The importance of environmental factors and matrices in the adsorption, desorption, and toxicity of butyltins: a review

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Abstract Butyltins (BTs) are considered as a group of the most important organometallic compounds in industry and agriculture. Due to their widespread use, large amounts of BTs including tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) have entered into the environment, and subsequently causing detrimental effects on humans and aquatic organisms. This work provides a critical review of recent studies on the adsorption, desorption, bioaccumulation, and toxicity of BTs that can notably influence the distribution of BTs in the environment. Influence of environmental factors (e.g., pH and salinity) and adsorbents in the matrices (e.g., minerals, organic carbons, and quartz) on the adsorption, desorption, and toxicity of BTs is particularly addressed.

Keywords Organotins · Adsorption · Desorption · Bioavailability · Toxicology

Introduction

As one of the most important organometallic compounds, butyltins (BTs) such as tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) have been widely used as additives of antifouling paints, biocides, and stabilizers (Fent 1996; Hoch 2001). Due to wide commercial applications, large amounts of BTs have been released into the ecosystems, and high levels of BTs have also been observed in freshwater systems and wastewater treatment plants (Bartlett et al. 2004; Sabah et al. 2016). The observation of causing sexual abnormality in gastropod mollusks (*Nucella lapillus*) and unnatural shell calcification in oysters by TBT has been receiving intense public attention, and consequently leading to its first legislation (Matthiessen and Gibbs 1998). More and more evidences have shown that BTs cause a significant reduction in the development, reproduction, and survival of many marine species (Frouin et al. 2008; Giraud-Billoud et al. 2013; Gumy et al. 2008; Lopes-dos-Santos et al. 2014). Of all butyltins, TBT presents the highest toxicity to aquatic organisms, by disturbing the function of mitochondria, while DBT and MBT are less toxic. However, DBT is reported to decrease lymphocyte proliferation of seals more than the other BTs (Frouin et al. 2008). The worldwide prohibition on the use of TBT came into effect in 2003 by the International Marine Organization (IMO), and the application of TBT-based antifouling paints has been totally phased out by 2008 (IMO 2005). However, no restriction has been implemented for DBT and MBT to date.

In spite of the restrictive regulation of TBT by the IMO, high concentration BTs still can be detected at high levels in many countries particularly from Asia and South America (Choi et al. 2013; Castro et al. 2012; Del Brio et al. 2016; Ho and Leung 2014; Paz-Villarraga et al. 2015). Adsorption and desorption processes of BTs by environmental matrices such as sediments and minerals play an important role in their levels in different

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environmental matrices, and consequently affecting the bioavailability and toxicity of BTs in the environment (Burton et al. 2004; Gao et al. 2015; Hoch 2001; Fang et al. 2010, 2012). Studies have also shown that the adsorption and desorption processes of BTs are highly dependent on the property of matrices. For example, Fang and coworkers reported that black carbons (BCs) as an important fraction of organic carbon can significantly contribute to the overall adsorption of BTs, consequently leading to overestimated toxicity of BTs to organisms (Fang et al. 2010, 2011). In addition, environmental factors such as pH and salinity can remarkably influence BT adsorption and desorption processes and their bioaccumulation and toxicity. Weidenhaupt et al. (1997) studied the adsorption of TBT to minerals at different pHs, showing that the adsorption of TBT was strongly pH-dependent. The similar findings have also been reported for DBT and MBT (Fang et al. 2012; Hoch et al. 2003).

Considering the importance of environmental factors and matrices in the bioavailability and toxicity of BTs in the environment, this work briefly reviews the physicochemical property, application, and distribution of BTs. In particular, this review focuses on recent studies on the adsorption, desorption,

toxicology, and bioaccumulation of BTs by emphasizing the effect of environmental conditions (e.g., pH and salinity) and matrices (e.g., minerals, BCs).

Properties, application, and distribution of BTs

BTs comprise a group of organometallic moieties, where the Sn atom is covalently bound to at least one organic group, such as alkyl and phenyl groups (Hoch 2001). Generally, BTs can be expressed by the formula $R_n\text{Sn}X_{4-n}$ (R denotes organic group; X denotes anionic group such as halide and hydroxide).

Synthesis and applications of BTs

According to the formula $R_n\text{Sn}X_{4-n}$, BTs comprise four compounds including tetrabutyltin (TeBT), TBT, DBT, and MBT. The main properties of the four BTs are listed in Table 1. TeBT as a precursor of the other BTs can be directly produced from SnCl_4 using a Grignard method (Peter 2003).

Table 1 Physicochemical properties of tetrabutyltin (TeBT), tributyltin chloride (TBT), dibutyltin dichloride (DBT), and monobutyltin trichloride (MBT)

	TeBT	TBTCl	DBTCl ₂	MBTCl ₃	References
CAS. No.	1461-25-2	1461-22-9	683-18-1	1118-46-3	
Formula	(C ₄ H ₉) ₄ Sn	(C ₄ H ₉) ₃ SnCl	(C ₄ H ₉) ₂ SnCl ₂	(C ₄ H ₉)SnCl ₃	
Molecular weight (g mol ⁻¹)	347.2	325.5	303.8	282.2	
Structure
Melting point (°C)	-97	-16	39-41	NA ^c	Hoch 2001
Boiling point (°C)	145/1.3 kPa	172/3.3 kPa	135/1.3 kPa	93/1.3 kPa	Hoch 2001
Density (g L ⁻¹)	1.1	1.2	NA	1.7	Hoch 2001
Solubility (mg L ⁻¹)	NA	1.0–2.0 ^a ; 5–17 ^b	4–50 ^a	NA	Hoch 2001; Inaba et al. 1995
LogK _{ow}	3.9	3.2 ^c ; 4.01 ^d	NA	NA	Arnold et al. 1997; Fent 1996; Vighi and Calamari 1985
pK _a	/	6.3–6.9	2.9–3.8 5.1	pK _{a,1} : 2.0–2.4 pK _{a,2} : 3.5 pK _{a,3} : 5.9	Fang et al. 2012; Tobias et al. 1966; Vighi and Calamari 1985

NA not available

^a Solubility in seawater

^b Solubility in distilled water

^c TBT in Tris-HCl buffer at pH 6

^d TBT in 10 mM NaClO₄ at pH 8

The Grignard reagent, BuMgX, acts as nucleophile and attacks the electrophilic Sn atoms, consequently yielding a polar bond between carbon and tin atoms.

By further reaction with tin(IV) chloride, other BTs can be formed as exemplified by the TBT formation.

The Sn-C bond is considered to be stable in water and the atmosphere and can resist heating (up to 200 °C), whereas UV radiation and biological activity can lead to debutylation (Hoch 2001; Peter 2003).

BTs have been applied for different purposes in the agricultural and industrial fields for decades, and their main application is listed in Table 2. TBT is used as biocide for antifouling paint and wood protection, while DBT and MBT are used as stabilizer additives in PVC products and polyurethane. TeBT is mainly used as precursor of the other BTs (i.e., TBT, DBT, and MBT).

Speciation of BTs

Knowledge about speciation is essential for understanding the chemistry of BTs in aqueous solutions and, hence, their environmental fate, bioavailability, and toxicity (Fent 1996). Several studies have found that the speciation of BTs (except TeBT) depends on the pH and anions in aqueous solutions (Arnold et al. 1997; Fent 1996; Weidenhaupt et al. 1997). It shows that TBT, DBT, and MBT can undergo hydrolysis in aqueous solutions (Table 3). These BTs are expected to be positively charged at low pH and predominate in neutral forms at pH > 7 (ionic strength 10 mM NaClO₄) (Arnold et al. 1997; Hoch 2001). The acidity constant (pK_a) value of TBT is found to be 6.3, estimated by potentiometric titration (Shoukry 1996), or 6.9 by modeling (Arnold et al. 1997; Vighi and Calamari 1985). Thus, at pH < 6.5, (C₄H₉)₃Sn⁺ (TBT⁺) dominates in water, whereas the neutral species C₄H₉)₃Sn-OH (TBTOH) is predominant at pH > 6.5 (Fig. 1). This has also been confirmed by ¹¹⁹Sn nuclear

magnetic resonance (Hynes and Odowd 1985) and Mössbauer spectroscopy (Eng et al. 1986).

DBT and MBT are expected to have two or three hydrolysis steps and hence two or three pK_a values, respectively. By potentiometric titration, estimated values of pK_{a,1} of 3.0 and pK_{a,2} of 5.1 were found for DBT and pK_{a,1} of 2.3, pK_{a,2} of 3.5 and pK_{a,3} of 5.9 for MBT (Table 2; Fang et al. 2012). These values are in good agreement with the findings (e.g., pK_{a,1} = 3.8 and 2.0 for DBT and MBT) by Vighi and Calamari (1985) and Shoukry (1996). According to the pK_a values, MBT and DBT mainly exist as a mixture of dicharged (i.e., MBT(OH)₂²⁺ and DBT²⁺) and monocharged species (i.e., MBT(OH)₂⁺ and DBT(OH)⁺) at pH < 4. In the pH range of 4 to 6, they dominate as monocharged species and as neutral species (i.e., MBT(OH)₃ and DBT(OH)₂) at pH > 6 (Fig. 1).

In addition, the dissociation reactions of BTs are influenced by temperature, ionic strength, and anionic composition (Fent 1996). In particular, ionic strength is highly related with salinity in marine and estuarine systems, which can determine the species of BTs. Studies show that the neutral TBTCI species account for 36–68% of total TBT in seawater at pH < 6 and even 2–3% of total TBT at pH 8 (formation constant of TBTCI, logK_i = 0.6) (Arnold et al. 1997; Burton et al. 2004). However, there is limited knowledge on the effect of salinity on the species of MBT and DBT, which should be further explored in future work.

BTs in different matrices

Due to their widespread applications, BTs have been found in many different matrices such as surface water, sediment/soil, and various organisms from different regions (Choi et al. 2009; Del Brio et al. 2016; Castro et al. 2012; Ho and Leung 2014; Jacobsen and Asmund 2000; Paz-Villarraga et al. 2015; Tang and Wang 2009). Comprehensive reviews on the occurrence and environmental levels of BTs in different regions have been well documented by other researchers such as Antizar-Ladislao (2008) and Sousa et al. (2014). This work emphasizes on the importance of environmental factors and matrices in the adsorption, desorption, bioaccumulation, and toxicity of BTs; hence, a few typical examples are summarized to show

Table 2 The hydrolytic reactions of butyltins (BTs) in water

Butyltin	Hydrolysis process	pK _a	Reference
TBT	TBT ⁺ + H ₂ O ⇌ TBTOH + H ⁺	6.3 ± 0.1 ^a	Arnold et al. (1997)
DBT	DBT ²⁺ + H ₂ O ⇌ DBT(OH) ⁺ + H ⁺	3.0 ± 0.1	Fang et al. (2012)
	DBT(OH) ⁺ + H ₂ O ⇌ DBT(OH) ₂ + H ⁺	5.1 ± 0.2	
MBT	MBT ³⁺ + H ₂ O ⇌ MBT(OH) ²⁺ + H ⁺	2.3 ± 0.1	Fang et al. (2012)
	MBT ²⁺ + H ₂ O ⇌ MBT(OH) ₂ ⁺ + H ⁺	3.5 ± 0.2	
	MBT(OH) ₂ ⁺ + H ₂ O ⇌ MBT(OH) ₃ + H ⁺	5.9 ± 0.1	

^a Value given as average ± standard deviation

Table 3 Application of butyltins (BTs)

Butyltin	Application	Main use	Reference
MBT	Catalyst Oxide films on glass Stabilization against heat and light	Industrial processes Glass treatment PVC stabilizer	Hoch (2001), WHO (1990)
DBT	Catalyst Stabilizers Dewormer	Polyurethane PCV and plastics stabilizer Poultry farming	Hoch (2001), Peter (2003)
TBT	Miticide, fungicide, insecticide Insecticide, fungicide Biocide	Agrochemicals Wood preservative Antifouling paints	Hoch (2001), WHO (1990)
TeBT	Precursor of TBT, DBT, and MBT	Produce TBT, DBT, MBT	Hoch (2001), Peter (2003)

Fig. 1 Speciation of TBT (a), DBT (b), and MBT (c) as a function of pH, respectively. The TBT species distribution as a function of pH is calculated according to pK_a of 6.3 (Arnold et al. 1997), while for DBT and MBT, they are calculated on the basis of pK_a values by Fang et al. (2012)

the BT distributions in various environmental matrices of different countries (Table 4). The concentrations of the three BTs exhibit a great variation in the different matrices and from place to place. High concentrations of BTs can still be detected in sediments and organisms of marine systems in South America according to the findings by Castro and coworkers (Del Brio et al. 2016; Laitano et al. 2015; Paz-Villarraga et al. 2015). The high content of BTs in marine sediments observed after the worldwide ban reflects the persistence of BTs in sediments and organisms (Strand et al. 2003, 2005). The enrichment of BTs in sediments can be due to the high distribution coefficients (K_d) of BTs ranging from 10^2 to 10^6 L kg⁻¹ in natural adsorbents such as organic matters and clay minerals (Burton et al. 2004), and high content of BTs in organisms is due to the high bioconcentration factor (BAF) values of TBT in bivalves ranging from about 16,000 to 400,000 (Tang and Wang 2008). On the other hand, adsorption to sediment and bioaccumulation in organisms can slow down the degradation of BTs from a few weeks to decades, which poses a threat to human and ecosystem (Nielsen and Strand 2002; Craig 2003; Peter 2003; Tang and Wang 2008).

Adsorption of BTs

Adsorption behavior is considered to be an important process affecting the transport, bioavailability, and toxicity of BTs in the environment (Weber et al. 1991). Studies on the adsorption of BTs to different matrices have been widely reported. These matrices include clays (Hermosin et al. 1993; Hoch et al. 2003; Weidenhaupt et al. 1997), quartz (Behra et al. 2003; Bueno et al. 1998), amorphous silica (Weidenhaupt et al. 1997), metal oxides (Randall and Weber 1986; Weidenhaupt et al. 1997), organic matters (Arnold et al. 1998; O'Loughlin et al. 2000; Said-Pullicino and Vella 2005), BCs (Brandli et al. 2009; Fang et al. 2010, 2012), natural soils, and sediments (Burton et al. 2004; Burton et al. 2006; Huang and Matzner 2004). Studies have demonstrated

Table 4 Selected studies on butyltin (BT) distribution in water, sediment, and organisms

Sample	Location	Year	Level of BTs			Reference
			TBT	DBT	MBT	
Water (ng Sn L ^{−1})						
	Korean coastal area	2001–2003	<d.l.–164	<d.l.	<d.l.	Choi et al. (2009)
		2004–2005	<d.l.–24	<d.l.	<d.l.	Choi et al. (2009)
	Estuary stream, Taiwan	2009	0.6–39.6	1.0–47.5	6.8–96	Tang and Wang (2009)
Sediments (ng Sn g ^{−1})						
	Korean coasts	2001–2003	<d.l.–9576	<d.l.	<d.l.	Choi et al. (2009)
	Crystal Lake, USA	2001–2003	1.5–14,000	59–350	21.3–320	Landmeyer et al. (2004)
	Estuary, Taiwan	2009	9–194	4–107	26–238	Tang and Wang (2009)
	Sanricu Coast, Japan	2005	2–14,000	<d.l.–3400	<d.l.–3300	Harino et al. (1998)
	Northwest Coast, Spain	2005	0.6–303	0.5–357	0.7–3.8	Üveges et al. (2007)
	Concepción, Chile	2013	1.2–122	4.7–103	3.1–118	Batista et al. (2016)
	Mar del Plata coast, Argentina	2012	<2–150	<3–12	<0.9–259	Laitano et al. (2015)
	Caribbean Sea, Venezuela	2015	84–1929	15–990	12–456	Paz-Villarraga et al. (2015)
Organisms (ng Sn g ^{−1})						
Bivalves	Korean coasts	2001–2003	20–6296	<d.l.	<d.l.	Choi et al. (2009)
Oyster	Estuary, Taiwan	2009	26–1071	10–957	4–1215	Tang and Wang (2009)
Mussel	Sanricu Coast, Japan	2005	3–287	3–92	4–32	Harino et al. (1998)
Mussel	Northwest Coast, Spain	2005	52.8–96.1	20–25.7	52–96	Üveges et al. (2007)
Human liver	Denmark	1999–2000	<d.l.–0.3	0.8–28.3	0.6–4.7	Nielsen and Strand (2002)
Gastropod	Valparaíso, Chile	2013	7.4–15.8	27.4–574.3	11.6–68.8	Batista et al. (2016)
Mussel	Caribbean Sea, Venezuela	2015	<d.l.–43.2	<d.l.–13.5	<d.l.–53.6	Paz-Villarraga et al. (2015)

d.l. detection limit

that the environmental factors (e.g., pH and salinity) and property of matrices can significantly affect the adsorption of BTs. In this section, the importance of these environmental factors and matrices in the adsorption of BTs is highlighted. In addition, the competitive adsorption and adsorption mechanism of BTs to different matrices is addressed.

Effects of environmental factors

Temperature

Temperature is an important factor that reflects the change of season (e.g., from winter to summer) and region (e.g., from high to low latitude region). Variation of BTs in sediment/soil has been observed in the literature due to the variable temperature and geological conditions (Quintas et al. 2016). However, only a few studies have been undertaken with respect to the effect of temperature on the adsorption of TBT to sediments. Bangkedphol et al. (2009) found that the distribution coefficient (K_d) of TBT between seawater (pH 8) and marine sediment (Bowling Basin, UK) significantly increases from 3981 L kg⁻¹ at 20 °C to 5012 L kg⁻¹ at 40 °C. A similar trend of TBT adsorption to estuarine sediment was also

observed by Ma et al. (2000), showing an increased K_d from 7511 to 8862 L kg⁻¹ from 25 to 35 °C. These findings may suggest that higher temperature favors the adsorption of BTs to sediments, which can affect the bioavailability of BTs in the environment.

Salinity

Salinity is an important environmental factor in estuarine, saline lake, and marine systems. Studies have demonstrated that salinity can alter the solubility, octane/water partition coefficient (K_{ow}) of BTs, as well as the ionic strength in solution (Laughlin et al. 1986; Inaba et al. 1995; Ni et al. 2000), and subsequently, salinity can influence the environmental behavior of BTs in the environment. A number of studies have shown that salinity can affect the BT adsorption (Table 5; Randall and Weber 1986; Unger et al. 1988; Burton et al. 2004; Hoch et al. 2002). In general, four different ways (i.e., types I, II, III, and IV) of salinity effect on the BT adsorption can be summarized according to Table 5 (Fig. 2).

Hoch (2004) observed a trend of type I for TBT adsorption to kaolinite from salinity of 0 to 32 at pH 4, where the predominant TBT species is positively charged TBT⁺ (Fig. 1).

Table 5 Summary of the experimental conditions collected from the literature for the determination of butyltin (BT) adsorption as a function of salinity

Butyltin	Adsorbent	Experimental condition	Result	Reference
TBT	Mixture of Fe-hydroxides and fulvic acid	TBT initial concentration 10 mg L ⁻¹ (as Sn); mixture of 10–1000 mg L ⁻¹ Fe-hydroxide and 10 mg L ⁻¹ fulvic acid; pH 6.2–8.2	The adsorption of TBT increases with increasing salinity from 0 to 3% (type II)	Randall and Weber (1986)
	Natural sediments	60 mg L ⁻¹ of sediments in solution; pH 8		Harris and Cleary (1987)
	Natural sediment	100 g L ⁻¹ of sediment; pH 8		Burton et al. (2004)
	Natural sediments	17 g L ⁻¹ of sediments	The adsorption of TBT decreases with increasing salinity from 0 to 3% (type IV)	Unger et al. (1988)
	Natural sediments	100 g L ⁻¹ of sediment; pH 4		Burton et al. (2004)
	Montmorillonite	Initial concentration of TBT was 400 and 1000 µg L ⁻¹ (as Sn); pH 8		Hoch et al. (2002)
	Montmorillonite or kaolinite	TBT initial concentration was 400 µg L ⁻¹ (as Sn); pH 6		Hoch (2004), Hoch and Schwesig (2004)
	Natural sediments	100 g L ⁻¹ of sediments; the initial concentration of TBT was 4 mg L ⁻¹ (as Sn); pH 7.9	No significant change of adsorption with increasing salinity from 0 to 3% (type I)	Ma et al. (2000)
	Kaolinite	TBT initial concentration 400 µg L ⁻¹ (as Sn); pH 4		Hoch (2004)
Butyltin	Kaolinite	Initial concentration of TBT 400 µg L ⁻¹ (as Sn); pH 8	The adsorption of TBT decreases with increasing salinity from 0 to 2–2.5% and then increases with increasing salinity from 2.5–10% (type III).	Hoch (2004)
	Sediments	Initial concentration of TBT 6–6000 ng L ⁻¹ (as TBT); 1.3 g L ⁻¹ sediments; pH 8		Langston and Pope (2001)
DBT	Montmorillonite sediments	DBT initial concentration 100–1000 µg L ⁻¹ (as Sn); pH 8	The adsorption of DBT decreases with increasing salinity from 0 to 3.2% (type IV)	Hoch et al. (2003)
	Mixture of Fe-hydroxides and fulvic acid	10 mg L ⁻¹ (as Sn) DBT; the mixture of 10 mg L ⁻¹ of Fe-hydroxides and 10 mg L ⁻¹ of fulvic acid; pH 8		Randall and Weber (1986)
	Mixture of Fe-hydroxides and fulvic acid	10 mg L ⁻¹ (as Sn) DBT; mixture of 1000 mg L ⁻¹ of Fe-hydroxides and 10 mg L ⁻¹ of fulvic acid; pH 8 and 6	The adsorption of DBT increases with increasing salinity from 0 to 3.2% (type II).	Randall and Weber (1986)
MBT	Mixture of Fe-hydroxides and fulvic acid	10 mg L ⁻¹ (as Sn) MBT; mixture of 10 mg L ⁻¹ of Fe-hydroxides and 10 mg L ⁻¹ of fulvic acid; pH 8 and 6	The adsorption of MBT decreases with increasing salinity from 0 to 3.2% (type IV)	Randall and Weber (1986)
	Mixture of Fe-hydroxides and fulvic acid	10 mg L ⁻¹ (as Sn) MBT; mixture of 1000 mg L ⁻¹ of Fe-hydroxides and 10 mg L ⁻¹ of fulvic acid; pH 8 and 6	No significant change of the MBT adsorption with increasing salinity from 0 to 3.2% (type I)	Randall and Weber (1986)

The authors suggest that the zero point charge (pH_{zpc}) of 4.9 for kaolinite is the determinant factor for the adsorption of TBT (Hoch 2004).

Harris and Cleary (1987) observed a sigmoidal trend (type II) for the adsorption of TBT to sediments at pH 8, showing an increasing TBT adsorption with the increase of salinity from 0 to 30. A similar trend was found for DBT adsorption to a mixture of iron hydroxides and fulvic acid at pH 8 (Randall

and Weber 1986). The type II adsorption trend can be due to “salting out” effect that increases the adsorption of neutral TBT and DBT species at pH 8. However, Ma et al. (2000) observed an adsorption trend of type I for adsorption of TBT to natural sediment at pH 7.9 by increasing the salinity up to 30, showing no significant salting out effect on the adsorption of neutral TBT species. This may be due to that salting out effect highly depends on the content of organic matter (Ma

Fig. 2 Four types of schematic tendencies for the adsorption of TBT as a function of salinity (type I, II, III, and IV). The four types of tendencies are summarized according to the data from the literature listed in Table 5

et al. 2000). Inversely, by increasing salinity from 0 to 32, the adsorption of TBT to kaolinite or montmorillonite at pH 8 decreases from 0 to 15 but then increases with further increasing salinity from 15 to 32 as shown as type III (Hoch 2004; Langston and Pope 2001). Because TBT predominates as neutral form at pH 8, there should be no competitive adsorption to minerals from background cations. However, the exact mechanism of type III adsorption for TBT is still not clear by far.

On the other hand, a trend of type IV was found for the adsorption of TBT to sediment at pH 4 and 6, showing that

TBT adsorption decreased by increasing salinity from 0 to 30 (Unger et al. 1988). This was also observed at the same pH range by Burton et al. (2004). As TBT mainly presents as cationic TBT^+ species at $\text{pH} < 6$, the strong competitive adsorption from background cations with positively charged TBT with the increase of salinity from 0 to 30 leads to a reduced TBT adsorption (Burton et al. 2004).

pH

pH can affect the speciation of BTs and the surface chemistry of adsorbents that carry dissociable functional groups, as a result, influencing the adsorption of BTs (Arnold et al. 1998; Burton et al. 2004; Fang et al. 2010, 2012; Hoch and Schwesig 2004; Hoch et al. 2003; Hunziker et al. 2001).

Representative findings of the pH effect on the BT adsorption by various adsorbents under different experimental conditions are summarized in Table 6. Studies show that the adsorption of TBT consistently increases with increasing pH from acidic to neutral condition but dramatically decreases with the further increasing pH to an alkaline condition (Table 6). However, Fang et al. (2010) reported that the adsorption of TBT to soot keeps constantly from neutral to alkaline condition. This inconsistent finding is ascribed to the absence of functional group upon the surface of soot that is

Table 6 The pH effect on the adsorption of butyltins (BTs) to adsorbents

Butyltin	Adsorbent	Media	Result	Reference
TBT	Municipal solid water	Seawater	Adsorption of TBT increases from pH 4 to 7, and then decreases at higher pH.	Sai-Pullicino and Vella (2005)
	Montmorillonite	Deionized water; 3.2% seawater		Hoch and Schwesig (2004)
	Sediment	Freshwater and seawater		Bangkedphol et al. (2009)
	Humic acid	10 mM NaClO_4		Arnold et al. (1998)
	Quartz	0.1 M NaNO_3		Bueno et al. (1998)
	Amorphous SiO_2	10 mM NaClO_4	Adsorption of TBT increases with increasing pH from 3 to 7 and then keeps constant at higher pH	Weidenhaupt et al. (1997)
	Kaolinite	10 mM NaClO_4		Weidenhaupt et al. (1997)
	Marine sediment	Seawater		Langston and Pope (1995)
	Charcoal	20 mM NaNO_3		Fang et al. (2010)
	Iron hydroxide	0–3.2% salinity		Randall and Weber (1986)
	Soot	20 mM NaNO_3		Fang et al. (2010)
DBT	Montmorillonite, kaolinite	3.2% saline water	Adsorption of DBT increases from pH 4 to pH 7 and decreases at higher pH.	Hoch et al. (2003)
	Estuarine sediment	Seawater		Dai et al. (2003)
	Iron hydroxide	0–3.2% salinity	DBT adsorption decreases from pH 6 to 8	Randall and Weber (1986)
	Charcoal	20 mM NaNO_3	No significant change from pH 4 to 7 and then decreases at higher pH	Fang et al. (2012)
MBT	Iron hydroxide	0–3.2% salinity	MBT adsorption decreases from pH 6 to 8	Randall and Weber (1986)
	Charcoal	20 mM NaNO_3		Fang et al. (2012)
	Estuarine sediment	Seawater		Dai et al. (2003)

different from other adsorbents such as humic acid and clays, implying the different adsorption mechanisms of soot from other adsorbents (Fang et al. 2010). Despite that findings of the pH effect on the TBT adsorption were obtained based on different experimental conditions with diverse salinity (e.g., from 0 to 32), it seems that the effect of salinity on the TBT adsorption is insignificant in comparison to pH (Langston and Pope 2001; Bangkedphol et al. 2009; Randall and Weber 1986). A similar trend is also found for the DBT adsorption towards sediment and clays from pH 4 to 8 and under various salinities reported by Dai et al. (2003) and Hoch et al. (2003), while Fang et al. (2012) found that the adsorption of DBT to charcoal remains constant from pH 4 to 7. Unlike TBT and DBT, the adsorption of MBT to sediment, iron oxide, or charcoal decreases consistently from pH 6 to 8, showing an opposite adsorption tendency to that for TBT and DBT from pH 6 to 7 (Dai et al. 2003; Fang et al. 2012; Randall and Weber 1986).

Environmental matrices

Soils and sediments are complex and heterogenic matrices containing clays, sand (quartz), natural organic matters (NOMs), and BCs. To illustrate the contribution of different components to the total adsorption of BTs, a “back of envelop calculation” is useful. We take TBT as an example where TBT is adsorbed at pH 6 and 8 by a sediment consisting of 95.4% sand (>90% quartz), 2% clay (kaolinite), and 2.6% C in NOM and BC with a BC to OM ratio of 0.25 (Burton et al. 2004; Hammes et al. 2007). A typical concentration range of TBT in water is from 0 to 500 ng L⁻¹ (Antizar-ladislao 2008; Nielsen and Strand 2002; Weidenhaupt et al. 1997). The TBT distribution coefficients of the adsorbents were taken from the literature (Arnold et al. 1998; Fang et al. 2010; Weidenhaupt et al. 1997). The total adsorbed TBT by the sediment, q_{total} , is given by the Eq. 3:

$$q_{\text{total}} = C_w f_k K_k + C_w f_s K_s + C_w f_{\text{OM}} K_{\text{OM}} + f_{\text{BC}} C_w K_{\text{BC}} \quad (3)$$

where f_k , f_s , f_{NOM} , and f_{BC} represent the fractions of kaolinite, sand, OM, and BC, respectively. K_k , K_s , K_{NOM} , and K_{BC} represent the distribution coefficients of TBT with kaolinite, sand, OM, and BC, respectively. C_w represents the concentration of TBT in aqueous phase.

On the basis of this rough calculation, the results are given in Table 7. It is shown that NOM contributes the most to the total adsorption of TBT ranging from 55 to 85% among the four adsorbents in all cases except that of 31% in the low TBT concentration at pH 8. BC is found to contribute the most (57%) to the total TBT adsorption in a low TBT concentration at pH 8 and shows the least contribution (10%) at high TBT concentration and pH 6, but is still considerably higher than clay (Table 7).

Table 7 Contribution of different natural adsorbents to the total tributyltin (TBT) adsorption

TBT concentration	pH	Contribution to the total adsorption of TBT (%)			
		Sand	Clay	NOM	BC
100 ng L ⁻¹	6	3%	1%	74%	22%
	8	10%	2%	31%	57%
100 µg L ⁻¹	6	4%	1%	85%	10%
	8	17%	4%	55%	24%

These findings indicate that the contribution by the adsorbents highly depends on the TBT concentration and pH.

Competitive adsorption

Competition for adsorption sites between the positively charged BTs and background ions such as Ca²⁺ and Mg²⁺ may seriously affect the adsorption of BTs to adsorbents, but very limited experimental evidence exists to date. Weidenhaupt et al. (1997) studied the adsorption of TBT to minerals at pH 4 in the presence of different cations and showed that the adsorption of TBT significantly declined when the monovalent cations' electrolyte (e.g., Na⁺ and K⁺) was replaced by bivalent cations (e.g., Ba²⁺, Ca²⁺, and Mg²⁺). The authors interpreted this decline due to the bivalent cations competing for exchangeable sites on the surface of minerals with cationic TBT⁺, the dominant species of TBT at pH 4 (Weidenhaupt et al. 1997). This is in good agreement with the finding by Hoch and Schwesig (2004) showing that the adsorption of TBT to sediment dramatically decreases in seawater compared to that in freshwater at the similar pH range. In addition, the influence of cations on TBT⁺ adsorption to negatively charged sites differs depending on the cation radius. The larger hydrated cations (e.g., Cs⁺) can decrease TBT adsorption more than the smaller ones (e.g., Na⁺) (Weidenhaupt et al. 1997). It was shown that the competitive adsorption can also occur between BTs (Fang et al. 2012); the presence of DBT with comparable concentration can significantly decrease the adsorption of TBT to charcoal at pH < 6, whereas the adsorption of TBT is irrespective to the presence of DBT at pH 8. However, it is suggested that the competitive effect of DBT is negligible in comparison to that of inorganic cations (e.g., Na⁺, Ca²⁺) in the environment, as the concentration of such cations are much higher than BTs.

Comparison of BT adsorption

Studies have shown that the adsorption behaviors of the three BTs are significantly different. Huang and Matzner (2004) studied the adsorption of the three BTs to soils in artificial rainwater at pH < 5, showing that the adsorption capacity of BTs to soils is in an order of MBT > DBT > TBT. A similar

finding was also reported on the BT adsorption to sediment and charcoals (Dai et al. 2003; Fang et al. 2012). This can be due to the fact that MBT is more positively charged than DBT and TBT, and hence, MBT can be more strongly bonded via electrostatic forces at $\text{pH} < 7$ (Huang and Matzner 2004). However, Fang et al. (2012) reported an opposite trend showing that the adsorption of BTs to charcoal is in an order of $\text{TBT} > \text{DBT} > \text{MBT}$ at $\text{pH} 8$. This can be due to that the predominant neutral TBT species at $\text{pH} 8$ shows a higher hydrophobicity than the neutral DBT and MBT species, and consequently leading to stronger hydrophobic adsorption to charcoal (Fang et al. 2012).

BT adsorption mechanisms

The adsorption of TBT is mainly governed by the adsorption of TBT^+ to the negatively charged surfaces via electrostatic forces at $\text{pH} < 6.3$. Although the fraction of TBT^+ decreases with increasing pH , the adsorption of TBT to adsorbents increases. This can be attributed to deprotonation of the functional groups enhancing the negative sites on the surfaces of adsorbents. It is considered to be a compromise of the fractions between TBT^+ and negative charge sites at the neutral pH range (Fang et al. 2011; Weidenhaupt et al. 1997). At $\text{pH} > 6.3$, the neutral TBTOH species dominates in water (Fig. 1), and hence, the hydrophobic adsorption of neutral TBTOH species to the hydrophobic surface of adsorbents is considered to be a prevailing mechanism for TBT adsorption (Arnold et al. 1998; Hoch et al. 2002).

MBT and DBT are mainly presented as a mixture of dicharged and monocharged species at $\text{pH} 3$ to 6 (Fig. 1; Fang et al. 2012). Hence, the electrostatic bonding of the positively dicharged and monocharged MBT and DBT species by the negatively charged sites on adsorbents can take place at $\text{pH} < 6$. Nevertheless, in comparison to the monocharged BT species (e.g., TBT^+), the dicharged BT species (i.e., $\text{MBT}(\text{OH})^{2+}$ and DBT^{2+}) may exhibit stronger affinity to the negatively deprotonated functional groups on adsorbents. This is also observed in the competitive adsorption of DBT and TBT at $\text{pH} < 6$ reported by Fang et al. (2012). At $\text{pH} > 6$, the neutral MBT and DBT species (i.e., $\text{MBT}(\text{OH})_3$ and $\text{DBT}(\text{OH})_2$) are presented as dominant species in water (Fang et al. 2012), and hence, the adsorption of MBT and DBT to adsorbents is prevailing by hydrophobic adsorption at $\text{pH} > 6$.

Several models have been suggested to describe the BT adsorption by various adsorbents, including the simplest linear isotherm for the adsorption of BTs to clays, humic acid, and metal oxides (e.g., Huang and Matzner 2004; Hoch et al. 2003; Weidenhaupt et al. 1997) and the nonlinear Langmuir and Freundlich models for BT adsorption to quartz and BCs (Bueno et al. 1998; Behra et al. 2003; Fang et al. 2010, 2012). In addition, a few semi-empirical models were developed to elucidate the mechanism of BT adsorption. Arnold et al.

(1998) modeled the humic acid to water partitioning of TBT by assuming that charged TBT^+ species adsorbs on four discrete bonding sites on humic acid. Hoch and Weerasooriya (2005) proposed a diffused double layer model (DLM) that treats the surface of montmorillonite as a nonpenetrable solid with three types of sites (i.e., pH -independently permanent charge sites, pH -dependent selective and nonselective charge sites). The model reveals that the adsorption of TBT to selective charged sites on the adsorbent remains constant and higher than to other two types of sites. Furthermore, a new pH -dependent dual Langmuir (pH -DL) model was proposed by Fang et al. (2012) giving a quantitative depiction of adsorption of the bicharged BT species (i.e., DBT^{2+} and $\text{MBT}(\text{OH})^{2+}$), the monocharged BT species (i.e., TBT^+ , $\text{DBT}(\text{OH})^+$, and $\text{MBT}(\text{OH})_2^+$), and the neutral BT species (i.e., TBTOH , $\text{DBT}(\text{OH})_2$, and $\text{MBT}(\text{OH})_3$) to BCs. It was shown that the electrostatic bonding of the dicharged BT species to a wheat charcoal is about 5 to 12 times stronger than that for the monocharged BT species, while the hydrophobic adsorption of the neutral BT species is much weaker than that of the monocharged BT species (Fang et al. 2012).

Desorption of BTs

Desorption behavior of BTs from environmental matrices is another important process, which can significantly alter the bioavailability and toxicity of BTs in the environment. In contrast to extensive studies on adsorption of BTs, only a few studies have been done in desorption of BTs (Berg et al. 2001; Burton et al. 2004; Gui et al. 2016; Huang and Matzner 2004; Ruiz et al. 2008; Watanabe et al. 1997). It suggests that desorption of BTs follows a biphasic kinetics with an initial rapid desorption and a later slower desorption (Ma et al. 2000). Desorption rate of BTs from sediment is highly dependent on the property of BTs with an order of $\text{TBT} > \text{DBT} > \text{MBT}$ at both $\text{pH} 8$ and 4 (Huang and Matzner 2004; Watanabe et al. 1997). Moreover, BT desorption from environmental matrices highly depends on environmental factors (e.g., pH and salinity) and property of matrices, which is specified as below.

Effect of salinity

There is limited knowledge on the effect of salinity on desorption of BTs to date. Burton et al. (2004) found no significant difference between the desorption rate of TBT from a marine sediment at the salinity of 5 and that at the salinity of 35 at the same pH conditions. Their findings also reveal that the effect of salinity on TBT desorption is not affected by pH , showing that both positively charged TBT species and neutral TBT species show the similar desorption rate. Conversely, Sakultantimetha et al. (2011) reported that the desorption rate

of TBT increases from 13 to 33% with the increase of salinity from 0 to 20 at pH 7.5, however decreases with further increasing salinity from 20 to 30. The increase of TBT desorption rate from salinity of 0 to 20 can be due to the competitive adsorption of cationic ions (e.g., Ca and Mg) to sediment, consequently stimulating the desorption of the positively charged TBT species (~10%) from sediment at pH 7.3. The decline of TBT desorption rate from salinity of 20 to 30 can be due to the salting out effect that increases the binding affinity of hydrophobic adsorption of the neutral TBT species. Nevertheless, contradictory findings have been observed between the studies by Burton et al. (2004) and Sakultantimetha et al. (2011), which can be due to different experimental methods used in the two studies; Burton et al. (2004) performed the adsorption and desorption experiments under the same salinity. However, Sakultantimetha et al. (2011) examined the desorption rate of TBT under different salinities after adsorption of TBT on sediment, which is more relevant for assessing the fate of TBT in TBT-adsorbed sediment particles transporting from freshwater to estuarine and marine system.

Effect of pH

Several groups investigated the effect of pH on the desorption of TBT and DBT from different adsorbents such as marine sediment, kaolinite, and montmorillonite, and a similar desorption behavior was observed showing that desorption of TBT and DBT can occur at a pH range from 4 to 8 (Burton et al. 2004; Hoch et al. 2002, 2003). Their results also show that desorption trend of BTs as a function of pH is in opposite to that of BT adsorption; the maximum desorption rate of BTs takes place at pH 8, and the minimum desorption rate occurs at pH ranging from 6 to 7. The higher desorption of BTs at pH 8 may be due to the fact that the hydrophobic interaction force of the neutral BT species with environmental matrices at pH 8 is weaker than the electrostatic force between the positively charged BT species and matrices at pH < 6.

Effect of environmental matrices

Desorption of BTs from environmental matrices is different depending on the property of matrices. The content of organic carbon is regarded as an important factor that affects desorption of BTs. Burton et al. (2006) observed a hysteric desorption of TBT from sediment at pH 8, which is due to the slow diffusion of TBT molecules from the internal sites of sediment with organic carbon content ranging from 0.2 to 4.8%. Huang and Matzner (2004) also reported a similar finding showing that TBT and DBT desorption rate remarkably declines from 33 to less 1% with the increase of organic carbon content from 1.6 to 44.3% even at pH < 5.5 where TBT and DBT are predominant as positively charged species. In addition, study shows that desorption rate of TBT from organic carbon-rich sediment becomes

more difficult by increasing the aging time from 24 h to 84 days (Ma et al. 2000). However, there is no significant difference for TBT and DBT desorption from kaolinite, illite, and montmorillonite in seawater at pH 8 where both of BTs are predominant as neutral species (Hoch et al. 2002, 2003).

Toxicity and bioaccumulation of BTs

Since the first evidence of TBT causing imposex in gastropod mollusks was reported in the 1970s, a number of studies have been devoted to assess the toxicity of BTs to different organisms (Matthiessen and Gibbs 1998; Giraud-Billoud et al. 2013; Graceli et al. 2013; Lopes-dos-Santos et al. 2014). The susceptibility of individuals to toxic exposure of BTs may differ due to their different genotypes, rate of metabolism, ontogenetic development, and environmental conditions (Fent 1996; Fernandez et al. 2005; Sahoo and Oikari 2016). As a consequence, the effect concentration (EC) of BTs to different organisms falls in a wide range. Determination of BT toxicity has been conducted in acute and chronic tests. For acute toxicity, the EC mainly relates to the mortality (immobilization of organism) and the growth inhibition during a short period of exposure, while the chronic effects of BTs are essentially of importance at low concentration and long-term exposure. In addition, studies demonstrated that bioaccumulation of BTs in organisms is an important parameter to predict BT toxicity and threats to higher trophic levels in the food chain. It is found that the bioaccumulation of BTs can be affected by many extrinsic factors such as the concentration of organic carbon, the presence of adsorbents, pH, water hardness, and salinity (Bartlett et al. 2004).

This section briefly reviews the acute and chronic toxicity of BTs to different species of organism and bioaccumulation of BTs in aquatic organisms. More importantly, influence of environmental factors and environmental matrices on toxicity and bioaccumulation of BTs is extensively addressed.

Toxicity of BTs

Among the three BTs, TBT is considered as the most toxic to aquatic organisms, while DBT is less toxic and MBT is the least toxic (Fent 1996; Li and Li 2015). Many studies have been undertaken on the toxicity of BTs to different life stages of organisms. The selected data are listed in Table 8.

The early stage of embryos and larvae is generally used as a model for assessing the water quality, since they are more susceptible to toxicant than in their adult stages (Sahoo and Oikari 2016). For instance, Lau et al. (2007) performed an acute toxicity test of TBT to different stages of polychaete, *Hydroides elegans*, i.e., eggs, two cells, trochophores, juveniles, and adults, in static seawater. The results showed that the 48 h LC₅₀ value (the concentration causing 50% of lethality in all test populations) for these stages from eggs to adults was 0.2, 1.0, 2.4, 2.9, and 4.4 µg (TBT)

Table 8 Selected studies on the acute toxicity results of butyltins (BTs) to aquatic organisms

Butyltin	Organism	Media	Time	LC ₅₀ (µg Sn L ⁻¹)	Reference
TBT	Nauplius neonate (<i>Eurytemora affinis</i>)	Artificial seawater	48–72 h	0.6–2.2	Hall et al. (1988)
	Crustacean neonate (<i>D. magna</i>)	Artificial freshwater	96 h	3.3–5.5	Meador (1986)
	Oyster (<i>C. virginica</i>), embryos	River water	48 h	1.3	Roberts (1987)
	<i>M. mercenaria</i> , embryos	River water	48 h	1.1	
	Crustacean juvenile (<i>Mysid shrimp</i>)	Seawater	96 h	0.3	Valkirs et al. (1987)
	Seabream larvae (<i>Sparus aurata</i> L.)	Seawater	24 h	38.6	Dimitriou et al. (2003)
	Echinoidea larvae (<i>P. lividus</i>)	Artificial seawater (salinity 3.4‰; pH 8)	24 h	0.3	Bellas et al. (2005)
	Crustacea larval (<i>P. serratus</i>)		24 h	17.5	
	Tilapia	Artificial seawater (salinity 1.5‰)	96 h	3.8	Lei et al. (1998)
	Crustacean neonate (<i>D. magna</i>)	Artificial freshwater at pH 6–8	48 h	2.7–3.4	Fang et al. (2011)
DBT	Crustacean neonate (<i>D. magna</i>)	M7 test media	24 h	900	Vighi and Calamari (1985)
	Crustacean neonate (<i>D. magna</i>)	Artificial freshwater at pH 6–8	48 h	330–484	Fang et al. (2011)
MBT	Crustacean neonate (<i>D. magna</i>)	M7 test media	24 h	49,000	Vighi and Calamari (1985)

L⁻¹. Another analogous finding was also reported for seabream (*Sparus aurata*) eggs and its larvae, which gave lower 24 h LC₅₀ of 28.3 µg L⁻¹ for the eggs than that of 38.6 µg L⁻¹ for larvae (Dimitriou et al. 2003). This is ascribed to the increased sensitivity of the earlier stage due to the rapidity of development and abundant availability (Antizar-Ladislao 2008; Dimitriou et al. 2003). In contrast, the later life stages of some organisms are found to be more sensitive to TBT than the earlier life stages. Novelli et al. (2002) observed that the EC₅₀ value of TBT for the egg stage of Mediterranean sea urchins, *Paracentrotus lividus*, was 5.8 µg L⁻¹ which was about two times higher than that of the embryonic stage (2.5 µg L⁻¹) and may be due to the different targets (DNA and protein synthesis inhibition) for this species. This is also in accordance with the findings of toxicity of TBT in the adult mollusk, *Mytilus edulis*, by Haggera et al. (2005).

For the acute toxicity of DBT and MBT, very little information can be obtained in the literature. Vighi and Calamari (1985) observed a 24 h LC₅₀ value of 900 µg L⁻¹ for DBT and 49,000 µg L⁻¹ for MBT, respectively, for the crustacean, *Daphnia magna*. Fang et al. (2011) has also found a 48 h EC₅₀ value of 330 to 484 µg L⁻¹ for DBT using the same test organism and experimental condition, which shows significantly higher LC₅₀ value than for TBT (3.2 µg L⁻¹; Fang et al. 2011). This may imply that the acute toxicity of TBT is significantly higher than that of DBT and MBT.

On the other hand, chronic toxicity of BTs can also highly depend on life stages of organisms (Leung et al. 2004; Li et al. 2014). For example, Ruppert et al. (2016) reported that the 18-day EC₅₀ (the concentration causing 50% of inhibition in all test populations) value (535 ng Sn L⁻¹) for adult snails is about 10 times higher than that for juvenile snails (50.8 ng Sn L⁻¹). Similarly, Lau et al. (2007) reported that the EC₅₀ value for the development of *H. elegans* (polychaete) from eggs to juveniles increases from 0.01 to 0.1 µg L⁻¹ for an exposure period of 17 days.

Bioaccumulation of BTs

Because bioaccumulation in organisms can be via adsorption from water and sediment, or via food chain, this section hereby discusses the bioaccumulation of BTs in the context of phytoplankton and zooplankton. Bioaccumulation of BTs from seawater by phytoplankton is considered to take place at a short timescale (minutes to hours). Coelho et al. (2002) studied the bioaccumulation of TBT by the microalgae, *Isochrysis galbana*, in seawater (salinity of 30). The results show that the bioaccumulation of TBT is rather fast and reaches steady state after exposure for 1 h, with a bioconcentration factor (BCF) of around 7000 L kg⁻¹. The rapid bioaccumulation of TBT by the microalgae can be attributed to the large surface area of microalgae. Besides, a BCF of 1000 to 10,000 L kg⁻¹ for TBT to the microalgae (i.e., *D. salina*, *D. vivides*, and *I. galbana*) exposed to 1 to 100 µg L⁻¹ of TBT has been reported in the literature (Guolan and Yong 1995; St-Louis et al. 1997; Coelho et al. 2002). St-Louis et al. (1997) studied the mechanism of TBT bioaccumulation by the marine microalga *Pavlova lutheri*. They demonstrated that bioaccumulation of TBT by algae could involve two independent processes: surface bioaccumulation of cells and intracellular uptake. The surface binding is the major process which also explains the reason of rapid bioaccumulation of TBT by algae.

On the other hand, bioaccumulation of BTs from water/sediment by zooplankton is found to be considerably slower than their bioaccumulation by phytoplankton (Seligman et al. 1996; Strand and Asmund 2003). For example, TBT was gradually taken up from water and sediment by the crustacean *Hyalella azteca* over the first 96 h and then reaches steady state after 25-day exposure, with a BCF around 1000 (Bartlett et al. 2004). The slow bioaccumulation rate is consistent with the findings of the bioaccumulation rate of TBT in fish larvae, *Thymallus* (Fent and Looser 1995), and fish muscles (e.g., *Megalaspis*

cordyla) with a BCF value of 590 to 3263 L kg⁻¹ (Shue et al. 2014). In addition, a very low BCF has been reported by Stronkhorst et al. (1999) who reported that the BCF of TBT for the heart urchin, *Echinocardium cordatum*, is only around 200. Bioaccumulation of TBT by zooplanktons is suggested to occur via the food chain, showing a relatively slow bioaccumulation rate (Coelho et al. 2002).

Effect of environmental factors

Environmental factors and matrices can alter the adsorption and desorption of BTs (Filipkowska et al. 2014; Furdek et al. 2016), consequently affecting the toxicity and bioaccumulation of BTs to organisms reported in many studies. In the following, the effect of different environmental factors and matrices on the toxicity and bioaccumulation of BTs is discussed.

pH

Depending on the pH of water, BT species can pose different physicochemical properties to organisms, such as lipophilicity/hydrophobicity. White and Tobin (2004) investigated the toxicity of TBT to yeast, *Candida maltosa*, at pH 5.5 and 7.5, and observed a slight increase in toxicity at higher pH. However, the membrane was found to be more damaged at pH 5.5 than that at pH 7.5. Fent and Looser (1995) reported that TBT causes a three times higher mortality for *D. magna* at pH 8 than that at pH 6 using a single TBT concentration of 4.8 µg L⁻¹. In contrast, Fang et al. (2011) reported that the 48-h EC₅₀ value of TBT and DBT to *D. magna* is 2.7 and 190 µg L⁻¹ at pH 6, respectively, and 3.2 and 331 µg L⁻¹ for TBT and DBT at pH 8. The results showed the consistently higher toxicity for the two BTs at pH 6, especially for DBT (Fang et al. 2011), and are consistent with the finding of the membrane-damaging effects of TBT to *C. maltosa*. Phosphate buffer can strongly bind with the cationic TBT⁺ species and has been used in Fent and Looser (1995). This may lead to the discrepancy between the two studies on the TBT toxicity to *D. magna*.

Several studies have also been involved in the effect of pH on the bioaccumulation of BTs by organisms. Fang et al. (2011) observed no significant difference between the BT bioaccumulations at pH 8 and pH 6 for both TBT and DBT. This is in accordance with the finding by Ciucani et al. (2004) showing no significant effect of pH on the bioaccumulation of TBT in willow trees.

Salinity and hardness

The effect of salinity and hardness on the toxicity of BTs has been reported. Hall et al. (2000) reported that the acute 10th percentiles of TBT for 43 saltwater species and 23 freshwater species are 320 and 103 ng L⁻¹, showing significantly lower toxicity to those organisms in saltwater than in freshwater. Kwok and Leung

(2005) stated that the acute toxicity of TBT to the crustacean, *Trissolcus japonicus*, is much higher at a salinity of 15 than that at 45. Fang and coworkers compared the acute toxicity of TBT and DBT to *D. magna* in media of different hardness and showed that the EC₅₀ values for TBT and DBT were enhanced with increasing the hardness from 0.6 to 2.5 mM (Fang et al. 2011). These findings reflect that the attenuated toxicity at a higher ionic strength (i.e., higher hardness or salinity) can be due to the competition of the background cations with BTs to biotic ligands on the organism. Nevertheless, the acute toxicity of TBT to the copepod, *Acartia tonsa*, slightly increased with an increase of salinity from 18 to 28 as reported by Kusk and Petersen (1997).

Although water salinity is also considered to be an important parameter for the bioaccumulation of BTs in organisms, very little work has been done on the effect of hardness or salinity on the bioaccumulation of BTs. It is noted that the BCF values of TBT in freshwater fish is also identical with those observed in fish in seawater at pH 8, showing insignificant effect of salinity on the bioaccumulation of TBT (Fent 1996).

Effect of environmental matrices

Environmental matrices such as humic acids and BCs can strongly associate with BTs, consequently affecting the BT bioavailability in the environment (Burton et al. 2004; Fang et al. 2011, 2012; Weidenhaupt et al. 1997). Bao et al. (1997) studied the acute toxicity of TBT to *D. magna* by the addition of different types of humic acids, and their results show that the 24 or 48 h EC₅₀ value for TBT remarkably increases after the addition of 40 mg L⁻¹ of humic acid, which indicates that the toxicity of organisms significantly decreases. The decrease of TBT bioaccumulation in the presence of humic acid was also observed by Fent and Looser (1995), which is in line with the findings by Fang et al. (2011) showing that the presence of nano-size charcoal can notably decrease the acute toxicity of TBT and DBT to *D. magna*. Conversely, Bartlett et al. (2004) found that the TBT bioaccumulation in *H. azteca* is much higher in the presence of sediment during exposure. Analogously, the presence of humic acid in the sediment-associated TBT was found to significantly increase the toxicity of TBT on the *Rhepoxynius abronius* and *Eohaustorius washingtonianus* (Meador et al. 1997).

Conclusion

BTs, namely TBT, DBT, and MBT, are the most important organometallic compounds in the industry and agriculture. The release of BTs into ecosystems can cause severely adverse effect to the environment and organisms. Study on the fate and toxicity of BTs in the environment has been intensively engaged during the past decades. This work reviews the recent progress of BT studies in relation with their physicochemical properties and environmental levels, adsorption and

desorption of BTs to different environmental matrices, and their bioaccumulation and toxicity to organisms. Lab-scale studies have demonstrated that environmental factors (e.g., pH, temperature, and salinity) and environmental matrices (e.g., minerals and BCs) can significantly influence the adsorption and desorption of BTs to matrices, and consequently altering their bioaccumulation and toxicity to organisms. These evidences can be useful for properly assessing the bioavailability and toxicity of BTs in the environment. However, further field study on the overall influence of these environmental factors is essentially demanded. Meanwhile, development of relevant remediation technology for BT-contaminant sediments particularly in marine systems is also highly required.

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