 5. This site was away from the Wangjiazhai village (Site 6, TAC, 80.57 ng g^{-1}). TACs ranged from 98.46 (Site 4) to 117.42 ng g^{-1} (Site 3) and 80.57 (Site 6) to 124.57 ng g^{-1} (Site 9) in Site 2–4 and Site 6–9, respectively, concentrations varying from <LOQ to 39.13 (TCs), <LOQ to 35.67 (SAs) and 7.41 to 84.17 ng g^{-1} (FQs). This broadly similar in those seven sampling sites further suggested the potential relationship between antibiotics and sediment. It was confirmed by the comparable residuals of OTC (mean, 15.66 ng g^{-1}), TC (mean, 25.71 ng g^{-1}), OFL (mean, 39.73 ng g^{-1}) and SMZ (mean, 1.47 ng g^{-1}) in sediment in Baiyangdian Lake (Cheng et al. 2014a; Li et al. 2012). Comparing the distribution of targeted antibiotics in both SPM and dissolved phase (Table 1), TCs and FQs had stronger sorption potentials than SAs. It was also proved that association of antibiotics with SPMs did not belong to hydrophobic interactions, due to the low log K_{ow} values of TCs (TC, −1.33; OTC, −1.22) and FQs (NOR, −1.7; OFL, −0.39) connected with the high sorption of antibiotics (Table S1), and the high log K_{ow} values of SAs (SMZ, 0.14; SDZ, −0.09) connected with the low sorption of antibiotic. This behavior could be because SAs have fewer ionic functional groups than TCs and FQs in the structures, as indicated by their chemical structures in Table S1 (Yi et al. 2013).

Similar seasonal variations to the dissolved phase were observed in the SPM (Fig. 3b). The total contents of both SAs and FQs at each sampling site were about 1–15 times greater in June than in October for SPM samples. In contrast, higher concentrations of TCs were observed in October instead of in June. These observations could be associated with the diffusive transfer of SAs and FQs from the soluble phase into the SPM due to the high concentration of those antibiotics in the soluble phase during June 2014, and vice versa for TCs in October 2013 (Sarmah et al. 2006). But it is worth attention that SMZ at Site 2 exhibited an opposite behavior compared to the other sites. The primary reason that causes this phenomenon is that there is the most abundant of SPM at

Site 2 in October (18.37 mg L^{-1}, data not shown) comparing in June (9.10 mg L^{-1}, data not shown). It was contributed by the lots of imports of SPM from farmland via overflow and drain flow in the period of winter wheat's planting in October from Fuhe River and the release of SPM from sediment into water by intensive shipping activity during the harvest season of October at Site 2 (Dai et al. 2013). The high concentration of SMZ in October may be contributed to the stronger adsorption of SMZ to the SPM than other three antibiotics. This is an interesting finding that needed to clarify the specific reasons in the further studies.

3.2.3. Occurrence of antibiotics in the soluble and colloidal phases

Concentrations of antibiotics ranged from 10.23 ng g^{-1} (SDZ) to 27,414 ng g^{-1} (SMZ) (mean, 1381 ng g^{-1}) in colloidal phase, and from <LOQ (OTC and SDZ) to 1641 ng L^{-1} (OFL) (mean, 101.70 ng L^{-1}) in soluble phase (Table 1). The concentrations of SAs in soluble phases in this study were much higher than those reported in Huangpu River (SDZ, 3.11–6.93 ng L^{-1}; SMZ, 1.85–38.61 ng L^{-1}) (Yan et al. 2015a). The concentrations of SDZ and SMZ in colloidal phases were 0.54–0.64 ng L^{-1} and 0.32–3.77 ng L^{-1}, respectively, in Huangpu River (Yan et al. 2015a). However, no reference data on the targeted antibiotic residual levels in colloidal phases has been reported. Therefore our results could not be compared with other areas.

The SDZ and NOR were dominant in both phases (Fig. 3c, d). The other antibiotics accounted for <10% and 15% of the TACs in colloidal and soluble phases, respectively. Similar to the dissolved samples, high antibiotic concentrations were detected in the colloidal samples at Site 1 (TAC, 28,095 ng g^{-1}) and Site 10 (TAC, 14,643 ng g^{-1}), and low TACs of 3130 ng g^{-1} and 3173 ng g^{-1} were detected at Site 5 and 8, respectively. Concentrations in colloids were 10–239 times greater than in the SPMs, suggesting that colloids were significant carriers of antibiotics than SPMs (Maskaoui and Zhou 2010). For the soluble phase, the spatial distribution was also very similar to that of the dissolved samples, and TACs ranged from 222 to 1963 ng L^{-1} in Site 4 and Site 10, respectively.

Similar seasonal variations in the dissolved phase were also observed in the colloidal and soluble phases (Fig. 3c, d). For the soluble phase, high concentrations of SAs and FQs were detected in June, especially for SAs that were approximately 2–129 times higher in June than in October (Fig. 3d). In contrast, the concentrations of TCs in October were almost 85 times those in June. The reasons for seasonal differences
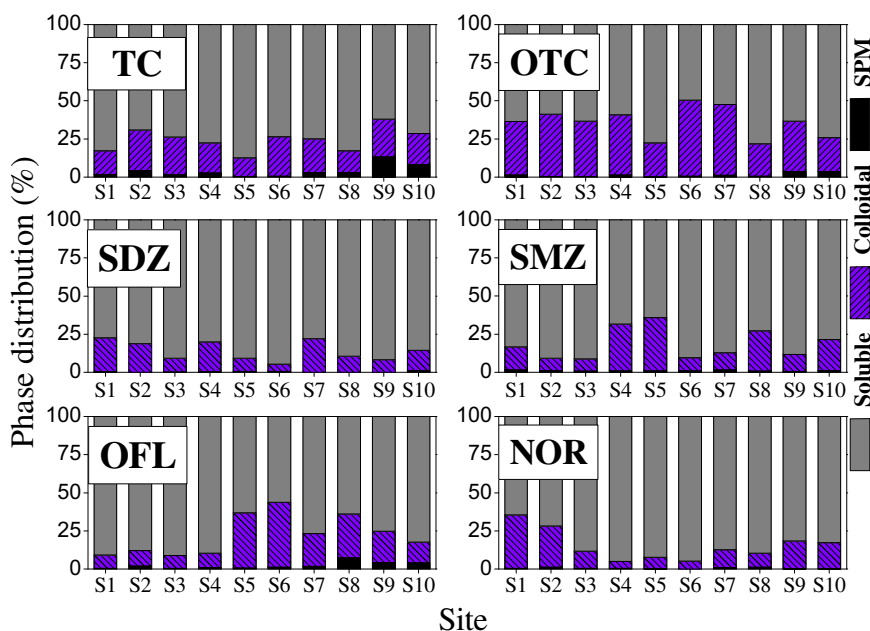

Fig. 4. Mass balance of antibiotic distributions among SPM, colloidal and soluble phases in water samples of Baiyangdian Lake.

Table 2
Partition coefficients of antibiotics between SPM and filtrate (K_p^{obs}), between SPM and permeate (K_p^{int}), between colloids and permeate ($K_{col.}$).

Antibiotic	K_p^{obs} (L kg^{-1})			K_p^{int} (L kg^{-1})			$K_{col.}$ (L kg^{-1})		
	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean
TC	4877–226	1691	1823	6173–221	1784	2572	93,604–8508	35,262	40,585
OTC	3797–41	803	566	5188–40	1118	1472	547,713–7278	69,447	117,374
SDZ	823–5	38	169	1167–5	56	249	47,666–1162	6860	12,289
SMZ	3384–29	777	938	4192–25	930	1220	97,996–611	7087	18,970
OFL	5587–98	979	1648	13,457–77	1144	3456	282,043–1915	8753	31,473
NOR	3553–70	293	541	3325–96	277	574	86,551–299	14,616	6218

in the soluble phases were much like the dissolved phases, due to variation in antibiotic consumption, physical and (bio-)chemical behaviors of the antibiotics (e.g., photo- and bio-degradation) in June and October in Baiyangdian Lake (Cheng et al. 2014a).

The total contents of both SAs and FQs at each sampling site were about 1–120 times greater in June than in October for colloidal phase samples. In contrast, higher concentrations of TCs were observed in October instead of in June (Fig. 3c). Like in SPM, the results could be explained as the transfer of antibiotics from the soluble phase to the colloidal phases because of the high concentration of those antibiotics in the soluble phase (Sarmah et al. 2006). For the colloidal phase, the obvious seasonal variations of antibiotics comparing in the SPM may be contributed to the higher content of colloid in June (range, 11.60–37.11 mg L^{-1}) than those in October (9.39–28.93 mg L^{-1}), and the special surface properties of colloid. The colloidal aggregation and adsorption of trace pollutants are dependent on the features of the colloid-colloid and colloid-water interfaces (Benedetti et al. 2003; Foster et al. 2003). For TCs, the other possible reason may be that traditional planting of winter wheat using excessive manure application and flood irrigation in late September or early October, that's lead to inputs colloids associated with TCs from manure into water via overflow and drain flow, especially for Site 1 that was located in the farming areas (Chang et al. 2010; Chen et al. 2011a; Muller et al. 2000).

To assess the efficiency of isolating the colloids using the CFUF system, the recovery values of organic carbon (OC) and antibiotics were calculated as the percentages of the measured total concentrations in colloidal and soluble phases to the concentration in the dissolved phase (Nie et al. 2014). The R values of OC were in the range of 74.66–138.52% (mean, 94.67%). Satisfactory recoveries were also obtained for TC (67.90–94.02%), OTC (72.15–93.13%), SDZ (77.63–97.43%), SMZ (79.28–115.06%), OFL (70.16–96.57%) and NOR (50.66–86.42%), with average recoveries of 82.49%, 83.62%, 90.08%, 92.12%, 88.62% and 76.95%, respectively.

3.3. Mass balance of antibiotics among SPM, colloidal and soluble phases

To further explore the role of natural colloids in the multi-phase distribution of antibiotics in Baiyangdian Lake, the mass balance of antibiotics among SPM, colloidal and soluble phases was calculated. The antibiotics were mainly in the soluble phase (49.59–94.97%), indicating high biological availability of these antibiotics (Fig. 4). Between 4.9% and 49.8% of the individual antibiotics were bound to the colloidal phase, as follows: TC, 12.37–26.75% (mean, 20.65%); OTC, 21.29–49.82% (mean, 34.69%), SDZ, 4.93–22.28% (mean, 13.71%); SMZ, 8.16–34.86% (mean, 17.46%); OFL, 8.42–42.61% (mean, 20.01%); and NOR, 4.71–35.03% (mean, 14.71%). However, only 0.24–13.31% of TCs, 0.01–1.13% of SAs and 0.09–2.27% of FQs were bound with SPMs. The results demonstrate that colloids can play an important role to remove the organic contaminants from aquatic environments (Lead and Wilkinson 2006; Liu et al. 2005).

3.4. Phases partitioning and statistical correlation

Since the adsorption to solid matrices is one of the critical steps limiting the fate and transport of antibiotics, it is necessary to calculate the

pseudo-partition coefficients of antibiotics between SPM and the dissolved phase (observed partition coefficients, K_p^{obs}), SPM and the soluble phase (intrinsic partition coefficients, K_p^{int}) and colloids and the soluble phase ($K_{col.}$):

$$K_p^{obs} = \frac{C_{SPM}}{C_{dis.}} \tag{2}$$

$$K_p^{int} = \frac{C_{SPM}}{C_{sol.}} \tag{3}$$

$$K_{col.} = \frac{C_{col.}}{C_{sol.}} \tag{4}$$

where C_{SPM} is the average concentration in the SPMs (ng g^{-1}), $C_{dis.}$ is the average concentration in the dissolved phases (ng L^{-1}), $C_{sol.}$ is the average concentration in the soluble phases (ng L^{-1}), and $C_{col.}$ is the average concentration in the colloidal phases (ng g^{-1}) (Kim and Carlson 2007; Li et al. 2012). Since the SPM, soluble phase and colloidal phase are not at equilibrium, those values cannot be regarded as true partitioning coefficients. However, calculated pseudo-partition coefficients can be a valuable indicator of the sorption characteristics of individual compounds. As shown in Table 2, the mean K_p^{obs} values varied from 169 L kg^{-1} for SDZ to 1823 L kg^{-1} for TC. These values are similar to reported values for OFL (1192–10,000 L kg^{-1}) and higher than those for SMZ (1.68–3.67 L kg^{-1}) (Carstens et al. 2013; Drillia et al. 2005; Petrie et al. 2014; Vithanage et al. 2014). Traditionally, the partition coefficient was decided according as the ratio of the contaminant contents in the SPM and dissolved phase. The K_p^{int} values were 6.18–109.66% higher than corresponding K_p^{obs} values. Hence, it was essential to derive K_p^{int} values. In addition, the calculations also showed that the mean $K_{col.}$ values ranged from 6218 to 117,374 L kg^{-1}, which were 1–2 orders of magnitude larger than the K_p^{int} values (Table 2). This clearly indicates that colloids are important carriers of antibiotics than SPM in the aquatic system (Maskaoui and Zhou 2010; Nie et al. 2014).

To further investigate the mechanisms of colloidal adsorption of antibiotics, the physicochemical properties of the aquatic colloidal phase were determined (Table S6). In Baiyangdian Lake, the concentrations of colloids ranged from 9.4 to 37.1 mg L^{-1}, the pH ranged from 6.89 to 8.62 and the COC content varied from 65.12 to 323.10 g kg^{-1}. The element concentrations for Ca, Mg, Na and K in the colloidal particle phase ranged from 0.82 to 193.34 g kg^{-1}, while the Fe content varied from 38 to 932 mg kg^{-1}. These results are consistent with those of other researchers who have shown that colloidal fractions contain significant concentrations of elements, especially Ca, Mg, Na, K and organic carbon (Ran et al. 2000; Sanudo-Wilhelmy et al. 1996), which may be ascribed to the high surface area, organic C content and cation-exchange capacity of colloids (Ran et al. 2000). Therefore, it is not surprising that the colloidal phase has a strong ability to fix dissolved cations by electrostatic interaction and cation exchange (Pan et al. 2012).

Pearson correlation analysis showed that the values of log $K_{col.}$ were mainly negatively correlated ($P < 0.01$) with binding of Ca and Mg, especially of OTC with Mg ($r = -0.643$) and OFL with both Ca (-0.595) and Mg (-0.593) (Table S7). This result may be attributed to the competitive adsorption between the antibiotics and cations, especially the

divalent cations such as Ca^{2+} and Mg^{2+}, in the colloidal phase (Chen et al. 2011b; Yusheng et al. 2011). Pan et al. (2012) have applied dialysis equilibrium system to investigate the role of cations in DOM-antibiotics interactions. It has been demonstrated that Mg^{2+} decreased DOM (dissolved organic matter)-OFL binding and OFL decreased DOM-Mg binding due to the competitive effect between Mg^{2+} and OFL. In addition, the strong complexation ability of antibiotics with divalent cations in solution could explain why divalent cations (Ca^{2+} and Mg^{2+}) were the main participants in the competitive adsorption (Figueroa et al. 2004; Martin 1979). It was confident that this phenomenon was due to the massive existence of COC and cations, such as Ca^{2+} and Mg^{2+}, and the strong binding ability between them (Table S5, 6). Since the 1960s, due to increasing human activities and climate change, Baiyangdian Lake has suffered from markedly shrinking and drying up several times. To maintain the existence and development of Baiyangdian Lake, anthropogenic water supplement plays a very important role, and from 1981 to 2003 this approach had been already carried out 15 times. (Yang et al. 2010). In this situation, both continuous water supplement and evaporation loss led to the accumulation of COC, Ca^{2+} and Mg^{2+}. High COC is also attributed by human activities (agriculture and domestic wastewater, food and excrement from aquaculture) and natural processes (microorganism and aquatic-plant activities) (Cui et al. 2016). It is generally accepted that natural organic matter adsorption masks the characteristics of the underlying mineral particles in aquatic environments (Roberts et al. 2004). Similarly it has also been found that the presence of cations influences the adsorption of TC to mineral particles due to the competitive adsorption between cations and antibiotics (Zhao et al. 2011). For SAs, the log $K_{col.}$ showed a weak correlation with divalent cations, especially of SMZ with Ca^{2+} ($r = -0.463$, $P < 0.05$). This result may be directly related to the weaker sorption of SMZ to natural colloids (Table 2).

Unexpectedly, pH was not found to be significantly ($P > 0.05$) correlated with log $K_{col.}$. This result may be due to the narrow ranges of pH (6.89–8.62) in our colloid solutions in comparison with the variation in soil solutions (4.01–8.84) (Gong et al. 2012; Zhao et al. 2015). In addition, it's worth mentioning that the correlation between COC and log $K_{col.}$ was not statistically significant ($P > 0.05$). This result was not surprising because the soluble phase and colloidal phase are not at equilibrium and most antibiotics were amphoteric molecules having ionizable functional groups. Compared with the $K_{col.}$ (299–547,712 L kg^{-1}), the target antibiotics had higher K_{COC} values (926–3,906,879 L kg^{-1}, data not shown) that were normalized by the COC, which suggests that the compounds were less mobile than their corresponding $K_{col.}$ values would indicate. Thus, the normalizing partition coefficients using COC are not recommended for antibiotics, as they do not reflect the reality of antibiotics in aquatic environments (Tolls 2001; Wegst-Uhrich et al. 2014).

As a heterogeneous mixture of particles, natural colloids often have different sizes, shapes, coatings and surface chemistry, as well as chemical composition, making sorption mechanisms complex. This study only started to explore the sorption mechanisms of antibiotics on colloids, and further research is needed to identify the interactions between antibiotics and colloids in natural environments.

4. Conclusions

This work provides the first seasonal data on the distribution of antibiotics in surface waters from the Baiyangdian Lake. The behaviors of the antibiotics were investigated by determining their contents in SPM, colloidal and soluble phases in aquatic environment. Antibiotic concentrations differed significantly with sampling location and sampling time. Binding with colloids plays a very significant role in the partitioning of antibiotics among different phases. Results of the Pearson correlation analysis between the log $K_{col.}$ of antibiotics and the physicochemical properties of natural colloids suggest that a competitive adsorption mechanism exists between the antibiotics and cations. The

normalized $K_{col.}$ with COC are not recommended for antibiotics because they do not reflect the reality of antibiotics in aquatic environments. Study results further demonstrated that sorption mechanisms were more complex than simple hydrophobicity bonding, and should also consider other mechanisms such as electrostatic interactions, cation exchange, competition and bridging.

A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.11.012.

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