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The partition behavior of tributyltin and prediction of environmental fate, persistence and toxicity in aquatic environments

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ABSTRACT

Tributyltin (TBT) is one of the most toxic anthropogenic compounds introduced into the aquatic environment. It has a relatively high affinity for particulate matter, providing a direct and potentially persistence route of entry into benthic sediments. To understand TBT behavior, computational programs are an exceptionally helpful tool for modeling and prediction. EPISuite program was used for evaluation of the prediction data including fate, persistence and toxicity from the partition coefficient values. Without experimental data, the model is useful for prediction but is essentially a default model. A site specific assessment is possible by measuring the partition coefficients and entering the experimental values obtained into the model. This paper describes the results of a study undertaken to determine the partition coefficients and the effect of various parameters on such partition coefficients. The octanol–water partition coefficient (K_{ow}) was determined by the OECD shake-flask method, with the logarithm values obtained ranging from 3.9 to 4.9 depending on salinity. The sediment–water partition coefficient (K_d) was determined by ASTM method of generating Freundlich adsorption isotherms, the obtained values ranged from 88 to 4909 L kg^{-1} depending on sediment properties, salinity, pH, and temperature. The experimental partition coefficient K_{ow} and K_{oc} (calculated from K_d) were used as input data into the prediction program to provide accurate values for the natural samples *in situ*. The experimental prediction showed lower toxicity than the default model, but represent actual toxicity and accumulation at the natural site. Moreover, the environmental fate was significantly different when the experimental values and the default values were compared.

1. Introduction

Tributyltin is one of the most toxic anthropogenic compounds introduced into the aquatic environment. It has been widely used mainly as antifouling paints and wood preservatives due to its biocidal property (Hoang et al., 1982; Rudel, 2003). Its production increased significantly in the 1950s which raised the level of TBT in the environment. Due to the persistent nature and bioaccumulative potential, TBT has been classified as a persistent organic pollutant (Langston and Pope, 1995) which also has a high toxicity towards organisms (Antizar-Ladislao, 2008). The usage of TBT and its derivatives has drawn concern about the potential damage to organisms and mammals in ecosystems. Following a recommendation by the International Maritime Organization (IMO, 2002), its application as an antifouling paints is now regulated in most countries. Nevertheless, TBT is still present in many aquatic systems at concentrations that cause adverse physiological effects on both organisms and mammals (Antizar-Ladislao, 2008). Therefore, the determination of partition coefficients and also the adsorption behavior are vital to verify the environmental fate and toxicity of TBT. The adsorption behavior of TBT in solid-water system has been investigated in terms of the solid-water partition coefficient, K_d (ASTM, 2001; Mackay, 2001). The partition coefficient K_d is found to fit the Freundlich equation depending on TBT concentration (Langston and Pope, 1995). The K_d values reported vary from 10^{-1} to 10^{6} L kg^{-1} depending on the conditions and method (Dowson et al., 1993; Langston and Pope, 1995; Burton et al., 2004, 2006). Moreover, partitioning of TBT, DBT and MBT by *in situ* solid/pore-water were determined at different depths at south-east Queensland, Australia. The partitioning, K_d and K_{oc} were varied at different estuarine sediment profile (Burton et al., 2005). The most comprehensive standard method published that was found suitable for this work in determining K_d is ASTM E1195-01. Quantification of the partition coefficient in the previous reports was not carried out precisely according to this standard method. Variations included for example, the use of dried or frozen sediment, the degree of water purity used, the ratio of solid:water

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for the experiments or the equilibrium time used. Moreover difference in the partition behavior of TBT reported in the literatures indicates variation of the partition coefficient as a function of salinity (Hoch, 2004). Previous studies on the effect of salinity have not covered the full salinity range and therefore interpretation may be erroneous as the effect of salinity is a parabolic curve (Harris and Cleary, 1987; Unger, 1988). Thus when the complete range is observed it leads to a contradiction of findings of relationships between K_d and salinity.

The influence of pH on K_{ow} is extensively reported (Tsuda et al., 1990; Avery et al., 1993; Arnold et al., 1998; White et al., 1999; Looser et al., 2000) but only one report also described the effect of salinity on K_{ow}. However, again the complete salinity range was not studied (Burton et al., 2004). In addition, partition coefficients of TBT are often only presented without the prediction of environmental fate, persistence and toxicity using the experimental partition coefficient values obtained to create accurate prediction values for each natural site.

Therefore, in this study, the experimental partition coefficients were derived based on standard methods. The variations of partition coefficients were investigated as a function of TBT concentration, time, solid:water ratio, pH, salinity, sediment type and temperature. Subsequently, the coefficients obtained from the experiments and program calculations from EPISuite (V4.0) were compared (EPA, 2009). Also the environmental fate, toxicity and persistence were predicted using the experimental partition coefficients as the input for the program to create a more accurate model for a specific site.

2. Materials and methods

2.1. Chemicals and instruments

All reagents were used without additional purification. The analytical standard, tributyltin chloride (96% purity), tropolone (98% purity) and hexylmagnesium bromide solution (2 M in diethyl ether) were obtained from Aldrich (Steinheim, Germany). Triethyltin chloride (98% purity) was purchased from VWR International Inc (West Chester, USA) and was used as an internal standard. All solvents were HPLC grade obtained from Merck (Darmstadt, Germany). All reagents used were of analytical grade. The PerkinElmer model 785A UV/VIS HPLC system (Waltham, Massachusetts, USA) was equipped with 20 μL injection loop. All HPLC tubing parts were replaced with polyether ether ketone (PEEK) components. The chromatographic column used was an ultra cyano column (5 μm, 250 mm × 4.6 mm i.d., Restek, UK). The powder X-ray Diffractometer (XRD) was carried on a Philips PW 1830 system (Almelo, Netherlands).

2.2. Sample collection

Sediment and water samples were collected from potentially polluted areas. The samples were collected in March 2008 at Bowling Basin and Port Dundas, Glasgow, UK. The study area is part of the Forth and Clyde Canal system which had been a main waterway between the west and east coast of Scotland. While boat activity is still present at Bowling Basin, Port Dundas has been inactive for many years and is no longer part of the canal network. In this study, samples collected from Bowling Basin were used to determine the partition coefficients and subsequently predict the behavior of TBT in the natural environment. Potentially uncontaminated sandy samples were collected from the Clyde River (taken six miles upstream from Glasgow) to study and compare the adsorption behavior of TBT.

All sediment samples were collected from the surface layer at the top 15 cm of the solid profile using a dredge sampler and passed through a 2 mm sieve before storage in polyethylene bags. Surface water samples were collected and stored in polypropylene bottles. The samples were kept refrigerated and analyzed within 3 d.

2.3. Octanol–water partition coefficient (K_{ow}) of TBT

The K_{ow} was determined by following the OECD guideline 107 (shaking flask method) at constant temperature, 20 °C (OECD, 1995). The method allows the user to select the TBT concentration in octanol and the ratios of octanol–water; however, a balance between these parameters is strictly required. The volume ratios between octanol and water studied were 1:1, 1:2 and 2:1. The Log K_{ow} value was obtained from the average results ($n = 3$) of each ratio, where the results varied by less than ±0.3 units, which was achieved by maintaining the concentration of TBT dissolved in the octanol less than 300 μg mL^{-1}. The effect of salinity on K_{ow} was studied. The salinity of the water was estimated using standard methods for the examination of water and wastewater which converts the conductivity measured into salinity (practical salinity units; psu) (APHA, 1999). Freshwater salinity is usually less than 0.5 psu, brackish or estuarine water is between 0.5 psu and 17 psu, and ocean salinity is between 32 psu and 37 psu (APHA, 1999). In addition, the K_{ow} value of the canal water sample from Bowling Basin was investigated.

For TBT analysis, 0.2% NaCl was added to a 10 mL aliquot of the aqueous phase, and then extracted at pH 1.7 with 0.05% tropolone in hexane. TBT was quantified using normal phase HPLC on cyanopropyl column with hexane containing 5% THF and 0.03% acetic acid at flow rate 0.8 mL min^{-1} (Bangkedphol et al., 2008). The amounts of TBT in organic phases were determined by subtraction from the total amount of TBT in the system (300 μg mL^{-1}). Then, the results were compared to the K_{ow} value from the computational program (default value).

2.4. Sediment characterization and TBT contamination

The sediment was characterized by pH, total organic carbon (TOC), moisture content, and particle size distribution. TOC and moisture content of the sediments were determined based on ASTM standard D2974-87 (ASTM, 2000). The carbonate content of sediment was assessed using the method from Horvath (Horvath et al., 2005). This simple method initially determines the presence of carbonates by the addition of HCl and confirms the presence of CO_2 by observation of the bubbles produced. Particle size distribution of the sediment was carried out using specific gravity measurements by hydrometer based on ASTM standard D422-63 (ASTM, 2002). The clay minerals in sediments were identified by XRD technique. The initial TBT concentration in sediments was determined from 5 g sample, on a dry weight basis. In water samples the initial concentration was determined from a 500 mL sample. The samples were extracted and analysed using NPHPLC method (Bangkedphol et al., 2008).

2.5. Solid-water partition coefficient (K_d) of TBT

The adsorption of pollutants from water to sediment is based on the Freundlich equation (EPA, 1999; ASTM, 2001; Mackay, 2001). K_d values of TBT were determined by ASTM standard E1195-01 to measure TBT adsorption behavior (ASTM, 2001). This involves 4 main steps. Firstly, in accordance with the standard method, ratios between the solid:water were optimized when the volume of water was fixed at 20 mL. The amounts of sediment used were 0.1, 0.2 and 0.4 g which represent 1:200, 1:100 and 1:50 sediment to water ratio, respectively. The concentrations of TBT in water were 40, 80, 120, 160, 200, 240 and 300 $\mu g\ mL^{-1}$. Secondly, the working range and highest concentration of TBT in water that was considered to follow the Freundlich adsorption isotherm was determined. Then, the adsorption times were varied from 15 min to 24 h at 20 °C using the highest concentration of TBT to achieve the equilibrium time, which was then set for the subsequent experiments. Finally, the K_d value was investigated by varying the TBT concentration in water and shaking at the equilibrium time. In addition, the standard method for K_d determination also requires specific Type IV reagent water, that is water of conductivity less than 5 $\mu S\ cm^{-1}$, electro-resistivity less than 0.2 ohm cm, and pH range from 5.0 to 8.0 (ASTM, 2008). The K_d value using natural water from Bowling basin was also examined and compared with the K_d value from Type IV water.

The major parameters that influence K_d studied in this work indicate TBT adsorption behavior and fate in the natural environment. This understanding leads to more efficient modeling and remediation processes. The parameters studied were sediment type, pH, salinity and temperature in the range where they practically occur in natural conditions. Sediment from Bowling Basin was used, and also sediment from the other two areas from the Forth and Clyde Canal, UK were considered and compared for sediment type variation. The salinities were studied at 0, 15, 32, 50 and 100 psu which represented the range of salinities from freshwater to greater than full strength seawater. The salinity of Type IV water was adjusted by adding KCl because potassium is absorbed in water better than NaCl (APHA, 1999). Water at various pH values (4, 5, 6, 7 and 8) was obtained by adjustment with 0.1 M HCl or 0.1 M NaOH. The pH of water was measured before and after the experiment. The study temperatures were varied from 20 to 50 °C using incubator shaker.

$K_{oc,}$ the organic carbon partition coefficient, was calculated from the obtained experimental K_d value as presented in Eq. (1) (ASTM, 2001; Mackay, 2001). Then, the results were compared to the K_{oc} value from the computational program (i.e. the default value).

$$K_{oc} = \frac{K_d}{\%OC} \times 100 \tag{1}$$

3. Results and discussion

3.1. Octanol–water partition coefficient (K_{ow})

TBT contamination in the environment has the potential for bioaccumulation. To predict the possible accumulation of TBT in organisms, the dimensionless octanol–water partition coefficient (K_{ow}) is used. Octanol represents lipids because of its similar carbon to oxygen ratio. The octanol–water partition coefficient is a measurement of the lipophilicity of a substance. K_{ow} value is defined by Eq. (2) (OECD, 1995).

$$K_{ow} = \frac{\text{Concentration in octanol } (\mu g/mL^{-1})}{\text{Concentration in water } (\mu g/mL^{-1})} \tag{2}$$

The Log K_{ow} values obtained from the experimental and default values are 3.95 ± 0.05 and 4.70, respectively. This shows a disparity in the experimental values and the values given from the computational model. Because the default values were estimated from the properties of TBT without accounting for local environmental conditions, the potentially influencing parameters were studied in an attempt to explain the difference of Log K_{ow}. Salinity affects water solubility and causes "salting out", which can change the K_{ow} value (Rydberg et al., 2004). Therefore, the K_{ow} value was examined in artificial water at various salinities, and also in the natural water from the site. The results are presented in Fig. 1.

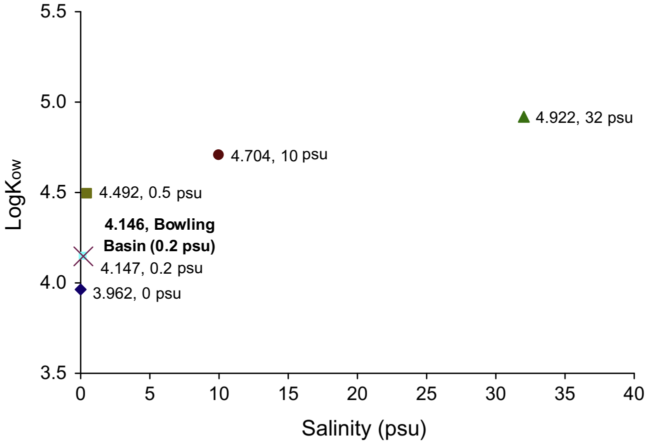

Fig. 1. Log K_{ow} of TBT in water of various salinities.

The results show the relationship between salinity of water and Log K_{ow}. Increased salinity resulted in higher Log K_{ow} values. Greater salinity is therefore likely to lead to higher accumulation of TBT within the lipid of organisms. The water from Bowling Basin, the salinity of which was 0.2 psu gave a similar Log K_{ow} value to synthetic water at 0.2 psu.

3.2. Solid-water partition coefficient (K_d)

The solid (soil and sediment)-water partition coefficient (K_d) is of paramount importance in order to predict the behavior and mobility of pollutants within the environment. The K_d value is determined as a plot of the Freundlich equation and yields the following linear relationship:

$$Q_e = K_d C_e^{1/n} \tag{3}$$

$$\text{Log } Q_e = 1/n \text{ Log } C_e + \text{Log } K_d \tag{4}$$

where Q_e ($mg\ kg^{-1}$) and C_e ($mg\ L^{-1}$) denote the sorbed and aqueous concentration at equilibrium, respectively.

The Eq. (4) is the Log plot of Eq. (3). A single point K_d value has been used and reported but this results in poor accuracy (Langston and Pope, 1995). The K_d value obtained from a slope is also used as presented in Eq. (3) this assumes that n is equal to 1 (Langston and Pope, 1995; Hoch et al., 2002, 2003; Burton et al., 2004; Keenan et al., 2008). The K_d value in the current study was obtained from intercept of a log plot of the Freundlich equation to improve the correlation coefficient and assess the actual adsorption behavior of TBT.

The appropriate sediment–water ratio was investigated in accordance with the standard procedure to obtain the maximum adsorption of TBT concentration that fitted the Freundlich equation (ASTM, 2001). The sediments from Bowling Basin were selected because the site is still active, with contamination present (Bangkedphol et al., 2008) and therefore the prediction will be applicable. Following Eq. (4), the working concentration range of TBT in water was decided for K_d identification (ASTM, 2001). At 20 °C, the samples were shaken for 24 h to reach the equilibrium and the results are presented in Fig. 2a.

Fig. 2a shows that the sediment–water ratio at 1:200 gave the maximum capacity of TBT on the sediments. The highest concentration of TBT tested in water (300 $\mu g\ mL^{-1}$) for sediment–water (1:200) was ignored as the adsorption behavior did not fit the Freundlich adsorption isotherm. Log K_d can be identified by the intercept on the y-axis of the Log plot in Fig. 2a. Under these conditions, the Log K_d of TBT for the Bowling sediments was 3.64. The maximum TBT concentration in water from the experiment with

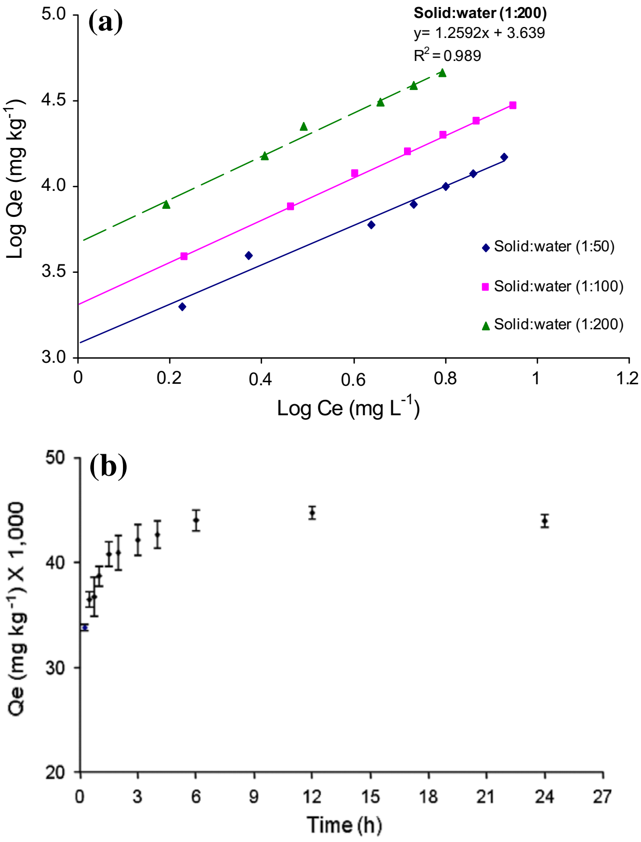

Fig. 2. (a) Freundlich adsorption isotherm of TBT on sediment from Bowling Basin at various sediment–water ratios and (b) adsorption of TBT on the Bowling sediment at various times.

sediment–water (1:200) was used to determine the equilibrium time. Time scales were varied from 15 min to 24 h. The results are presented in Fig. 2b. This figure shows that the adsorption of TBT on the sediment was almost steady after 6 h. Therefore, the shaking time was fixed at 12 h. The optimum conditions so established were used in subsequent studies on the influence of other parameters on the partition coefficient K_d.

3.3. The effect of sediment properties, salinity, pH and temperature on K_d

The quality of water affects the adsorption of TBT on sediment. The Log K_d values were 3.64 for Type IV water and 3.34 L kg^{-1} for water taken from the Bowling Basin. The lower Log K_d in the natural water is possibly due to the pH (pH 8) and salinity (0.2 psu) which were different from the Type IV water at pH 7.0 and zero salinity. Therefore, the effects of these parameters on the adsorption behavior were studied. The results were input into the modeling program with the new values obtained providing a more accurate assessment for the natural conditions in terms of the toxicity, persistence and fate of TBT.

3.3.1. Effect of sediment properties

The characteristics of the sediments collected are presented in Table 1. The sediment samples were also tested for carbonate which proved negative. Therefore, the total organic carbon is considered similar to the organic matter in sediment (ASTM, 2000).

The isotherms of TBT on sediments were obtained at the optimum condition for the adsorption i.e. a sediment–water ratio of 1:200 and 12 h shaking time. The results from adsorption isotherm show that the Log K_d of sediments from Bowling Basin, Port Dundas and the Clyde River were 3.64, 3.48 and 1.95, respectively. The sediments from Clyde River which contains considerably less organic carbon than the other sites had the lowest Log K_d. The result supports previous findings that organic matter in sediment increases the adsorption of TBT (Unger, 1988). Conversely, even though the organic carbon content in Bowling Basin sediments was lower than in Port Dundas, a higher Log K_d was found. It is possible that this phenomenon could be explained by the types and proportions of clay minerals present. Therefore the clay minerals in the three sediment samples were identified by XRD. Results of semi-quantitative analysis of the clay minerals are presented as relative intensity ratios of kaolinite/illite/quartz. The 2θ of the main peak of montmorillonite, kaolinite, illite, quartz are 5.89, 14.05, 16.93 and 26.65, respectively. Montmorillonite in the Forth and Clyde Canal samples was below the limit of detection. The relative intensity ratio (kaolinite/illite/quartz) of clay minerals in sediments from Bowling Basin, Port Dundas and the Clyde River were 1/3.0/1.5, 1/2.8/0.8 and 1/1.8/3.8, respectively. Generally, the affinities of the sorbents for TBT at pH 8 are reported to be in the order of kaolinite < kaolinite-illite mixture < montmorillonite ≈ illite (Hoch et al., 2002). In addition, low adsorption affinity of kaolinite was supported by the hydrogen bonding in the structure. Hydrogen bonds keep the structure relatively rigid and prevent the entering atom or molecule being adsorbed on the kaolinite structure (O'Neill, 1998). The Bowling Basin sediment appears to contain the highest proportion of illite, therefore this can explain why it showed a greater Log K_d even though it contained lower organic carbon content than the sediment from Port Dundas.

Table 1
Properties of the sediment from the three study sites.

Sediment sample	pH	Moisture content (%)[a]	TOC (%)	Particle size analysis (%)		
				Sand	Silt	Clay
Bowling Basin	8.0	3.23	12.1	7.67	63.5	28.8
Port Dundas	8.0	2.85	17.4	17.4	53.0	29.6
Clyde River	7.5	0.37	1.21	79.5	0.97	19.5

[a] Wet sample moisture content required for recalculation to dry basis.

In general, organic carbon is believed to be a major factor to predict the adsorption behavior of TBT on sediment. However, this study demonstrates that the clay minerals are also important. In samples with similar organic carbon content, the nature of the clay minerals present may strongly affect TBT sorption behavior.

3.3.2. Effect of salinity

The effect of salinity was studied on the Bowling Basin sediments with water at various salinities. The salinity range was varied from 0 to 100 psu. Following the Eq. (4), The K_d values at various salinities of water were investigated. The results are shown in Fig. 3.

Fig. 3 shows that adsorption was greatest in freshwater, decreased at low and intermediate salinities, and then increased again at high salinities. This could be explained by the capacity of TBT to show characteristics of both metal ions and hydrophobic properties with respect to partitioning. It is typical of hydrophobic compounds that the adsorption of TBT increases with salinity because of "salting out" (Harris and Cleary, 1987). However, at low salinity the decreasing of TBT adsorption is more consistent with the behavior of metal cations (Unger, 1988). At higher salinities, more competition for adsorption sites by cations, in this case K^+, led to less negatively charged particulate matter and resulted in decreased adsorption.

3.3.3. Effect of pH

The pH is an important factor in controlling the partitioning of butyltin compounds, since this parameter not only affects the

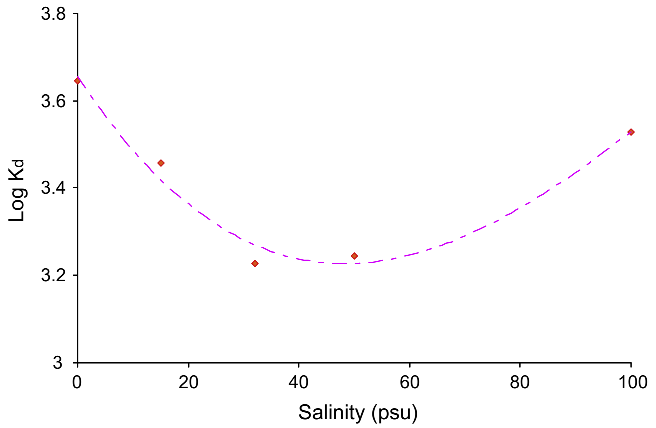

Fig. 3. Relationship between Log K_d (from Freundlich adsorption isotherm; $n = 3$, SD < 0.0023%) and salinity of water.

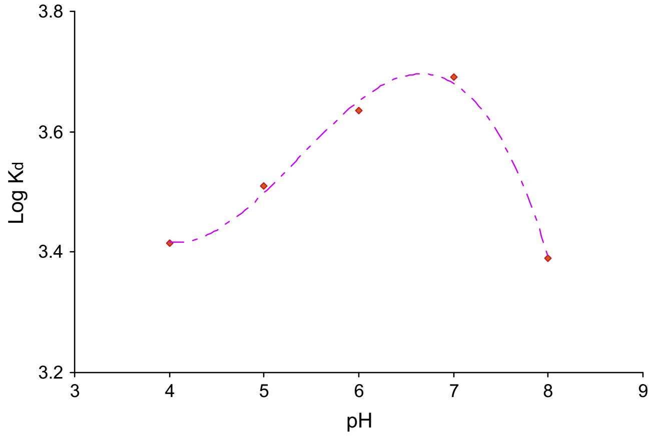

Fig. 4. Relationship between Log K_d (from Freundlich adsorption isotherm; $n = 3$, SD < 0.0013%) and pH of water.

surface properties of the clays but also the aquatic chemistry of the organotin species (Hoch et al., 2002). Varying the pH of the system was achieved by addition of acid or base (0.1 M) (Burton et al., 2004). The effect of pH on K_d was studied for the Bowling Basin sediments with water at various pH. The pH of water was measured before and after the adsorption experiment to confirm that it was constant. The variation of Log K_d values are presented in Fig. 4.

The results show the highest adsorption of TBT occurs at approximately pH 7. The finding was support by Said-Pullicino and Vella, 2005 who demonstrate the highest adsorption of TBT on municipal solid waste at pH 6.7 (Said-Pullicino and Vella, 2005). There are two main reasons as to why this should occur:

1. The pKa of TBT is approximately 6.51 depending on the experimental conditions (Fent and Looser, 1995). At pH < pKa, cations are formed as the predominant species in water, when pH > pKa the neutral hydroxo-complex TBTOH dominates as shown in Eq. (5).

$$\mathrm{TBT}^{+} \cdot n\mathrm{H_2O} \leftrightarrow \mathrm{TBTOH} + \mathrm{H}^{+} \quad \mathrm{pKa} = 6.51 \tag{5}$$

2. The zero point of charge (pHzpc) is the pH at which the surface exhibits a neutral net electrical charge. The pHzpc of clay minerals including kaolinite, illite, montmorillonite is approximately 4 (Hoch et al., 2003). Thus, raising the pH over 4 increases the negative charge on the surface of the clay minerals. In contrast, these clays exhibit a positive charge at pH < 4. Therefore, the adsorption zone is in the range of pH 6–7 and this gives the highest adsorption of TBT on sediment surface. At pH 7, number of cationic species exist are sufficient to bind with negative charge clay surface. Therefore, this suggests that electrostatic attraction is the driving force for adsorption between the negative charged clay surface and the positive charged TBT molecules. Additionally, both cationic and neutral hydroxotin species are presented at pH 6.5 ($[\mathrm{TBT}^{+}] = [\mathrm{TBTOH}]$) which neutral species can adsorb on the organic matter in sediment. Then partitioning at pH 6.5 was high but still lower than at pH 7.

3.3.4. Effect of temperature

The effect of temperature was studied on the Bowling Basin sediments with water at various temperatures. The study temperatures were varied from 20 to 50 °C using an incubator shaker. The results are shown in Fig. 5.

The adsorption of TBT on sediment slightly increases at higher temperature. This can be clarified in that the adsorption of atoms/molecules on surfaces and interlayers of sorbents is related to the Gibb's surface free energy (Bajpai and Vishwakarma, 2003). Increasing temperatures reduce the surface tension of water (Rinker et al., 1994), which then lowers the surface free energy (Ip and Toguri, 1994). These lead to increased adsorption on the sediment surface.

3.4. Prediction of environmental fate, persistence and toxicity

The experimental values of Log K_{oc} and Log K_{ow} calculated by the Eqs. (1) and (2), respectively, were compared to calculation values from EPISuite, as presented in Table 2.

Table 2 shows the considerable difference between experimental values obtained and the values given from the computational model, the EPISuite program underestimates K_{oc} but overestimates K_{ow}. The program calculation uses only the inherent chemical and physical properties of TBT and does not account for local environmental conditions. The different coefficients lead to dissimilar predictions of environmental fate, persistence and toxicity. Subsequently, the experimental values of K_{oc} and K_{ow} were entered into the program to create a more accurate prediction based on natural conditions.

A comparison of the prediction data, using both the input from the experiment and default values, is presented in Table 2 (see bold font). These include considerable difference between predicted

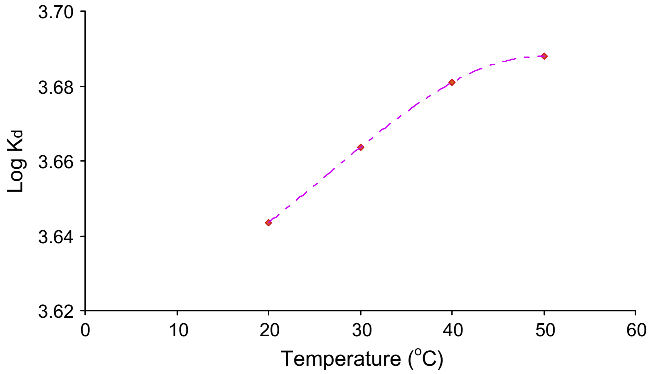

Fig. 5. Relationship between Log K_d (from Freundlich adsorption isotherm; $n = 3$, SD < 0.0004%) and temperature of water.

Table 2
The partition coefficients and comparison of the predictions obtained using experiment and default values as the input for the EPISuite program.

Parameter	Log K_d (L kg^{-1})	$K_{oc} = K_d \times 100/\%OC$ (L kg^{-1})	Log K_{oc} (L kg^{-1})	Log K_{ow}	Partitioning[a] (%)/half-life[a] (h)			Toxicity in fish[a] (μg mL^{-1})	
					Air	Water	Solid	LC_{50}[c] (14 d)	ChV[d] (30 d)
Bowling Basin: experimental	3.34[b]	18 087 (%OC = 12.1)	4.26 (K_{oc} = 18 197)	4.15 [b] (K_{ow} = 14 125)	**1.98/6**	**22.3/208**	**75.7/1870**	**3.37**	**0.39**
EPISuite program: default	Not available	12 023	4.08 (K_{oc} = 12 023)	4.70 (K_{ow} = 50 118)	**3.65/6**	**33.9/208**	**62.4/1870**	**1.11**	**0.13**

[a] The prediction data using K_{oc} and K_{ow} as the input values.
[b] The experimental partition coefficients obtained from Bowling Basin's sediment and water.
[c] Lethal concentration 50 is the concentration of a material that will kill 50% of the test subjects.
[d] Chronic value is the geometric mean of the lower and upper chronic limits.

environmental fate and toxicity of TBT depending on whether experimental or default input values were used, but the persistence (half-life) was no different because the experimental K_{oc} and K_{ow} input values affect mainly on the partitioning behavior calculated by EPISuite. Whereas, half-life of TBT in natural conditions is depend on the surrounding biological and physical properties. The experimental prediction showed lower toxicity than the default model for Bowling Basin but this represents the actual toxicity and accumulation at the natural site. Moreover, the environmental fate in term of partitioning for TBT was very different for the experimental values compared to the default values obtained. The percent partitioning to solid was increased. It appears therefore that bioaccumulation might be greater in mud-dwelling bottom feeding fish than the program predicates.

The default model is useful as a general indicator of environmental fate and toxicity. However, results based on experimental data differ greatly from those predicted by EPISuite. Therefore, experimentally-derived parameters (K_{oc} and K_{ow}) are necessary for site-specific investigations. This can help with an understanding of real behavior of TBT in a local area and provide more effective remediation solutions.

One of the most significant findings of this work is the underestimate of K_{oc} in the computational model as presented in Table 2. If the computational calculation in default mode is used in decision-making, there may be a danger that the solids are not properly treated and remediated. This could lead to more widespread contamination through environmental transport pathways, risk maybe magnified, and subsequent costs of remediation maybe increased. It is thus clear that the default model, although useful as a general indicator of TBT behavior, is imprecise when applied to a specific site and thus cannot replace experimentation.

4. Conclusions

From default prediction of EPISuite, the partitioning coefficients were calculated from the inherent chemical and physical properties of TBT but did not account for the site-specific environmental conditions. Therefore, K_{ow}, K_d and K_{oc} were derived by experiment. Experimental values can estimate the actual toxicity, accumulation at a specific site. The variations of partition coefficients were studied by Freundlich adsorption isotherms. The K_d values were depended on the following:

(i) Organic carbon and clay mineral content which refers to the sorption behavior.
(ii) Salinity, TBT showed characteristics of both metal ions and hydrophobic properties with respect to partitioning. The sorption was greatest in freshwater and decrease at low and intermediate salinities indicate that bioavailability is enhanced in the marine environment. Then the K_d increased again at high salinities but at values not typically experienced in the environment (100 psu).
(iii) pH, the highest TBT adsorption of this study was at pH7 due to the charge contained on clay surfaces and dominant species of TBT.
(iv) Temperature, the adsorption of TBT on sediment slightly increases at higher temperature due to the reduction of surface tension and Gibb's surface free energy.

It could be concluded that modeling based on chemical and physical properties although a useful tool should never replace realistic experimentation. In this instance it is inappropriate for scientists to move entirely away from laboratory testing toward computational models.

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References

Antizar-Ladislao, B., 2008. Environmental levels, toxicity and human exposure to tributyltin (TBT)-contaminated marine environment: a review. Environ. Int. 34, 292–308.
APHA, 1999. Standard methods for the examination of water and waste water (APHA: 2520B). American Public Health Association, Water Environment Federation, Washington, DC.
Arnold, C.G., Ciani, A., Muller, S.R., Amirbahman, A., Schwarzenbach, R.P., 1998. Association of triorganotin compounds with dissolved humic acids. Environ. Sci. Technol. 32, 2976–2983.
ASTM, 2000. Standard test methods for moisture, ash, and organic matter of peat and other organic soils (ASTM: D 2974-87). ASTM international publisher, Philadelphia.
ASTM, 2001. Standard test methods for determining a sorption constant (K_{oc}) for an organic chemical in soil and sediments (ASTM: E 1195-01). ASTM international publisher, West Conshohocken.
ASTM, 2002. Standard test methods for particle-size analysis of soils (ASTM: D 422-63). ASTM international publisher, West Conshohocken.
ASTM, 2008. Standard specification for reagent water (ASTM: D 1193-99). ASTM international publisher, West Conshohocken.
Avery, S.V., Codd, G.A., Gadd, G.M., 1993. Biosorption of tributyltin and other organotin compounds by cyanobacteria and microalgae. Appl. Microbiol. Biot. 39, 812–817.
Bajpai, A.K., Vishwakarma, N., 2003. Adsorption of polyvinylalcohol onto Fuller's earth surfaces. Colloid. Surface. A 220, 117–130.
Bangkedphol, S., Keenan, H., Davidson, C., Sakultantimetha, S., Songsasen, A., 2008. Development of a low-cost method of analysis for the qualitative and quantitative analysis of butyltins in environmental samples. J. Environ. Sci. Heal. A 43, 1744–1751.
Burton, E.D., Phillips, I.R., Hawker, D.W., 2004. Sorption and desorption behavior of tributyltin with natural sediments. Environ. Sci. Technol. 38, 6694–6700.
Burton, E.D., Phillips, I.R., Hawker, D.W., 2005. In-situ partitioning of butyltin compounds in estuarine sediments. Chemosphere 59, 585–592.
Burton, E.D., Phillips, I.R., Hawker, D.W., 2006. Tributyltin partitioning in sediments: effect of aging. Chemosphere 63, 73–81.
Dowson, P.H., Bubb, J.M., Lester, J.N., 1993. A study of the partitioning and sorptive behavior of butyltins in the aquatic environment. Appl. Organomet. Chem. 7, 623–633.
EPA, 1999. Understanding variation in partition coefficient, K_d, values (EPA 402-R-99-004A). United States Environmental Protection Agency, Washington, DC.
EPA, 2009. Internation Estimation Program Interface (EPI) Suite Version 4.0. United States Environmental Protection Agency, Washington, DC.

Fent, K., Looser, P.W., 1995. Bioaccumulation and bioavailability of tributyltin chloride – influence of ph and humic acids. Water Res. 29, 1631–1637.

Harris, J.R.W., Cleary, J.J., 1987. Particle water partitioning and organotin dispersal in an estuary. In: Proceeding of the fourth international organotin symposium.

Hoang, T.V., Michel, A., Guyot, A., 1982. Polyvinylchloride stabilisation with organotin compounds—Part III: effect of lewis acidity and co-ordination of organotin chlorides upon their catalytic activity towards dehydrochlorination. Polym. Degrad. Stabil. 4, 213–222.

Hoch, M., 2004. Assessment of salinity variations in TBT adsorption onto kaolinite and montmorillonite at different pH levels. Water Air Soil Pollut. 152, 349–362.

Hoch, M., Alonso-Azcarate, J., Lischick, M., 2002. Adsorption behavior of toxic tributyltin to clay-rich sediments under various environmental conditions. Environ. Toxicol. Chem. 21, 1390–1397.

Hoch, M., Alonso-Azcarate, J., Lischick, M., 2003. Assessment of adsorption behavior of dibutyltin (DBT) to clay-rich sediments in comparison to the highly toxic tributyltin (TBT). Environ. Pollut. 123, 217–227.

Horvath, B., Opara-Nadi, O., Beese, F., 2005. A simple method for measuring the carbonate content of soils. Soil Sci. Soc. Am. J. 69, 1066–1068.

IMO, 2002. International maritime organization TBT antifouling ban: account of discussion at IMO-MEPC47.

Ip, S.W., Toguri, J.M., 1994. The equivalency of surface tension, surface energy and surface free energy. J. Mater. Sci. 29, 688–692.

Keenan, H.E., Sakultantimetha, A., Bangkedphol, S., 2008. Environmental fate and partition co-efficient of oestrogenic compounds in sewage treatment process. Environ. Res. 106, 313–318.

Langston, W.J., Pope, N.D., 1995. Determinants of TBT adsorption and desorption in estuarine sediments. Mar. Pollut. Bull. 31, 32–43.

Looser, P.W., Fent, K., Berg, M., Goudsmit, G.H., Schwarzenbach, R.P., 2000. Uptake and elimination of triorganotin compounds by larval midge Chironomus riparius in the absence and presence of Aldrich humic acid. Environ. Sci. Technol. 34, 5165–5171.

Mackay, D., 2001. Multimedia Environmental Models: The Fugacity Approach, second ed. Lewis Publishers, London.

OECD, 1995. Organization for Economic Cooperation and Development (OECD) guideline for the testing of chemical: partition coefficient (*n*-octanol/water): shake flask method (107). OECD publisher, Paris.

O'Neill, P., 1998. Environmental Chemistry, third ed. Blackie Academic & Professional, an Imprint of Thomson Science, London.

Rinker, E.B., Oelschlager, D.W., Colussi, A.T., Henry, K.R., Sandall, O.C., 1994. Viscosity, density, and surface tension of binary mixtures of water and N-methyldiethanolamine and water and diethanolamine and tertiary mixtures of these amines with water over the temperature range 20–100 °C. J. Chem. Eng. Data 39, 392–395.

Rudel, H., 2003. Case study: bioavailability of tin and tin compounds. Ecotoxicol. Environ. Safety 56, 180–189.

Rydberg, J., Cox, M., Musikas, C., Choppin, G.R., 2004. Solvent Extraction Principles and Practice, second ed. Marcel Dekker, Inc., New York.

Said-Pullicino, D., Vella, A.J., 2005. Adsorption characteristics of tributyltin on municipal solid waste compost. Appl. Organomet. Chem. 19, 719–726.

Tsuda, T., Aoki, S., Kojima, M., Harada, H., 1990. The Influence of ph on the accumulation of tri-normal-butyltin chloride and triphenyltin chloride in carp. Comp. Biochem. Phys. C 95, 151–153.

Unger, M.A., 1988. Sorption behaviour of butyltin on estuarine and freshwater sediments. Environ. Toxicol. Chem. 7, 907–915.

White, J.S., Tobin, J.M., Cooney, J.J., 1999. Organotin compounds and their interactions with microorganisms. Can. J. Microbiol. 45, 541–554.