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Sorption of tetracycline, oxytetracycline and tylosin to eight surface sediments of Taihu Lake

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Abstract

The objective of the present study is to investigate the mechanism of tetracyclines and macrolieds absorption on Taihu Lake sediments. In the study, batch technique was used to study the adsorptive behavior of three pharmaceutical antibiotics (tetracycline, oxytetracycline and tylosin) from several sediments of Taihu Lake, Zhushan Bay, Western Lakeshore, Lake Center, Southern Lakeshore, East Tai Lake, Eastern Lakeshore, Gonghu Bay and Meiliang Bay. The eight sediments showed extraordinarily high absorption affinity for all the tested antibiotics. However, especially the sediments of East Tai Lake was exceptional. The observed sorbent to solution distribution coefficient (K_d, l kg^{-1}) was 10^2-10^4. The sediment of East Tai Lake showed highest organic carbon content and cation exchange capacity. A remarkably strong sorption of antibiotics to the sediment of East Tai Lake can be attributed to the cation exchange and complexation reactions between the functional groups of antibiotics and the respective charged and polar sites of the sorbents. The sorption affinity of tetracycline and oxytetracycline from the eight sediments was higher than tylosin. Tetracycline and oxytetracycline had multiple polar and ionizable functional groups. In the study within the tested pH, the zwitterion speciation is predominated; therefore, the sorption interaction (cation exchange and surface complexation) between tetracycline and sediments was expected stronger than tylosin.

Key words

Sediment, Sorption, Taihu Lake, Tetracycline, Tylosin

Introduction

Taihu Lake is situated in the south of Yangtze Delta, China, among 30°55'–31°33'N and 119°52'–120°36'E with a land area of 2338 km^2 and an average water depth of 1.9 m. It is one of the five largest freshwater lakes in China. Taihu Lake has almost the highest population density and is situated in one of the most heavily industrialized areas in China. It covers only 0.4% of total territory of the country, but contributes 3.1% of the national food production and 10% of the gross domestic product. After decades of intensive industrial development accompanied by the production of thousands of various chemicals in this densely populated area, the quality of Taihu Lake water has degraded 2–3 levels from 1970 to 1990. Serious blue–green algae water blooms have been frequently occurring in recent years. Organic and heavy mental contaminants in Taihu Lake have been studied, however, distribution, transport and fate of pharmaceutical antibiotics in Taihu water sediment system is limited.

Pharmaceutical antibiotics are heavily used as veterinary therapeutics and growth promoters for animals. Most of the antibiotics used in the farming industry are excreted via fecal matter and urine as unmodified parent compounds, with only small fractions being metabolized. China has the largest population in the world, and antibiotics are of common use, with annual consumption being over 25,000 tons (Kummerer, 2010). Antimicrobials constitute more than 6% of all prescriptions in human medicine, and more than 70% pharmaceuticals are consumed in veterinary medicine (Thiele-Bruhn, 2003). Antimicrobials are often not completely metabolized by livestock and up to 90% of the antimicrobials administered may be excreted either as a parent compound or in a partially metabolized form (Huang *et al.,* 2001; Ingerslev and Sorensen, 2000; Tolls, 2001). The fate and transport of antibiotics in the environment has been focus of research in recent years. The presence of antibiotics in the environment has raised significant concern because these bioactive compounds may promote development and spread of antibiotic resistant genes among the bacterial population or induce biological responses due to prolonged exposure to low-level antibiotics (Chee-Sanford *et al.,* 2001; Roy *et al.,* 2015; Arias-Andres *et al.,* 2014; Daughton and Ternes, 1999). In the Netherlands and the Weser-Ems district of Germany, more than 50% of veterinary antimicrobial agents are used as tetracyclines, approximately 20% as sulfonamides, and 12% as macrolides (Winckler and Grafe, 2001).

Tetracyclines, a wide-spectrum antibiotic, constitute one of the most important antibiotic families, ranking second in production and usage worldwide (Levy, 2002). Tetracyclines have been detected in sediments, soils, surface waters; groundwater samples collected near waste and wastewater lagoons samples (Kulshrestha *et al.,* 2004; Jacobsen *et al.,* 2004; Meyer *et al.,* 2000). Tylosin, a wide-spectrum, macrolide antibiotic is a veterinary antibiotic widely used as therapeutic and subtherapeutic levels and for increases in rates of weight gain and improved feed efficiency in companion animals, cattles, chickens, turkeys and swine (Kumar *et al.,* 2005). Tylosin is one of the most common antibiotics present in swine and turkey manures, with concentrations as high as 4 mg l^{-1} as measured in swine manure (Kumar *et al.,* 2004).

Pharmaceuticals released in aquatic systems are expected to absorb to the sediments to varying degrees. Their sorption is likely to influence their fate and transport, which ultimately pose risk to the aquatic organisms. Sorption to solid surface is an important process for deciding the transport and fate of organic chemicals, such as antibiotics, in environment (Drillia *et al.,* 2005). Like other organic chemicals, the sorption behavior of antibiotics is also not only influenced by their own properties, including water solubility, acid-dissociation constant (pK_a) and octanol-water partition coeffcient (K_{ow}) (Drillia *et al.,* 2005; Lorphensri *et al.,* 2006), but also by sediment properties such as quality and quantity of organic matter, type and amount of clay minerals, cation exchange capacity (CEC) and pH value. The adsorbent-to-solution distribution coeffcients, K_d, presented in the literature strongly suggest that the tendency of antibiotics to sorb to soil and sediment cannot be predicted from their lipophilicity alone. While estimating the K_d value of antibiotics, the specific chemical structure of antibiotics, such as functional groups, hydrogen bonds, has to be considered carefully at a relevant pH value. The antibiotics may interact with sediments via metal complexation, hydrogen bonding and electrical interactions or polarization besides hydrophobic interaction (Tolls, 2001).

Persistence of antibiotics in terrestrial environment ranges from less than one day to week or even months depending primarily on temperature and chemical structure of the antibiotics. However, knowledge on the behavior and fate of currently unregulated chemicals, such as tetracyclines and macrolides into the aquatic environment is still limited. Moreover, research about the interaction mechanisms of sediments and antibiotics is meagre. The sorption behaviour of tetracycline, oxytetracycline and tylosin on sediments has not yet been fully elucidated in the literature. Thus, the present study, focused on the sorption of tetracycline and tylosin on sediments collected from different sites in Taihu Lake, China. Particular emphasis was given on investigating the following : sorption of tetracycline and tylosin on sediments in different sites; impact of different structure of antibiotic sorption on sediments. The results obtained are important to evaluate the migration tendency of tetracycline, oxytetracycline and tylosin on sediments and to assess the fate and risk of lake contamination.

Materials and Methods

Sorbents and sorbates : The sediment samples were collected from eight different sites in the Taihu Lake (Zhushan Bay S1, Western Lakeshore S2, Lake Center S3, Southern Lakeshore S4, East Tai Lake S5, Eastern Lakeshore S6, Gonghu Bay S7, Meiliang Bay S8). The location of chosen sites is shown in Fig. 1 and the latitudes/longitudes of sites are represented in Table 1. The sampling sites were selected to provide almost total coverage of the Taihu Lake. The sediments were collected from the surface at 0–5 cm depth, and then thoroughly homogenized, freeze-dried, sieved using a 100-mesh opening sieve, and stored in dark. The properties of eight sediments are presented in Table 1. Soil organic carbon content was determined by CO_2 evolution on combustion of freeze-dried soil samples after removal of inorganic carbons by adding 0.01 M HCl. Analysis of cation exchange capacity(CEC) was performed using 1 M NH_4Ac and 0.005 M EDTA at pH 7.0.

The three tested pharmaceutical antibiotics are tetracycline (95%, Biosharp), oxytetracycline (95%, Biosharp), and tylosin (99%, DeBiochem). Solute aqueous solubility (S_w), n-octanol-water partition coefficient (K_{ow}), and acid dissociation constant (pK_a) are listed Table 2.

Batch sorption : Batch sorption experiments were performed using 22 ml glass vials equipped with polytetrafluoroethylene-lined screw caps. Vials were fitted with 50 mg of selected sediments and a full volume of background solution containing 0.02 M NaCl. The sorbents were prewetted for 24 hrs. The pH of sediment suspension was adjusted to about 6.5 by 0.05M HCl and 0.01 M NaOH. The sediment slurries were then spiked with the test sorbate in methanol carrier that was kept below 0.1% (V:V) to minimize cosolvent effects. The initial concentration rage of tetracycline was 3.1×10^{-3}-7.1×10^{-2} mmol l^{-1}, the initial concentration of oxytetracycline was 2.7×10^{-3}-6.1×10^{-2} mmol l^{-1} and the initial concentration of tylosin was 2.1×10^{-3}-2.6×10^{-2} mmol l^{-1}. The samples were then mixed end-over-end at room temperature for 3 day. The 3 days incubation time was selected for batch equilibrium study because previous studies showed that 24 hrs time was found effective for sufficient equilibration time (Rabølle and Spliid, 2000). Afterward, the samples were left undisturbed for more than 12 hrs to allow complete settling of the sorbent, and then centrifuged at 4000 r/min for 10 min.

The sorption on to the tubes and caps were assumed to be negligible (<5%). Tetracycline, oxytetracycline and tylosin were analyzed by HPLC (High-Performance Liquid Chromatography, HPLC, Waters e2695) using a Bridge C18 column (4.6×150mm). Isocratic elution was performed with a UV detector under the following conditions: 0.01M oxalic acid, acetonitrile and methanol (80:16:4; v:v:v) with a wavelength of 360nm for tetracycline and oxytetracycline, 0.02 M ammonium acetate and acetonitrile (65:35; v: v) with a wavelength of 290 nm.

Results and Discussion

Characterization of sediments : The results of pH, oxidation-reduction potential (Eh), cation exchange capacity (CEC), and organic carbon (OC) content of different sediments from different sites are summarized in Table 1. According to Table 1, the pH values of eight sediments from different sites did not vary much; they were all near to neutral ranging from 7.33 to 7.74. The range of Eh widely changed from -111 to 534, which indicated that both oxidation and reduction conditions exist in the sediments. The cation exchange capacity in the collected sediments ranged from 18.99 to 33.33 cmol kg^{-1}, which was noted in the samples as follows: East Tai Lake, Meiliang Bay > Gonghu Bay > Zhushan Bay > Southern Lakeshore > Eastern lakeshore > Western Lakeshore, Lake Center.

The pH values of eight sediments from different sites did not change much. East Tai Lake sample showed largest OC content, and Lake Center sample showed smallest OC content, OC content of other samples were nearly similar. Considering all the parameters, the East Tai Lake sample had the highest CEC and OC content.

Sorption isotherms of tetracycline, oxytetracycline and tylosin on different sediments : The tetracycline, oxytetracycline and tylosin sorption isotherms on tested sediments within the concentration range were regressively analyzed using Freundlich model. $q=K_F C_e^n$, where, q (mmol kg^{-1}) is solid concentration and C_e (mmol/L) is liquid concentration in balance of liquid and solid. Freundlich model is a nonlinear sorption model, which suggests the heterogeneity of surface and exponential distribution of sites and their energies. It can be assumed that the sediments have a range of sorption sites and the capacity for multilayer sorption. In the Freundlich sorption model, K_F is a measure of the degree of sorption strength which can be regarded as a relative indicator of sorption capacity, while n is used as an indicator of whether sorption remains constant (n = 1) or decreases with the increasing solute concentration (n < 1). The sorption is linear when n = 1 and the sorption is nonlinear when n < 1, it indicates nonlinear sorption isotherms is larger. Freundlich model parameters for isotherms measured for sorption are shown at Table 3. For tetracycline, the n value of sorption isotherms on Zhushan Bay (n=0.82±0.03) is less than n value of sorption isotherms on East Tai Lake (n=0.60±0.03), which indicates that a more heterogeneous distribution of sorption sites on East Tai Lake. In the present study, the obtained sorption isotherms were used mainly for comparing the sorption affinity between different antibiotic/sediment combinations.

From all the Figures, it can be stated that solid concentration increased with increasing the liquid concentration. Fig. 2 shows sorption of tetracycline on sediments from East Tai Lake and Zhushan Bay were strongest. The calculated K_d (calculated from the Freundlich model at middle equilibrium aqueous concentration) of East Tai Lake (E) was 15400 l kg^{-1}, and the K_d of Zhushang Bay was 11300 l kg^{-1} which is slightly lower than East Tai Lake. Sorption of tetracycline on sediments from Southern Lakeshore and Lake Center are weakest. The calculated K_d was 1600 l kg^{-1} and 2000 l kg^{-1} which was nearly one tenth of East Tai Lake's. Fig. 3 shows that sorption of oxytetracycline on sediment from East Tai Lake and Zhushan Bay was strongest. The calculated K_d was 3300 l kg^{-1} and 6200 l kg^{-1}. Sorption of oxyetracycline on sediments from Southern Lakeshore and Lake Center were weakest. The calculated K_d was 1350 l kg^{-1} and 1600 l kg^{-1}. This trend was similar to tetracycline. Fig. 4 shows sorption isotherms of tylosin on eight sediments were close. Sorption of tylosin on East Tai Lake was strong at low concentration (the calculated K_d is 260 l kg^{-1}), while the others were slightly lower. Sorption of tylosin on Lake Center was lowest (the calculated K_d was 200 lkg^{-1}).

Sorption of tetracycline, oxytetracycline and tylosin on sediment from East Tai Lake was strongest (Fig. 2, 3 and 4). The sediment from East Tai Lake had highest OC content and CEC (Table 1). Usually, there are different conformation of antibiotics accompany with different pH value. For example, tetracycline carries a positive charge throughout the environmentally relevant pH range. Generally, tetracycline has four different species in various pH ranges (Sassmann and Lee, 2005). The cationic form (+00) is present up to pH 5.6, the zwitterion (+ – 0) is present up to pH 9.5, and the net negative charge ion (+ – –) is present at pH > 7.0. At pH 7.0, tetracycline is about 75% neutral zwitterions (ionization is +– 0) and 25% zwitterions with a net negative charge (ionization is + – –) (Sassmann and Lee, 2005). Therefore, with the increased solution pH value, the concentration of anionic form of tetracycline increased accordingly and non-ionized tetracycline would be less. Essentially, the anionic form of tetracycline appeared to sorb less than the non-ionized form. The trend observed in the present study was similar to the study reported by Sassmann and Lee (2005), Pils and Laird (2007). In order to investigate the mechanisms of tetracycline, oxytetracycline, and chlortetracycline sorption by soil and its constituents, batch studies were conducted in several soil with various pH, cation exchange capacity (CEC), anion exchange capacity (AEC), clay content and type, and OC content under various background electrolyte concentrations (Sassman and Lee, 2005). Their results supported the hypothesis that pH and CEC play an important role in tetracycline sorption as pH value was less than pK_{a3}, the main conformation is non-ionized tetracycline. Cation exchanges have dominated effects on sorption. The positive charge amino groups take cation exchanges with the negatively charge sediments. A study by Kulshrestha *et al.* (2004) showed that when oxytetracycline had a net positive charge at lower pH values, they tend to have greater sorption affinity with cation exchange as the dominant mechanism. For further insight into the effects of pH on drug sorption in soil and clay, similar conclusions were drawn using batch studies and empirical modeling (Tolls, 2001; Sassman and Lee, 2005; Jones, 2005). The sediments from East Tai Lake showed highest CEC content, so had strongest sorption capacity. Strong sorption mechanism of antibiotics on sediment was probably due to multiple simultaneous interactions between polar and charged functional groups of tetracycline and surface charge sites on the sediments. The positively charged ammonium functional groups interact with negatively charged sites via cation exchange. The result is in accordance to the previous study. Laak *et al.* (2006) found that sulfachloropyridazine, tylosin, and oxytetracycline had stronger sorption in acidic conditions, these antibiotics were in non-ionized form and cation exchange played dominate role in sorption. Hydrogen bonding between polar groups and acidic groups in sediments and humic substance surfaces may also contribute to sorption (Pils and Laird, 2007).

The OC content also had effect on the sorption. The sorption behavior of pharmaceutical antibiotics in soil is depended upon the soil properties under different conditions. Organic matter and clay fractions had strong influence on the sorption of antibiotics (Rabølle and Spiild, 2000; Jones *et al.,* 2005; Kolz *et al.,* 2005). Organic matter play an important role in sorption of organic pollutant, but poor correlation between f_{OC} and OTC sorption on 30 soil samples was observed (Jones *et al.,* 2005). It was found that the K_d of many organic chemicals depends on the organic carbon content ($f$oc) of the sorbent and that $f$oc (the content of organic matter in soil), as well as pH in the matrix play primary role for the distribution behavior of non-ionic compounds in the soil. From Table 1, highest OC content was found in sediment from East Tai Lake. Accordingly, the K_d value of East Tai Lake was largest, while lowest OC content was found in the sediments from Lake Center. Accordingly, the K_d value of Lake Center (E) was minimum. For the organic matter on the sediment, the organic carbon normalized sorption constant, K_{OC}, was calculated, based on the organic carbon content f_{OC} (%), using the equation below:

$$K_{OC} = K_d / f_{OC}$$

The K_{OC} values obtained from the study ranged from 0.130 to 0.851 l g^{-1} for tetracycline, 0.026 to 0.108 l g^{-1} for oxytetracycline, 0.004 to 0.005 l g^{-1} for tylosin. K_{OC} values typically indicate the effect of organic carbon on sorption of organic compounds. In previous studies, the K_{OC} values of oxytetracycline was 8.16 l g^{-1} for sewage sludge (Stuer-Lauridsen *et al.,* 2000), 27.8–93.3 l g^{-1} for various soil types (Rabølle and Spliid, 2000), and 0.195 l g^{-1} for pig manure (Loke *et al.,* 2002) have been reported. Considering the *n* values ($n < 1$) in this study, K_{OC} values reported in this study is comparable to the above studies. Hydrogen bonding between polar function group in OC and antibiotics might be a strong sorption mechanism.

Comparison of tetracycline, oxytetracycline and tylosin sorption behavior on different sediments : Tetracycline, oxytetracycline and tylosin sorption isotherms on the Lake Center and East Tai Lake sediment are shown in Fig. 5. According to Table 3, regression coefficient ($R^2 > 0.97$) and linear index (n = 0.34-0.82) indicate that sorption data were fitted well by Freundlich model. In previous studies, the sorption of tetracycline on humic acid and peat soil (Sassmann and Lee, 2005), oxytetracycline on clay (Kulshrestha *et al.,* 2004) soil (Rabølle and Spliid, 2000) were described in terms of Freundlich type isotherms. It was found that all the *n* values of the Freundlich model were less than 1 (Table 3), the nonlinear sorption isotherms of three antibiotics exist in the sorption sites of sediments. It reflects the situation that at higher liquid concentrations, it becomes more and more difficult to sorb additional molecules on sediments. This might occur in cases where specific binding sites become saturated or remaining sites are less attractive to the sorbate molecules. When Zhushan Bay (n=0.82) and East Tai Lake (n=0.60) for tetracycline was compared, *n* of Zhushan Bay was close to 1, which indicates homogeneity of sorption sites in Zhushan Bay. According to Fig. 2, sorption of tetracycline on sediment from Zhushan Bay was slightly higher than East Tai Lake at high concentration. The distribution coefficients K_d (l g^{-1}) of tetracycline, oxytetracycline and tylosin were 10^3-10^4, 10^3-10^4 and 10^2-10^3, respectively.

From Fig. 5, the trend of tetracycline, oxytetracycline and tylosin Sorption isotherms was similar and the sorption of tetracycline and oxytetracycline was much stronger than tylosin. The calculated K_d value of tetracycline, oxytetracycline and tylosin was 14700 l g^{-1}, 13200 l g^{-1} and 340 l g^{-1}, respectively, which was much lower than tetracycline and oxytetracycline. Laboratory studies were conducted to characterize metronidazole, olaquindox, oxytetracycline and tylosin with regard to sorption and mobility in various soil types by Rabølle (2000), that showed oxytetracycline sorption was stronger (K_d is 1026 l g^{-1}) than tylosin sorption (K_d is 62.3 l g^{-1}). The main reason about disparity between the three antibiotics was due to the difference of the molecular structure. As reported by Kolz *et al.* (2005) and Thleie and Aust (2004), carboxyl group and amine group in antibiotics could form chelates and complexions with organic matter and inorganic matter in the sediment for sorption. The positively charged $-NH(CH_3)_2$ group of tetracycline bind with sorption sites *via* electrostatic interaction and have cation exchange with sediments (Figueroa *et al.,* 2004). Negatively charged tricarbonyl methane keto-enol moiety of tetracycline might interact with negatively charged sites via cation bridging. Some polar function groups have hydrogen bonding with the sediment polar fraction. It is known that oxytetracycline binds strongly to the sediments and that the binding is dependent on the physical and chemical characteristics of the sediment. Oxytetracycline easily forms strong complexes with divalent cations like Mg^{2+} and Ca^{2+} and it is therefore believed that sorption of oxytetracycline to soil and sediments is dominated by binding of oxytetracycline to mineral cations and organic matter such as humic acids. The –OH and $-CONH_2$ function groups in oxytetracycline could form complex to the surface of metal oxide via metal ions that makes the complex stable (MacKay and Canterbury, 2005; Wessels *et al.,* 1998). There were five –OH, two -C=O, one

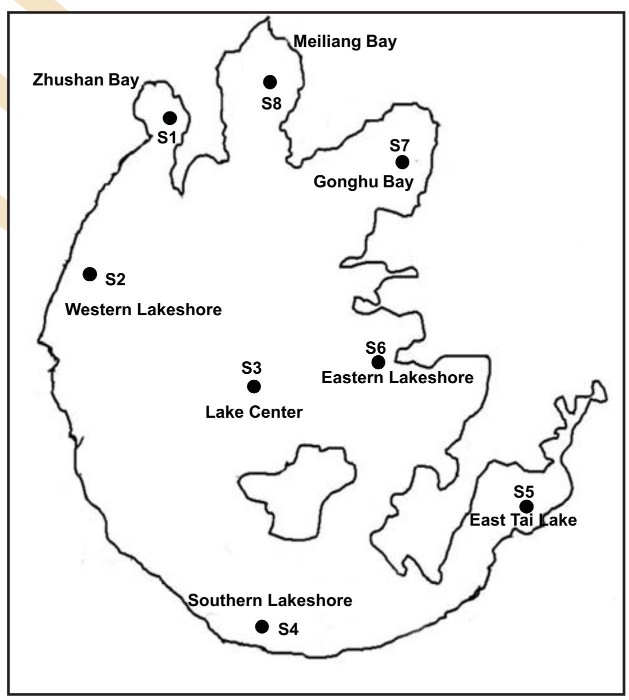

Fig. 1 : Location of sampling sites at Taihu Lake

Table 1 : Selected physical and chemical properties of sediments

Sediment	Site	pH	Eh	CEC (cmol/kg)	OC (%)
Zhushan Bay	(31°27'585"N, 120°02'533"E)	7.33	86	27.66	4.23
Western Lakeshore	(31°18'145"N, 119°58'350"E)	7.44	219	19.12	2.49
Lake Center	(31°06'074"N, 120°08'109"E)	7.51	155	18.99	1.92
Southern Lakeshore	(30°57'196"N, 120°14'493"E)	7.51	241	25.58	2.23
East Tai Lake	(31°02'823"N, 120°28'420"E)	7.74	-111	33.13	4.66
Eastern Lakeshore	(31°12'373"N, 120°19'271"E)	7.41	534	22.87	2.30
Gonghu Bay	(31°26'782"N, 120°22'794"E)	7.37	248	30.12	3.50
Meiliang Bay	(31°29'575"N, 120°12'442"E)	7.36	106	33.38	3.70

Table 2 : Sorbate water solubility (S_w), *n*-octanol-water partition coeffient (K_{ow}) and acid dissociation constants (pK_as)

Compound	S_w (mmol/L)	K_{OW} (L/L)	pK_{aS}
Tetracycline	3.8	0.0646	3.30(1), 7.68(2), 9.69(3)
Oxytetracycline	2.2	0.0603	3.27(1), 7.32(2), 9.11(3)
Tylosin	5.5	3160	7.1

-refered by Tolls (Tolls, 2001)

Table 3 : Freundlich model parameters K_F and $n \pm$ standard deviation for isotherms measured for sorption, along with OC-normalized sediment-to-water distribution coefficient (K_{OC}) at 0.01 S_w and 0.1 S_w

Antibiotic	Sediment	K_F (mmol^{1-n}L^{n}kg^{-1})	n	R^2	K_{OC}(L kg^{-1}) 0.01 S_w/0.1 S_w
Tetracycline	Zhushan Bay	3600±700	0.82±0.03	0.99	1500/1000
Tetracycline	Western Lakeshore	900±200	0.72±0.03	0.98	900/470
Tetracycline	Lake Center	350±30	0.66±0.02	0.99	550/250
Tetracycline	Southern Lakeshore	290±30	0.62±0.02	0.99	450/190
Tetracycline	East Tai Lake	800±100	0.60±0.03	0.98	630/250
Tetracycline	Eastern lakeshore	570±60	0.69±0.02	0.99	680/330
Tetracycline	Gonghu Bay	1400±300	0.76±0.03	0.98	870/500
Tetracycline	Meiliang Bay	1000±200	0.70±0.03	0.99	720/360
Oxytetracycline	Zhushan Bay	250±20	0.49±0.01	0.99	410/130
Oxytetracycline	Western Lakeshore	130±20	0.47±0.03	0.97	390/120
Oxytetracycline	Lake Center	170±20	0.57±0.03	0.98	460/170
Oxytetracycline	Southern Lakeshore	150±8	0.55±0.01	0.99	370/130
Oxytetracycline	East Tai Lake	400±30	0.53±0.01	0.99	520/170
Oxytetracycline	Eastern lakeshore	150±20	0.52±0.03	0.99	410/130
Oxytetracycline	Gonghu Bay	500±60	0.60±0.02	0.99	660/260
Oxytetracycline	Meiliang Bay	120±10	0.40±0.01	0.99	320/80
Tylosin	Zhushan Bay	16±1	0.44±0.01	0.99	20/5
Tylosin	Western Lakeshore	9.3±0.6	0.34±0.01	0.98	25/6
Tylosin	Lake Center	9.2±0.7	0.35±0.01	0.98	32/7
Tylosin	Southern Lakeshore	23±2	0.51±0.02	0.99	42/14
Tylosin	East Tai Lake	12.1±0.6	0.35±0.01	0.99	17/4
Tylosin	Eastern lakeshore	12.1±0.7	0.37±0.01	0.98	33/8
Tylosin	Gonghu Bay	15±1	0.42±0.01	0.99	23/6
Tylosin	Meiliang Bay	15.5±0.8	0.40±0.01	0.99	24/6

–CHO and one -$NH(CH_3)_2$ in one tylosin molecule, whose function groups were less than the function groups of tetracycline. In the present study pH, tetracycline, oxytetracycline and tylosin were all ionized, and tetracycline and oxytetracycline were predominated by the zwitterions speciation, and tylosin was predominated by cation speciation. Moreover, stereo chemical structure of tylosin, reveals that it is a large molecule which inhibits the exchange between aliphatic ammonia and sediment surface particles. Therefore, the sorption interaction (cation exchange and surface complexation) between tetracycline/oxytetracycline and sediments was expected to be stronger than tylosin.

The sorption of tetracycline, oxytetracycline and tylosin on eight sediments from different sites of Taihu Lake were investigated in the study. A nonlinear sorption isotherms of three antibiotics indicate heterogeneous distribution of sorption sites on the surface sediments. The

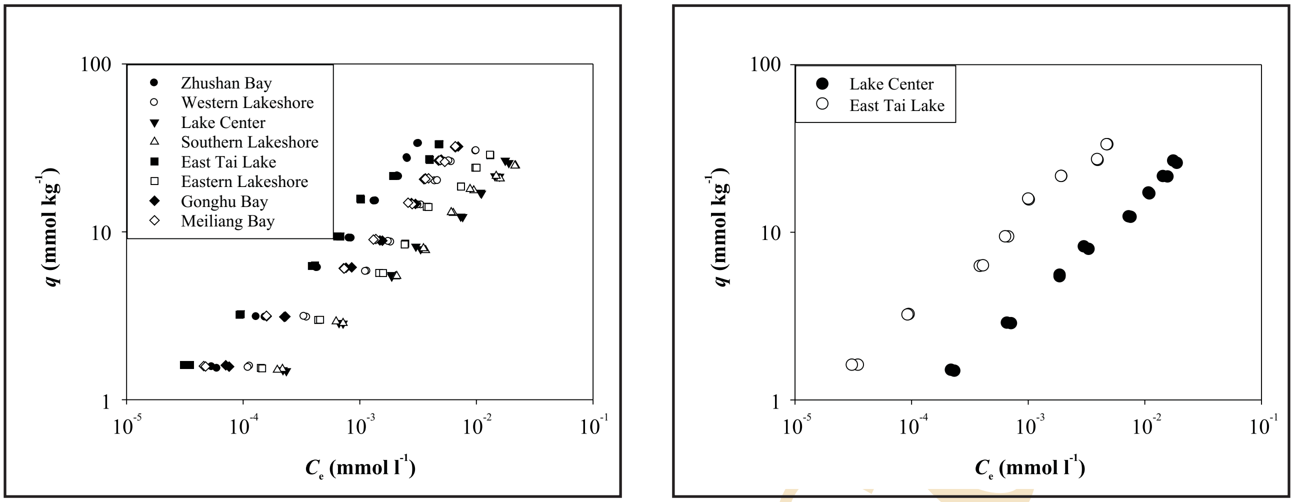

Fig. 2 : Sorption isotherms of tetracycline on eight sites sediments

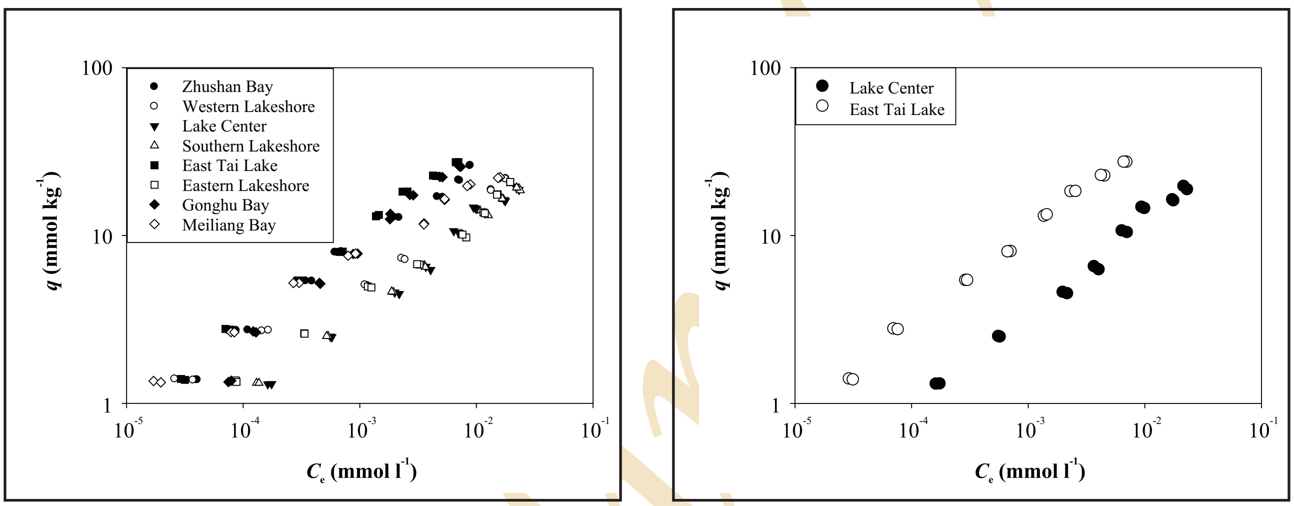

Fig. 3 : Sorption isotherms of oxytetracycline on eight sediments

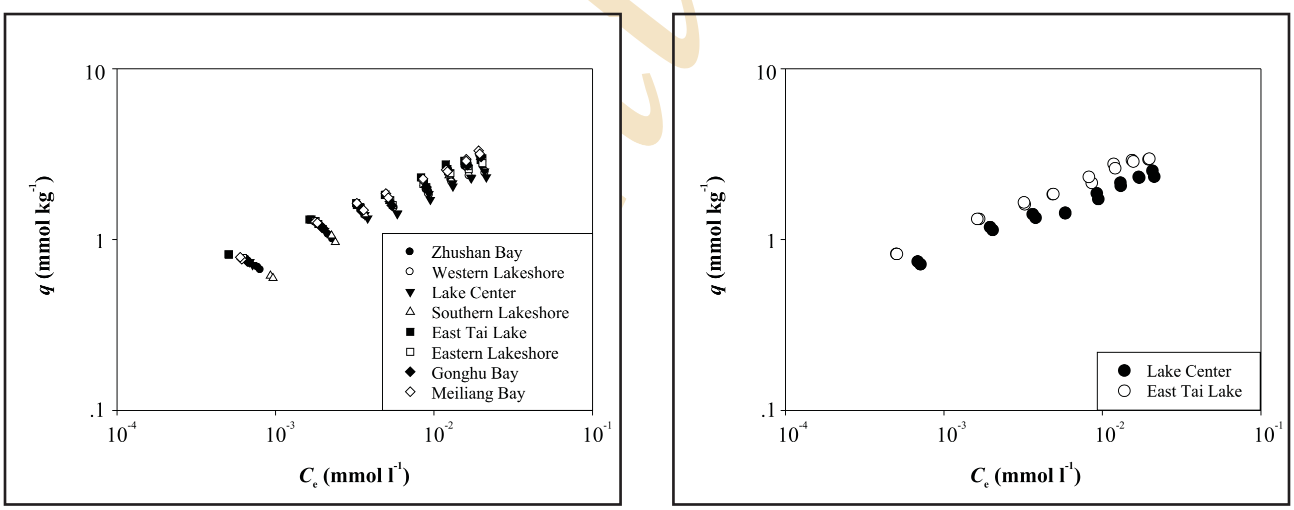

Fig. 4 : Sorption isotherms of tylosin on eight sediments

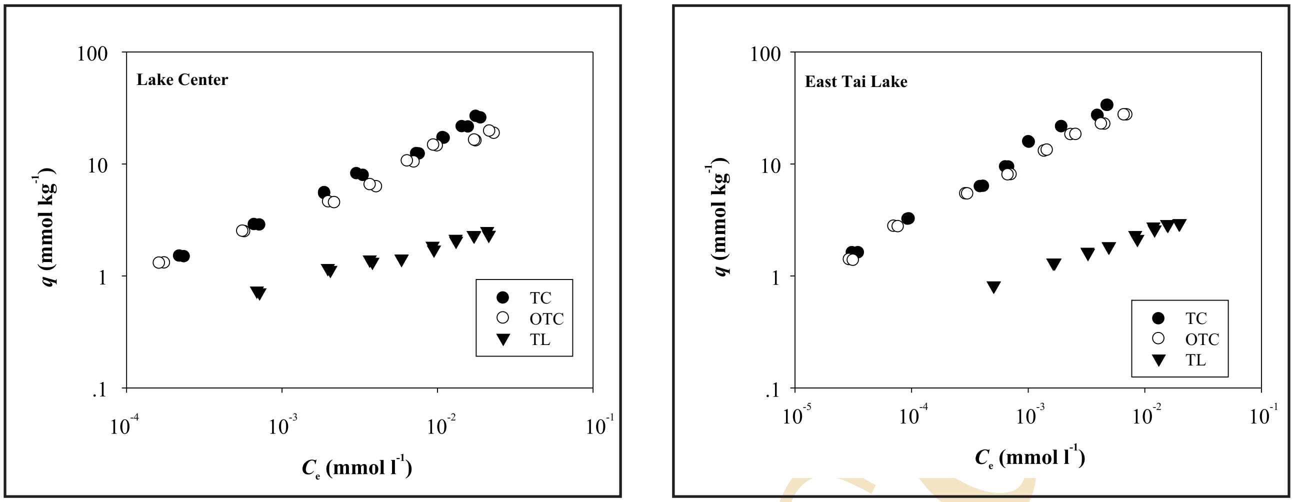

Fig. 5 : Comparison of sorption date between tetracycline, oxytetracycline and tylosin on sediments of Lake Center and East Tai Lake.

observed sorbent-to-solution distribution coefficients K_d (l g^{-1}) of tetracycline, oxytetracycline and tylosin were 10^3-10^4, 10^3-10^4 and 10^2-10^3, respectively. The East Tai Lake had the strongest sorption capacity, because it had the highest CEC and OC content. The functional groups of antibiotics could strongly interact with their respectively charged and polar sites of sediments *via* cation exchange effect and surface complexation reaction. For given sediment, the K_d value of tetracycline and oxytetracycline was nearly and much higher than tylosin. Compared to tetracyclines, the function groups of tylosin were less and its molecular structure was large which made it hard to sorb on the sediment. Tetracycline and oxytetracycline are amphoteric molecules which can make cation exchange and surface complexion stronger and easier.

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