Simultaneous determination of organotin pesticides by HPLC-ICP-MS and their sorption, desorption, and transformation in freshwater sediments

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ABSTRACT

In order to better assess their environmental risks, the sorption and degradation of triphenyltin hydroxide, azocyclotin and fenbutatin oxide were studied in two sediments under varying laboratory conditions in this study. An analytical method for simultaneous determination of the three organotins in environmental samples was firstly developed using high performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS). The limit of detection and limit of quantification for standards ranged from 0.13 to 1.46 µg/L. Fortification study showed that when spiked at 2–250 µg/kg the mass recoveries were 73.7–119.6%. Sorption isotherm experiments indicated that the organotins could be strongly adsorbed by the sediments, and organotin sorption kinetics obeyed the pseudo second-order kinetic model. The sorption affinity was inversely related to their water solubility. All isotherms fitted with the Henry mode fairly well ($r^2 > 0.96$) with distribution coefficients (K_d) ranging from 746.1 to 2465.2 mL/g. The three organotins could rapidly move from the upper water layer to the lower sediment layer, and they were all of moderate degradation compounds with the degradation half lives varying from 38.3 to 84.5d in anaerobic and aerobic water-sediment systems. The degradation rate seemed to be positively related to organic matter content of sediment. Result inferred that the three organotins had the low risks to pollute groundwater when applied on dry land and could moderately degrade in water-sediment system. However, more attention should still be paid to these organotins due to the wide application on agricultural field.

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1. Introduction

Organotin compounds (OTCs) are a class of organic chemicals with at least one carbon-tin (C–Sn) bond in their molecular structures. To date, more than 800 OTCs have been reported, most of which are artificially synthesized (Xu, 2013). In the past six decades, OTCs were extensively used as thermal stabilizers in plastics industry and as biocides in shipyards, marine buildings, and agricultural fields (Hoch, 2001; Liscio et al., 2009; De Carvalho Oliveira and Santelli, 2010; Campillo et al., 2012; Hu and Xu, 2000). As a result of their widespread use, OTCs have been detected in soils, sediments, and water around the world (Deng et al., 2008; Yang et al., 2006; Furdek et al., 2012; Jacobsen, 2000). For instance, butyltins were measured up to 152 ng/L in water from Shekou Harbor, Shenzhen, China (Deng et al., 2008), 182 µg/kg in sediments from Taihu Lake, Wuxi, China (Yang et al., 2006), 102 ng Sn/L and 5000 µg Sn/kg in water and sediment from Danish marinas, respectively (Jacobsen, 2000), and 30 ng Sn/L and 12 µg Sn/kg in

Tejo river water and Tejo estuary sediment in Japan (Díez et al., 2005). In addition to their ubiquitous presence in the environment, some of triphenyl- or tributyl-substituted OTCs such as tri-n-butyltin (TBT), tri-n-butyltin chloride (TBTC), bis (tri-n-butyltin) oxide (TBTO), triphenyltin (TPT) and triphenyltin chloride (TPTC) were found to have genotoxicity (Wexler, 2014; Olegário de Campos Júnior et al., 2015) and/or developmental toxicity (Wu et al., 2014) to lower marine organisms. TBT had been confirmed as an endocrine disruptor by World Wildlife Fund (WWF) in 1999 (WWF, 1999). Given their adverse ecosystem impacts, OTCs were regarded as one class of the most harmful anthropogenic chemicals introduced into the environment (Fent, 1996), and thus were prohibited or limited for use in many countries. For instance, since 2001 OTCs were completely banned for agricultural use in Germany (Hu, 2001). The application of TBT-based paints was prohibited for all vessels by International Marine Organization (IMO) starting January 1st, 2008 (IMO, 2001). Tri-substituted OTCs were strictly restricted with concentration less than the equivalent of 0.1% by weight of tin in all consumer products in European Union (EU) from July 1st, 2010 (EU, 2004).

However, organotin pesticides (OTPs), as an important class of OTCs, are still used in many developing countries including China at present due to their high efficiencies for controlling plant pathogens and/or acarid, and sometimes the total usage is even increasing. Triphenyltin hydroxide (TPTOH, Fig. 1a), azocyclotin (ACT, Fig. 1b) and fenbutatin oxide (FBTO, Fig. 1c) are three of the most popular OTPs as acaricides (Qerhaili and Halloum, 2012) and/or fungicides (Bock et al., 2012). Typically, these chemicals are considered of low acute toxicity to mammals and humans (ChemBlink), and low residues in crops. It was reported that the concentrations of OTPs on plants decreased rapidly with sunlight, rainfall, wind and other environmental factors (Suzdalev et al., 2015). Field trials showed that the degradation half lives ($t_{0.5}$) of TPTOH in potato plant and soil ranged from 4.4 to 25.7 days and 1.1–3.1 days, respectively (Shou, 2006). The $t_{0.5}$ values of ACT in orange fruit and soil varied from 3.1 to 3.9 days and 2.9–10.3 days, respectively (Zhang and Zhao, 1999). The $t_{0.5}$ value of FTBO in soil was found to be around 10 days (Wu et al., 2011). However, in contrast to the reported rapid degradation of OTPs in aerobic environment such as soils, their degradation in anaerobic marine and freshwater sediments remained largely unknown. Nonetheless, OTCs could conceivably persist in sediments for a long time (EU, 2004) and then their slow release from sediments to overlying water column over time could inflict lasting negative impacts on aquatic species. Therefore, environmental behaviors of trace-level OTPs, and their environmental exposure and chronic effects on non-targeted organisms need to be better studied. Unfortunately, many previous studies focused on industrially used OTCs, especially TBT and TPT (Langston and Burt, 1991; Jacobson and Willingham, 2000; Díez et al., 2002; Shi et al., 2002; Dubey and Roy, 2003; Wang, 2003), and there is a paucity of research on more agriculturally-relevant OTPs.

To study the environmental behaviors of OTPs, accurate and efficient analytical methods are needed to detect OTPs in environmental samples. Analysis for TPTOH, ACT and FBTO have traditionally been performed by gas chromatography (GC) with electron capture detector (ECD) (Wu et al., 2011) and flame photometric detector (FPD) (Li, 2010; Liu et al., 2009), GC coupled with mass spectrometry (GC–MS) (Qi, 2013; Devos et al., 2005; Cui et al., 2014; Wang and Zhang, 2015) and high performance liquid chromatography (HPLC) with ultraviolet detector (UVD) (Shou et al., 2006; He et al., 2011). After derivatization, GC and GC–MS can analyze many different groups of OTCs such as butyl-, phenyl-, octyl- and propyl-OTCs in a single run (Rajendran et al., 2000). However, derivatization is often time-consuming with varying derivatization yields among OTC species and sample matrices. Conversely, the HPLC methods do not require derivatization, thus eliminating a potential uncertainty source in the analytical results and substantially reducing analysis time. However, the sensitivity of reported HPLC methods was lower than that of GC and GC–MS. Recently, HPLC tandem mass spectrometry (HPLC-MS/MS) has emerged as an alternative for the trace-level analysis of OTPs. Ma et al. (2015) analyzed the residue of ACT in orange, peach, apple, and grape using HPLC-MS/MS. Moreover, inductively coupled plasma mass spectrometry (ICP-MS) for trace element determination has been well developed, and is particularly advantageous due to its sensitivity, selectivity, and simultaneous measurements of multiple elements and isotopes. Therefore, ongoing efforts have been devoted to GC or HPLC coupled with ICP-MS to analyze many OTCs such as DBT (dibutyltin), TBT, TPT, DOT (dioctyltin) and DMT (dimethyltin) in wines, oyster, mussel, marine products, water and sediment samples (Ritsema et al., 1998; Chiron et al., 2000; Fairman and Wahlen, 2001; Yu et al., 2008, 2011; Li et al., 2011; Liu et al., 2014). However, the simultaneous measurements of OTPs in environmental samples using HPLC-ICP-MS is lacking with only one reported study on analyzing TPTOH and ACT in pear (Wang, 2011), to our best knowledge.

Therefore, there is a significant need to develop a sensitive and rapid HPLC-ICP-MS method for measuring OTPs in environmental samples such as water, soils, and sediments. This study selected TPTOH, ACT and FBTO as model compounds for development and validation of this analytical method for water, soil and sediment samples. Then, this analytical method was used to investigate sorption, desorption and transformation of the three OTPs in two varying sediments. Sorption kinetics and equilibrium isotherms were conducted on two sediments using batch sorption technique. The transformation study was performed under aerobic and anaerobic conditions using simulated sediment microcosms consisted of a sediment layer overlaid by a water column.

2. Materials and methods

2.1. Chemicals and materials

Triphenyltin Hydroxide (98.0% purity) and fenbutatin oxide (97.0% purity) standards were purchased from J&K Scientific Co. Ltd. (Beijing, China), and azacyclotin (99.7% purity) standard from Qindao Dongsheng Pharmaceutical Co. Ltd. (Qindao, China). Acetonitrile (HPLC grade), methanol (HPLC grade), acetone (analytical grade), dichloromethane (analytical grade) and petroleum ether (30–60 °C, boiling point, analytical grade) were purchased from Sigma–Aldrich (Shanghai, China). Triethylamine (TEA) and acetic acid of HPLC grade were purchased from TEDIA (Shanghai, China). Ultrapure water was obtained from a water purification system (Pall Corporation, Port Washington, USA). Other chemicals and solvents were of analytical grade or better. Mixed
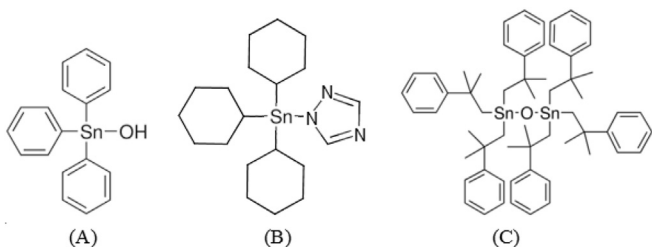

Fig. 1. Chemical structures of the three organotins (A: triphenyltin hydroxide (TPTOH); B: azocyclotin (ACT); C: fenbutatin oxide (FBTO)).

standard stock solutions of 100 mg/L (for each analyte) were prepared in methanol. A series of mixed working standard solutions (0.5–1000 μg/L) were prepared from the stock solutions through serial dilution with methanol. A TPTHO standard stock solution of 50 mg/L was prepared in methanol and a working standard solution of 50 μg/L in methanol was diluted from the stock solution. All of the solutions were stored at 4 °C in the dark prior to use. The working standard solutions were prepared weekly, whereas the standard stock solutions could be preserved for three months.

Three types of soils and two types of sediments were sampled from various locations in China and used in this study, including a black soil from Harbin, Heilongjiang Province, a paddy soil from Wuxi, Jiangsu Province, a red soil from Quzhou, Zhejiang Province, a pond sediment from Zhuji, Zhejiang Province, and a lake sediment from the West Lake, Hangzhou, Zhejiang Province. Soil samples were air-dried, passed through a 2-mm sieve, and then stored at room temperature for later use. Sediment samples (0–10 cm depth) were collected by a stainless steel grab, and meanwhile water samples (0–6 cm depth of top water) from the same site were also collected. For the sorption and desorption experiments, the sediments were first centrifuged at 4000 rpm for 10 min using a centrifuge (Anke DL-5-B, Shanghai Flying Pigeon, China) and the sediments were collected, air-dried, and then passed through a 100-mesh (1.49 mm, pore size) sieve prior to use. For the sedimentary microcosm experiments, the slurry of water and sediments were first wet-sieved to a fraction of less than 2 mm and then allowed for quiescent settling of two weeks at 4 °C to separate the sediments from the water phase.

The pH, organic matter content (OMC) and cation exchange capacity (CEC) of soil and sediment samples (Supplementary material, Table S1) were measured following the ISO methods (ISO, 2005, 1995, 2007), and particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986).

2.2. Development of HPLC-ICP-MS method

In this study a HPLC-ICP-MS method was first developed to analyze TPTOH, ACT and FBTO simultaneously in water, soil, or sediment samples. At the following we first attempted to optimize separation conditions and extraction efficiencies, and then validate the developed method.

A Flexar HPLC system (PerkinElmer, USA) coupled with a NexION300 ICP-MS (PerkinElmer, USA) was used. Sample injection volume was set at 50 μL, and the column temperature maintained at 30 °C. Among 10 isotopes and 7 isobaric interferences of element Sn (Supplementary material, Table S2), the isotope ^{118}Sn was selected for quantification purpose, due to its relative high abundance and absence of isobaric interference. While ICP-MS is ideal for analysis of inorganic samples, organic matrix could lead to instability of plasma torch in ICP, and even blockage in the interface cones (Yu et al., 2010). As organic solvent must be added into the mobile phase of HPLC to achieve proper separation of the three OTPs, adequate flow rate of oxygen must be provided so that organic matter could be fully oxidized in the plasma without leaving carbon deposit on the cone surface, thus improving the sensitivity and stability of plasma. It was found that at oxygen flow rate of 0.055 L/min the high response and stable plasma in the torch were obtained when injected with the TPTOH standard solution (50 μg/L). Optimized ICP-MS operating parameters were listed in Supplementary material of Table S3.

To achieve adequate separation of the three OTPs, it is important to properly select the mobile phase composition, solution pH, and type of LC columns. TPTOH standard solution of 50 μg/L was used for optimizing the mobile phase composition. As most of organotin compounds had low water solubility, water-soluble organic solvents including acetonitrile and methanol were added to the mobile phase at varying solvent-to-water ratios. The composition of the mobile phase was then optimized by examining plasma stability, and signal intensity of peaks. It is known that solution pH of the mobile phase sometimes could influence peak resolution in HPLC for certain analytes. Therefore, to select the optimal solution pH, the mobile phase pH was varied from 2.8 to 5.0 by acetic acid and TEA buffer and the separation was performed with a DELTA-PAK C18 column for an injection of 10 μg/L mixed standard solution. Using the above optimized conditions, we further selected the best C18 column for this analysis. Four types of C18 columns were tested, including Gemini C18 (250 × 4.6 mm and dp = 5 μm, Phenomenex, USA), Luna C18 (250 × 4.6 mm and dp = 5 μm, Phenomenex, USA), DELTA-PAK C18(150 × 3.9 mm and dp = 5 μm, Waters, USA) and Ultrasphere ODS C18 (150 × 4.6 mm, dp = 5 μm, BECKMAN, USA).

Since the success of the HPLC-ICP-MS method is highly dependent on sample pre-treatment to extract the OTPs from environmental samples, the extraction methods were developed for water, soil, and sediment samples. It was previously reported that acidic condition could facilitate the extraction of organotins (Wang, 2011). Therefore, acetic acid was added to adjust solution pH to 3–4. Each sample of 20 g air-dried soils, 20 g air-dried sediments, or 20 mL water sample was spiked with 0.1 mL of the working standard solution (50 mg/L). Then, for soil and sediment samples, 20 mL deionized water was added in a 250-mL plastic centrifuge bottle. After 30 min, 60 mL of either acetone/acetic acid mixed solution (99:1 by volume) or petroleum ether/acetic acid mixed solution (99:1 by volume) were added to soil samples, whereas either acetone/acetic acid mixed solution or acetone/petroleum ether/acetic acid mixed solution (49/49/2 by volume) was added to the sediment samples. This would allow for selection of extractant solution for optimizing the extraction efficiency. The mixture was shaken on a temperature-controllable incubation shaker (ZHWY-2012C, Shanghai Zhicheng Analysis Instrument Manufacturing Co., Ltd., China) at 180 rpm (revolutions per minute) and 25 °C for 60 min. After centrifugation at 4000 rpm for 5 min on a centrifuge (Anke DL-5-B, Shanghai Flying Pigeon, China), the supernatant was transferred to a 250-mL glass flask. The remaining solids were extracted again with the same procedure. The resultant two supernatants were combined, decompressed and evaporated to a volume of 15–20 mL at 40 °C using a rotary evaporator (RE-2000, Yarong Biochemical Instrument, Shanghai, China) in a water bath. Subsequently, 10 mL 10% (by mass) NaCl aqueous solution was added to the concentrated supernatants, followed by the liquid–liquid extraction (LLE) with 50-mL dichloromethane for either 2 or 3 times to maximize the extraction efficiency. The dichloromethane phases were collected, combined, and then passed through anhydrous sodium sulfate to remove trace water. This extractant was decompressed and evaporated again to dryness at 30 °C. The residue was re-dissolved with 10 mL methanol. Followed by a 5-fold dilution with methanol, the final solution was filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane microfilter (MITEX, Millipore, USA), transferred into an autosampler vial, and then analyzed by the HPLC-ICP-MS.

For water samples, the liquid–liquid extraction was directly applied. Briefly, 1 mL acetic acid was added to 20 mL water samples, followed by extraction with 40-mL dichloromethane twice by vigorous hand-shaking for 2 min. After 15-min standing, the bottom dichloromethane layer was collected, dehydrated by passing through anhydrous sodium sulfate, and then decompressed and evaporated at 30 °C to dryness. The residue was re-dissolved with 20 mL methanol, then filtered through the 0.22-μm membrane microfilter, and analyzed with the HPLC-ICP-MS.

The developed analytical method was further validated by

examining the method sensitivity characterized by method limits of detection (MLODs) and quantification (MLOQs) as well as fortification recoveries using working standard solutions. The MLOD and MLOQ values were defined as the lowest concentration that could be detected or quantified for signal-to-noise (height/height) ratio of 3 and 10, respectively. A standard concentration range of 5–250 μg/L was used for calibration. For fortification recovery experiments, the three soil samples, two sediment samples, and three water samples (i.e., lake water, pond water and 0.01 M CaCl₂ solution) were spiked with TPTOH, ACT and FBTO each at three concentrations (i.e., 10, 100 and 250 μg/kg). Non-spiked soil, sediment and water samples were set as controls. Then the OTP-loaded sediment, soil and water samples and control samples were extracted according to the abovementioned extraction method, and analyzed by the HPLC-ICP-MS.

2.3. Sorption and desorption in sediments

Batch sorption experiments were conducted for sediment samples. Aqueous solution of 0.01 M CaCl₂ at pH 6.9 was used as background solution. A pre-determined volume (V_0) of each OTP solution (i.e., either TPTOH, ACT, or FBTO) at a given concentration (C_0) in CaCl₂ background solution was added to 5 g of each sediment sample in a glass Erlenmeyer flask. A pre-determined volume of methanol was added as cosolvent and the added methanol was less than 1% of water volume. Either OTP-free or sediment-free solutions were used as control treatments. The mixture was then shaken on a temperature-controlled incubation shaker at 200 rpm and 25 ± 2 °C for pre-determined equilibration time (ZHWY-2012C, Shanghai Zhicheng Analysis Instrument Manufacturing Co., Ltd., China). After sorption, the mixture was centrifuged at 4000 rpm for 10 min, and then the supernatant was collected for OTP analysis by the established HPLC-ICP-MS method to obtain the equilibration concentration (C_e).

For the desorption experiments, the supernatant volume (V) after the sorption experiments was measured, and the CaCl₂ background solution of equal volume was then added to the remaining sediments in the centrifuge tube. The sediments were then re-suspended and shaken for 5 h. Then, the mixture was centrifuged again, and the supernatant (volume of V) was collected. The same desorption procedure was repeated, and the two supernatants were individually taken for the analysis of each OTP by the HPCL-ICP-MS to obtain equilibration concentrations of C_1 and C_2 for the first desorption and the second desorption, respectively. The OTP remaining in the sediment was then extracted with the above mentioned extraction procedure and analyzed with the HPLC-ICP-MS.

The water/sediment ratio was varied at 100:1, 40:1, or 20:1 (volume/mass) in CaCl₂ background solution containing 0.1 mg/L of each OTP to select the proper water/sediment ratio for sorption kinetics and isotherm experiments. Typically, the water/sediment ratio should increase with water solubility of sorbate, but no greater than 100 (Administration of Quality Supervision, (2014)). The reaction time was set at 24 h. The sorption experiments were carried for the three water/sediment ratios, where the desorption experiments were only carried for the water/sediment ratio of 100. Sorption efficiency (S), desorption percentage (D) or total recovery (R_t) was calculated as per Eqs. (1)–(3), respectively.

$$S\% = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

where C_0 (μg/L) is the initial OTP concentration in aqueous solution, and C_e (μg/L) is the final equilibrium OTP concentration in aqueous solution.

$$D\% = \frac{(C_1 + C_2)V_0 - (C_e + C_1)(V_0 - V)}{(C_0 - C_e)V_0} \times 100 \tag{2}$$

where C_1 and C_2 (μg/L) are the OTP concentrations in supernatant after the first desorption and second desorption, respectively, and V (mL) was the supernatant volume after sorption or desorption. The OTP in deposit phase after centrifugation and separation included the OTP truly sorbed by the sediments and the OTP remaining in the residual water phase. The latter should not be considered as the OTP sorbed by the sediments, and could be easily released to the desorption. Hence, this amount of OTP must be deducted to reduce the error of calculation.

$$R_t\% = \frac{(M_{wa} + M_{wd} + M_{sd})}{M_0} \times 100 \tag{3}$$

where M_0 (μg) is the initial OTP mass, M_{wa} (μg) is the OTP mass in aqueous solution after sorption, M_{wd} (μg) is the total desorbed OTP mass, and M_{sd} (μg) is the OTP mass remaining in the sediments after the second desorption.

In order to select equilibration time in the sorption isotherm experiments, sorption kinetics experiments were conducted at a water/sediment ratio of 100:1 and the concentration of each OTP at 0.1 mg/L. The experiments were continued up to 24 h. In the isotherm experiments, five concentrations of mixed organotins (20, 100, 200, 500 and 1000 μg/L for each OTP) were used. The sorbed OTP concentration in the sediments was plotted against the final equilibrium concentration in aqueous solution to obtain the isotherm curves.

2.4. Sorption equilibrium and kinetic models

Pseudo first-order and pseudo second-order kinetic models were used to fit the sorption kinetics of OTPs on the sediments. The pseudo first-order kinetic model was expressed via Eq. (4):

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \tag{4}$$

where Q_e and Q_t are the sorbed concentrations of OTP in sediments (μg/g) at equilibrium and at contact time t (h), respectively, and k_1 is the pseudo first-order rate constant (h⁻¹). The model parameters can be estimated by plotting $\ln(Q_e - Q_t)$ versus t linearly to obtain the slope of k_1 and the intercept of $\ln(Q_e)$.

The pseudo second-order kinetic model was stated via Eq. (5):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{5}$$

where k_2 is the pseudo second-order rate constant (g/(μg h)). The model parameters can be determined by plotting t/Q_t versus t linearly to produce a slope of $1/Q_e$ and the intercept of $1/k_2 Q_e^2$.

The third model, intraparticle diffusion model (Weber and Morris, 1963) as described in Eq. 6, was used to assess the role of diffusion. An empirical model applicable to many adsorption processes, it stipulates that the sorption amount is proportional to $t^{0.5}$ t.

$$Q_t = k_p \cdot t^{0.5} + C \tag{6}$$

where k_p (μg/(g h⁰·⁵)) is the intraparticle diffusion rate constant that can be estimated from the linear slope of Q_t versus $t^{0.5}$, and C is the parameter of the boundary layer effect. For the larger C, surface adsorption is the major rate-limiting process. For the linear regression of Q_t versus $t^{0.5}$ through the origin (i.e., $C = 0$), intraparticle diffusion is the only rate-limiting process.

The linear Henry model was used to fit the sorption isotherms and K_d (distribution coefficient, mL/g) was estimated via Eq. (7):

$$Q_e = k_d \times C_e \tag{7}$$

The amount of OTP sorbed per unit mass of sediment at contact time t, Q_t, is calculated by Eq. (8),

$$Q_t = \frac{(C_0 - C_t)V_0}{m} \tag{8}$$

where C_t (μg/L) is the OTP concentration in aqueous solution at time t, and m is the mass of the sediment (g).

2.5. Transformation in sediment microcosms

Transformation kinetics of each OTP was investigated in sedimentary microcosms under both aerobic and anaerobic conditions. Wet lake sediment of 195 g of wet weight (i.e., 150 mL of wet bulk volume, equivalent to 50 g dry weight) or wet pond sediment of 118 g wet weight (i.e., 80 mL of wet bulk volume, equivalent of 50 g dry weight) was placed to a glass beaker to form a layer of 2.5 ± 0.5 cm thickness. Then, the previously separated water of approximately 3-fold of the sediment layer volume was gently added without disturbing the underneath sediment layer. The beaker was then sealed with a cotton plug. This experimental microcosm setup mimicked the interface of the sediment and overlying water column. The microcosoms were then statically incubated in darkness at 25 ± 1 °C for 7 days prior to the transformation experiments. To commence the transformation experiments, 10 mL of 10 mg/L mixed standard solution containing 0.1 mg each OTP was added dropwise on the water surface. Co-solvent methanol was adjusted to 5% (methanol/water, by volume) after the OTP addition. The microcosms were again sealed with the cotton plug and statically incubated in darkness. The microcosms free of any OTP or OTP-spiked sediment-free water samples were used as control treatments. Each treatment had 45 replicate microcosms to start with, and 3 microcosms were withdrawn periodically for measurements of OTP residues in water and sediment phases. For anaerobic transformation experiments, the microcosms were filled with nitrogen gas, sealed airtight and placed in a nitrogen-filled cabinet during incubations. To minimize the oxygen exposure, the addition of OTP to the microcosms was performed quickly, and the microcosms were again filled with nitrogen gas, sealed airtight and placed in the cabinet.

The transformation kinetics of the OTPs in lower sediment phases, upper-water phases and whole water-sediment microcosms (the total amount of OTP in the whole microcosm was

Fig. 2. Recoveries of three organotin pesticides at varying spiked levels in sediment, soil and water samples. Data were the mean of five replicates (n = 5).

Fig. 3. Plots of (A) C_t versus t, (B) t/Q_t versus t (pseudo second-order kinetics) and (C) $\ln(Q_e - Q_t)$ versus t (pseudo first-order kinetics) curves of OTPs sorbed by sediments. Square: TPTOH in pond sediment; Circular: TPTOH in lake sediment; Up-triangle: ACT in pond sediment; Down-triangle: ACT in lake sediment; Diamond: FBTO in pond sediment; Left-triangle: FBTO in lake sediment).

calculated by combining the amounts of OTP in the two phases) were evaluated by plotting OTP residue against time, and the transformation kinetics was fitted with the first-order equation (Eq. 9). The goodness of fit was judged by coefficient of determination (r^2).

$$Q_t = Q_0 e^{-kt} \tag{9}$$

where k is the first-order rate constant (d^{-1}).

The persistence of a chemical in environment can be characterized by half life ($t_{0.5}$, d) which means the time required for a

Table 1
Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental Q_e values of the OTPs sorbed by the two sediments.

OTP/Sediment	$Q_{e, exp.}$ (μg/g)	Pseudo first-order kinetic model			Pseudo second-order kinetic model		
		$Q_{e,cal}$ (μg/g)	k_1 (h^{-1})	r^2	$Q_{e,cal}$ (μg/g)	k_2 (g/μg h)	r^2
TPTOH/Pond sediment	6.669	4.620	0.577	0.888	6.688	0.242	0.996
TPTOH/Lake sediment	7.605	7.201	1.061	0.981	7.736	0.293	0.998
ACT/Pond sediment	5.843	3.641	0.499	0.838	6.097	0.246	0.999
ACT/Lake sediment	6.229	3.405	1.095	0.847	6.242	0.536	0.998
FBTO/Pond sediment	7.199	2.007	0.705	0.619	7.133	0.634	0.998
FBTO/Lake sediment	7.108	1.399	0.935	0.668	7.141	0.834	0.999

Triphenytin hydroxide = TPTOH, azacyclotin = ACT and fenbutatin oxide = FBTO.

concentration of a chemical to be reduced to one half. The $t_{0.5}$ was calculated via Eq. (10):

$$t_{0.5} = \frac{\ln(2)}{k} \tag{10}$$

3. Results and discussion

3.1. HPLC-ICP-MS method development and validation

Once the ICP-MS operating parameters were optimized, the critical elements of the HPLC-ICP-MS were the separation of three OTPs by HPLC and OTP extraction from environmental samples such as soils, sediments, and waters. During optimizing the mobile phase, acetonitrile was eliminated as co-solvent because the plasma extinguished due to its low tolerance of carbon content in the mobile phase at > 5% of acetonitrile in water by volume, and no peak was observed at < 5% of acetonitrile in water by volume. No peak was observed at < 80% of methanol in water by volume, and good response and sharp peaks were obtained at 90% of methanol in water by volume (Supplementary material, Fig. S1). Thus, the mobile phase was optimized to 90% of methanol and 10% of water. It was observed that TPTHO could be easily separated from the other two organotins, and the retention times of the three compounds were slightly increased when pH varied from 2.8 to 5.0. However, the R (resolution) value between ACT and FBTO was 0.93, 1.15, 1.09, and 0 for pH 2.8, 3.0, 4.0 and 5.0, respectively, suggesting incomplete separation of the ACT and FBTO (Supplementary material, Fig. S2). Therefore, pH 3.5 was selected due to the high signal

response and an R value of 1.47. The optimized mobile phase consisted of a phase A (TEAA buffer, prepared by ultrapure water (containing 7% (by volume) of acetic acid with solution pH of 3.5 adjusted by triethylamine) and a phase B (methanol) at a flow rate of 1.0 mL/min (A:B = 10:90 by volume). In terms of column selection, ACT and FBTO could not be well separated on Gemini and Ultrasphere ODS C18 columns, whereas the three OTPs could be absolutely separated from each other on Luna and DELTA-PAK C18 columns (Supplementary material, Fig. S3). However, as the retention times of ACT and FBTO on Luna C18 column were two times longer than those on DELTA-PAK C18 column, thus the DELTA-PAK C18 column was selected to reduce the analysis time.

With regard to sample pretreatment, the extraction efficiencies of the three OTPs from the sediment, soil and water samples using the tested extraction methods were shown in Table S4. The extraction of the lake and pond sediments with the acetone/petroleum ether/acetic acid mixed solution and subsequent LLE with dichloromethane for 3 times showed better extraction efficiencies of 83.1–94.6% for the three OTPs. For soil samples, the extraction of the three OTPs with acetone/acetic acid mixed solution and subsequent LLE with dichloromethane for 3 times resulted in extraction efficiencies of 74.9–93.3%. For water samples, satisfactory extraction efficiencies were measured at 82.2–88.7% by direct LLE twice with dichloromethane. Therefore, these extraction methods were used for the soil, sediment, and water samples in this study.

The method validation results were discussed at the following. The developed HPLC-ICP-MS method had a great linearity over the concentration range of 5–250 μg/L with determination coefficients (r^2) greater than 0.999 (Supplementary material, Table S5). The MLODs and MLOQs for TPTOH, ACT and FBTO were 0.13, 0.44 and 0.39 μg/L (or, 7.50×10^{-13}, 2.20×10^{-12} and 1.95×10^{-12} g), and 0.43, 1.46 and 1.39 μg/L (or, 2.15×10^{-12}, 7.30×10^{-12} and 6.95×10^{-12} g), respectively. The obtained MLODs were slightly or much better than those previously reported (all MLODs in present and previous studies were obtained by non-matrix matched standards), e.g., 0.25 μg/L (1.25×10^{-12} g) and 0.47 μg/L(2.35×10^{-12} g) for TPTOH and ACT analyzed by HPCL-ICP-MS, respectively (Wang, 2011), 1×10^{-10} g by GC-ECD (Wu et al., 2011), 0.1 mg/kg (5.0×10^{-10} g) by GC-FPD (Li, 2010; Liu et al., 2009), 3.4 μg/kg(1.7×10^{-11} g) by GC–MS (Devos et al., 2005), 20 μg/kg (1.0×10^{-11} g) by (GC–MS) for FBTO (Cui et al., 2014), and 2×10^{-10} g (HPLC-UV) for TPTOH (Shou et al., 2006).

Spiking recovery experiments were performed to determine the precision and accuracy of the developed pretreatment method for TPTOH, ACT and FBTO (The typical HPLC-ICP-MS chromatograms for three OTPs in all samples were showed in supplementary material, Fig. S4.). As listed in Fig. 2, the average recoveries obtained for each of the three analytes at all spiked levels ranged between 73.7% and 119.6% with relative standard deviation (RSD) between 1.2% and 16.3%, which conformed to the requirement of guideline on pesticide residue trials (China, 2004). In addition, the lowest fortification level, i.e. 10 μg/kg for all three analytes in soil
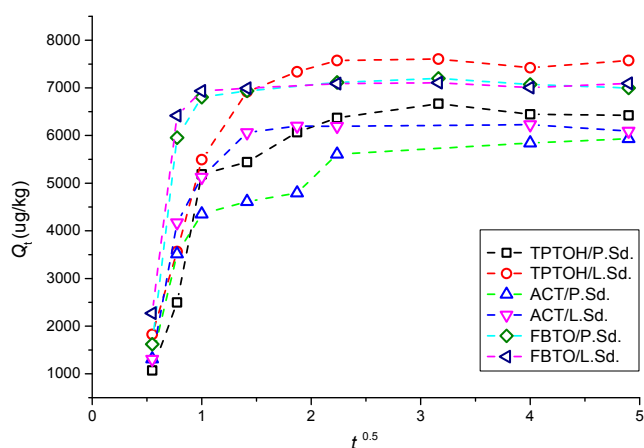
Fig. 4. Intraparticle diffusion plot of Q_t versus $t^{0.5}$ for the three organotins on two sources of sediments. Square: TPTOH in pond sediment; Circular: TPTOH in lake sediment; Up-triangle: ACT in pond sediment; Down-triangle: ACT in lake sediment; Diamond: FBTO in pond sediment; Left-triangle: FBTO in lake sediment).
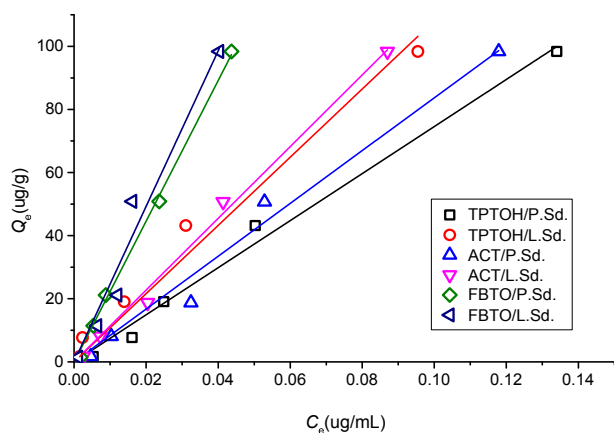
Fig. 5. Observed and fitted sorption isotherms of three organotin pesticides on lake and pond sediments. The lines were fitted with the linear Henry model. Square: TPTOH in pond sediment; Circular: TPTOH in lake sediment; Up-triangle: ACT in pond sediment; Down-triangle: ACT in lake sediment; Diamond: FBTO in pond sediment; Left-triangle: FBTO in lake sediment).

and sediment samples and 2 μg/L for $CaCl_2$ solution, respectively, were recommended as the sample limits of quantification (SLOQs), defined as the minimum analyte concentrations in sample matrix measurable by an analytical method.

3.2. Sorption and desorption in sediments

3.2.1. Selection of water:sediment ratio

The removal efficiencies decreased with increasing water/sediment ratios for a given OTP (Supplementary material, Table S6). Moreover, the three organotins were strongly sorbed by both sediments with the removal efficiencies greater than 90% at the water/sediment ratio of 20 and 40. The removal efficiencies varied from 79.5% to 93.5% at the water/sediment ratio of 100. To allow for accuracy of OTP measurements in the aqueous phase in the sorption kinetics and equilibrium isotherm experiments, the water/sediment ratio of 100 was selected. Furthermore, at the water/sediment ratio of 100, the desorbed percentage ranged from 6.5% to 11.9%, indicating a strong binding between sorbed OTPs and sediments. The total recoveries in the sorption and desorption experiments ranged from 82.3% to 96.6%, thus meeting the quality control of the tests (Administration of Quality Supervision, (2014)).

3.2.2. Sorption kinetics

The three organotins could be quickly sorbed by both sediments, resulting rapid reducing of the OTPs in liquid phase (Fig. 3A), and the sorption rate was greatest within 1 h from the start of the experiments. Organotin sorption reached the plateau after 5 h. Therefore, the equilibration time for the sorption isotherm was selected at 5 h. The sorption kinetics were characterized by a fast initial sorption followed by a much slower sorption. Additionally, the pseudo second-order kinetics model fitted the sorption isotherms well with $R^2 > 0.99$ (Fig. 3B). Compared to the pseudo second-order kinetics model, the pseudo first-order kinetics model could not well fit the sorption isotherms (R^2 ranging from 0.619 to 0.981) (Fig. 3C). The k_1, k_2, model-calculated Q_e and experimental Q_e were presented in Table 1 along with the corresponding coefficients of determination. The fitted sorption rate constant (k_2) were 0.242, 0.246 and 0.635, and 0.293, 0.536 and 0.834 for TPTOH, ACT and FBTO in pond sediment and lake sediment, respectively. Furthermore, there was no agreement between experimental and calculated Q_e for the pseudo first-order model, opposite to the results of the pseudo second-order model (Table 1). Similarly, the

adsorption of pesticides 2,4-D (Hameed et al., 2009), carbofurn (Salman and Hameed, 2010a), and ametryn, aldicarb, dinoseb and diuron from aqueous solution onto activated carbon-cloth (Ayranci and Hoda, 2005) followed the pseudo second-order model. Endo-sulfan and methoxychlor removal from water by carbon slurry also obeyed the pseudo second-order model (Gupta and Ali, 2008).

It is well known that hydrophobic interactions greatly contribute to the adsorption of chemicals in aqueous solution (Moreno-Castilla, 2004). The adsorbate with higher hydrophobicity tend to be more strongly adsorbed and retained on particle surface or interior pores. As suggested by the solubilities (TPTOH 8.0 mg/L (PMEP), ACT: 0.12 mg/L (Tomlin, 1994), and FBTO: 0.0127 mg/L(PPDB)), the hydrophobicity of these OTPs is significant, resulting in enhanced sorption affinities. The OMC in the two sediments (i.e., the lake sediment had a higher OMC than the pond sediment) provided another evidence. The k_2 value obtained from the OTP sorption on lake sediment was always higher than that from the OTP sorption on pond sediment.

3.2.3. Sorption mechanism

In order to elucidate the mechanisms and rate controlling steps governing the sorption kinetics, the kinetic experimental results were fitted to the intraparticle diffusion model. Generally, the plot of Q_t versus $t^{0.5}$ (Fig. 4) was not linear but might be multi-linear, which indicated that two or more steps might occur in the sorption. For TPTOH and ACT, three linear stages (0—1 h, 1—5 h and 5—24 h) were involved with a strong adsorption rate in the initial stage (0—1 h), characterizing the instantaneous adsorption on external surface due to the rapid mass transfer of sorbate from bulk solution to the sorbent surface. Subsequently, the slower sorption at the second stage (1—5 h) was controlled by intraparticle diffusion. The third stage (5—24 h) of the sorption, intraparticle diffusion was diminished due to the depletion of sorbate concentration in solution. Thus, predominantly, the sorption of TPTOH and ACT occurred through rapid external surface adsorption followed by intraparticle diffusion. For FBTO, only two linear stages, i.e., strong adsorption process (0—1 h) and equilibrium adsorption process (1—24 h) were observed, whereas the slower sorption stage was absent because of the predominant adsorption of sorbate on the external sediment surfaces. Based on the intraparticle diffusion model, if the linear regression of Q_t versus $t^{0.5}$ has zero intercept, intraparticle diffusion is the only rate-limiting step. However, as the linear plots for all stages did not pass through the origin (lines were not shown, Fig. 4), it confirmed that the intraparticle diffusion was not the sole rate limiting process during the sorption. This result was similar to the trend for dye adsorption on palm kernel fiber (Ofomaja, 2007), fungicide 2,4-D adsorption on activated carbon (Hameed et al., 2009), and 2,4-dichlorophenoxyacetic acid and carbofuran pesticides adsorption onto granular activated carbon (Salman and Hameed, 2010b).

3.2.4. Sorption isotherms

The Henry model fitted the isotherm data satisfactorily ($r^2 > 0.97$), as shown in Fig. 5. The estimated K_d values were 746.1 and 1072.4 for TPTOH in pond and lake sediments, 837.9 and 1138.0 for ACT in pond and lake sediments, and 2230.9 and 2465.2 for FBTO in pond and lake sediments, respectively (Supplementary material, Table S7). It indicated that the sorption affinity on the sediments followed the order of FBTO > ACT > TPTOH, which was inversely related to their water-solubility. Additionally, for a given OTP, the K_d value in the lake sediment was higher than that in the pond sediment. This might be because the lake sediment had a higher organic matter content and more finer fractions than the pond sediment. The lake sediment had 6.47% organic matter and 83.7% of particle finer than 0.05 mm, whereas the pond sediment
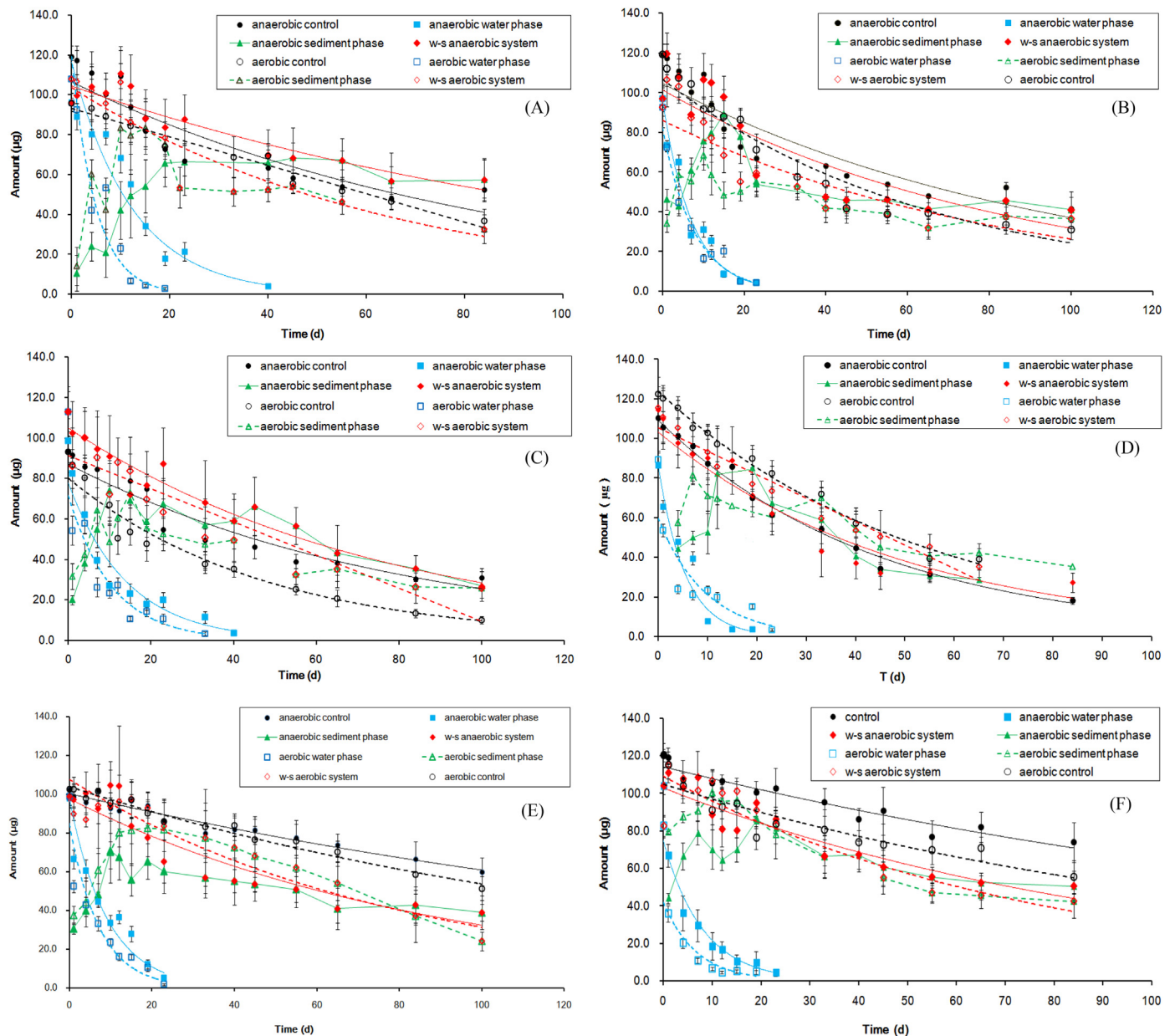
Fig. 6. The transformation dynamic curve of the three pesticides in the two water-sediment systems (A: TPTOH in pond water-sediment system; B: TPTOH in lake water-sediment system; C: ACT in pond water-sediment system; D: ACT in lake water-sediment system; E: FBTO in pond water-sediment system; F: FBTO in lake water-sediment system).

only had 0.46% organic matter content, and 63.9% of <0.05 mm fractions (Supplementary material, Table S1).

3.3. Transformation in sedimentary microcosms

Fig. 6 displayed the transformation kinetics of the three OTPs in the lake and pond sediment microcosms under aerobic and anaerobic conditions. Results showed that all transformation kinetics fitted with the first-order kinetic equation satisfactorily with $r^2 > 0.89$ in 27 out of 36 cases, and r^2 between 0.79 and 0.89 in 9 cases. All three pesticides could rapidly move from upper water column to the bottom sediment layer with the transformation half lives ($t_{0.5}$) ranging from 4.9 days to 9.9 days. The amounts of the pesticides in the sediments gradually increased in the first two or three weeks, and then tended to decrease slightly. The total three organotins in the entire microcosms (including the

organotin amount in the water column and the sediment layer) showed moderate degradation with $t_{0.5}$ ranging from 38.3 days to 84.5 days. However, only TPTOH and ACT showed moderate degradation with $t_{0.5}$ from 21.3 days to 66.6 days in the sediment-free water controls, whereas FBTO was difficult to be transformed with $t_{0.5}$ from 90.0 to 138.6 days (data were listed in Supplementary material, Table S8). It was also found that ACT was the easiest, but FBTO the hardest to be degraded among the three pesticides. Additionally, the transformation rates of the pesticides in the lake sediment microcosms were in general greater than those in the pond sediment microcosms. This observation corroborated with the results of sorption kinetics and isotherms, likely resulted from greater organic matter content, finer texture, and subsequent more active microbial community in the lake sediments. It should be noted that the transformation products or metabolites of the organotins in the sediment microcosms could

not yet be separated and identified, which should be a topic of further investigation.

4. Conclusions

In conclusion, we have successfully developed and validated a HPLC-ICP-MS method for simultaneous determination of TPTOH, ACT and FBTO in environment samples with high sensitivity and accuracy. Considering the variety of soils, sediments, and water samples used, this method could have a broader application in analyzing organotins in other environmental samples not covered in this study. Sorption and desorption results showed that the three compounds could be strongly sorbed by the sediments. The sorption was followed the pseudo second-order kinetic model and external mass transfer was the rate-controlling step. The hydrophobic interaction might play the key role in adsorption process. Sorption tests implied a lower risk of the OTPs release from the sediments. Nonetheless, how sorption in the sediment may influence the bioavailability of organotins to aquatic organisms should be further investigated. The transformation studies suggested that the three OTPs were of moderate degradation in the sedimentary microcosms. More intriguingly, the three OPTs showed migration from water surface to and accumulation in the sediment layers, implying that once these contaminants reach the natural water bodies, such as pond, lake, stream, and ocean, they tend to be enriched in the sediment layer. Therefore, how this sedimentary enrichment could negatively affect the benthonic aquatic organism requires further studies.

Conflicts of interest

The authors have declared no conflict of interest.

Acknowledgment

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.02.056.

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