Environmental Science
Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

In this paper, a fugacity-based model was developed to simulate the bioaccumulation of butyltins in the food web of the Jincheng Bay mariculture area using the water and sediment concentrations, and based on the estimated tissue residues, an ecological risk assessment (ERA) for the marine biota and a health risk assessment (HRA) for seafood consumers were performed, which could provide a refinement for the aquatic ERA and HRA together with a basis for both the protection of marine ecology and the security of fishery products.

Risk Assessment of Butyltins Based on a Fugacity-based Food Web Bioaccumulation Model in the Jincheng Bay Mariculture Area: Ⅰ. Model Development

Yanbing Hu[abc], Xianghong Gong[b], Yingjiang Xu[b], Xiukai Song[b], Huihui Liu[b], Xuxiu Deng[b], Shaoguo Ru[*a]

[a]. College of Marine Life Sciences, Ocean University of China, Qingdao 266003, China

[b]. Shandong Provincial Key Laboratory of Restoration for Marine Ecology, Shandong Marine Resource and Environment Research Institute, Yantai 264006, China

[c]. Research Center for the Environment Administration and Development Strategy, Third Institute of Oceanography State Oceanic Administration, Xiamen 361005, China

Abstract

A fugacity-based model was developed to simulate the bioaccumulation of butyltins in the food web of the Jincheng Bay mariculture area. The predicted biological tissue residues of tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) were 0.04-17.09, 0.14-53.54, and 0.27-108.77 ng-Sn/g, respectively, and the predicted values in six mollusca agreed well with the measured ones. The lipid-normalized concentrations did not significantly increase up trophic levels, indicating no biomagnification across aquatic food webs. These results were highly consistent with those observed both in the laboratory and field, which had been reported in numerous references. The explanation was that butyltins were primarily taken in *via* respiration from the water column by marine organisms, by calculating their flux equilibrium in the food web. The sensitivities of the model parameters were analysized, revealing that the hydrophobicity of butyltins played the dominant role in their bioaccumulation phenomena. The verified model predictions of the biotic tissue concentrations of the butyltins could be readily applied to perform an internal ecological risk assessment and a human health risk assessment in this area.

Keywords

Bioaccumulation; Food web; Fugacity; Mariculture area; Risk assessment; Organotin

1. Introduction

Butyltins, including tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT), are extensively distributed offshore around the world and can be taken up by organisms through multiple pathways. They can accumulate in biotic tissues and thereby cause the imposex of female gastropods.[1-3] For example, TBT was reported to induce the formation of a penis and a pallial oviduct in female *Nucella lapillus* at a level of 1-2 ng-Sn/L, thereby

* Corresponding author. Address: College of Marine Life Sciences, Ocean University of China, No.5 of Yushan Road, Qingdao 266003, China. Tel/fax: +86 532 82031962.

Email address: rusg@ouc.edu.cn (S. Ru).

significantly decreasing the ratio of females to males.[4] Moreover, by virtue of their high bioaccumulation potency with a large bioaccumulation factor ranging from several hundred to tens of thousands, butyltins can induce multiple detrimental effects, especially the impairment of immunity in humans from seafood consumption.[5,6] As reported by Thomas et al.[7] and Catlin et al.[8], both TBT and DBT significantly degraded the immune function of human natural killer cells at the level of 200 nM. Thus, butyltins could adversely affect marine organisms and human beings even at trace levels.

An aquatic ecological risk assessment (ERA) is usually based upon the external aqueous exposure of target pollutants or environmental quantity guidelines[9-11], which could be termed an external ecological risk assessment (EERA). However, the exposure *via* diet and the toxicity kinetics of a target toxicant are not under consideration in an EERA, which appears to underestimate the true risk for some chemicals such as those which are highly hydrophobic and poorly depurated[12, 13]. As demonstrated by Landrum et al.[14], the uptake rates and bioconcentration factors of four polycyclic aromatic hydrocarbons (PAHs), naphthalene, fluorene, phenanthrene, and pyrene, in *Diporeia* sp. decreased significantly with increasing concentrations under a 28 d static exposure. Furthermore, the mutual differences of the median lethal residue concentrations of the four PAHs to *Diporeia* sp. were just within 2-fold, whereas those of their median lethal aqueous concentrations were greater than one order of magnitude. Consequently, an ERA based on biotic tissue residues was deemed to be more reliable[12, 13], which could be termed an internal ecological risk assessment (IERA). Leung et al. [10] calculated the risk quotient (RQ) of TBT to *Thais clavigera* and *Thais luteostoma* in the Hong Kong coastal waters by dividing the tissue residues by the corresponding predicted no-effect tissue concentration, and the probability of RQ > 1 was determined to be 0.054 by applying the Monte Carlo simulation accordingly, indicating the possibility to perform an IERA. As a biocommunity normally comprises diverse species with different bioaccumulation potentials, the acquisition of the tissue residues of a specific pollutant in multiple species pertaining to all trophic levels through field investigation requires enormous expenses. To this end, a fugacity-based model was developed by Campfens and Mackay[15] to simulate the transportation and transformation of organic pollutants in a complex food web based on the water and sediment concentrations. Using this model, Nfon and Cousins[16] estimated the distributions of polychlorobiphenyls (PCBs) in the food web of the Baltic Sea, which were generally within a factor of 3 of the measured values, indicating the reliability of the model. Wang et al.[17] employed this model to estimate the tissue residues of dichlorodiphenyltrichloroethanes (DDTs) in the food web of Bohai Bay and conducted an ERA based on the estimated internal tissue concentrations. However, this approach has not yet been applied to implement a human health risk assessment (HHRA) for the consumption of aquaculture products to our knowledge.

Jincheng Bay, located south in the Bohai Sea, is an important mariculture area in North China, with the

primary cultivated species being *Argopecten irradias*, along with varieties of the wild shellfishes inhabiting the area, such as *Crassostrea ariakensis* and *Neverita didyma*, most of which are relatively sensitive to butyltins.[18] In this study the concentrations of butyltins were determined to be 23.9-44.8 ng-Sn/L in the surface water of the area in 2009, with TBT accounting for 0.60-2.90 ng-Sn/L, just comparable with or greater than the critical level (1-2 ng-Sn/L) to induce imposex in female *N. lapillus*, which related to the Environmental Quality Standard (2 ng/L) in the European Union and UK and the Canadian Water Quality Guideline (1 ng/L) for the protection of marine life[19, 20]. As the biota in this area was similar to that in the Bohai Sea[21], the biocommunity in the Jincheng Bay mariculture area (JBMA) could be divided analogously to those in the Bohai Sea into thirteen functional groups (FGs), including phytoplankton, microzooplankton, etc. On this basis, a fugacity-based bioaccumulation model could be constructed to estimate the distributions of butyltins in the thirteen FGs with the water and sediment concentrations in the JBMA. Based on the prediction of the internal tissue residues of butyltins, an ERA for the biota and an HHRA for the consumers *via* seafood were implemented to provide a basis for the protection of the marine ecology and the security of fishery products and to simultaneously provide a refinement for the HHRA of aquatic products. For the large and complex scope of work, the results are presented in two papers. This paper discusses the development of the fugacity-based food web bioaccumulation model and the subsequent paper discusses the risk assessment.

2. Materials and methods

2.1 Model development

Aquatic pollutants are taken up and removed by organisms through multiple pathways. The former includes respiration and diet, and the latter includes respiration, egestion, metabolism, and growth dilution.[22] Specifically, TBT can be biodegraded to DBT, MBT, and ultimately inorganic tin through successive dealkylation.[1] Under conditions of long-term exposure, the biological intake and removal of butyltins would reach equilibrium, which could be profiled by the fugacity equation as follows:[15]

$$f_W D_W + f_A D_A + k_R f_R D_R = f_B \left(D_W + D_E + D_M + D_G \right) \quad (1)$$

where f_W, f_A, and f_B represent the chemical fugacities in the water, food, and tissue, respectively; D_W, D_A, D_E, D_M, and D_G represent the transportation-/transformation-relevant parameters for respiration, diet, egestion, metabolism, and growth dilution, respectively; f_R and D_R represent the fugacity and transformation-relevant parameter, respectively, of the maternal chemical; and k_R is the corresponding transformation coefficient. As one molecule of TBT could be transformed to an equivalent amount of DBT and similarly for DBT to MBT, k_R could be assigned a value of 1 when all these compounds are given in Sn-normalized units. Accordingly, equation (1) reduces to:

$$f_W D_W + f_A D_A + f_R D_R = f_B \left(D_W + D_E + D_M + D_G \right) \quad (2)$$

Provided $\begin{cases} D_T = D_W + D_E + D_M + D_G \\ A = D_A / D_T \\ W = D_W / D_T \\ R = D_R / D_T \end{cases}$

equation (2) reduces to:

$$f_B = f_W W + f_A A + f_R R \quad (3)$$

where W, A, and R are the fugacity factors for respiration, food, and the maternal compound, respectively, and $f_W W$, $f_A A$, and $f_R R$ are the fugacities in the biota due to the relative exposure pathways. Given that benthos respire in the sediment for a fraction of time, the respiration term $f_W W$ should be modified to be $W(X_W f_W + X_S f_S)$, where f_S is the fugacity in the porewater and X_W and X_S are the fractions of respiration from the overlying water column and porewater, respectively. The fugacity equilibrium equation is applicable to a complex food web with a general equation for FG i:

$$f_i = W_i \left(X_{iW} f_W + X_{iS} f_S \right) + \sum A_{ji} f_j + R_i f_{iR} \quad (4)$$

which can be rewritten as:

$$f_i - \sum A_{ji} f_j = W_i \left(X_{iW} f_W + X_{iS} f_S \right) + R_i f_{iR} \quad (5)$$

For a whole food web, the fugacity-equilibrium equation is written as:

$$\begin{bmatrix} 1-A_{11} & -A_{21} & \cdots & -A_{n1} \\ -A_{12} & 1-A_{22} & \cdots & -A_{n2} \\ \vdots & \vdots & \ddots & \vdots \\ -A_{1n} & -A_{2n} & \cdots & 1-A_{nn} \end{bmatrix} \begin{pmatrix} f_1 \\ f_2 \\ \vdots \\ f_n \end{pmatrix} = \begin{pmatrix} W_1 \left(X_{1W} f_W + X_{1S} f_S \right) \\ W_2 \left(X_{2W} f_W + X_{2S} f_S \right) \\ \vdots \\ W_n \left(X_{nW} f_W + X_{nS} f_S \right) \end{pmatrix} + \begin{pmatrix} R_1 f_{1R} \\ R_2 f_{2R} \\ \vdots \\ R_n f_{nR} \end{pmatrix} \quad (6)$$

The chemical fugacity (f_i) in each FG can be calculated by editing a Matlab procedure (Box S1 of the Supplementary Information), and then the corresponding internal tissue concentration can be calculated as:

$$C_i = f_i Z_i \quad (7)$$

where Z_i represents the fugacity capacity in FG i. The uptake and removal flux for FG i *via* pathway j is:

$$FLX_{ij} = f_{ij} D_{ij} \quad (8)$$

where f_{ij} and D_{ij} are, respectively, fugacity and the transportation-/transformation-relevant parameter for FLX_{ij}.

2.2 Model parameterization and implementation

All the Z-values and D-values for the model were calculated according to Campfens and Mackay[15] and Mackay[23], which involved multiple parameters pertaining to physicochemical, biological, and environmental

properties. The log*Koc* of butyltins and the log*Kow* of TBT were cited from Berg et al.[24] and Arnold et al.[25], and the log*Kow* of DBT and MBT were linearly converted from their log*Koc*, referring Seth et al.[26], and the biological half-lives of butyltins were extracted from the WHO[27] and the HSDB database (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB). The concentrations of butyltins in the water and sediment were monitored in 2009, along with the total organic carbon contents (*TOC*) in the sediment (Table 1). The density of the suspended particles and the volume fraction of sediment solids were cited from Mackay[23]. All the physicochemical and environmental parameters cited from the references are listed in Table 2.

Table 1 Butyltin levels in the surface water, surface sediment, and marine species in the JBMA

Compound	n	Min	Max	GM	GSD
Water concentration (ng-Sn/L)					
TBT	120	0.69	2.90	1.52	1.40
DBT	120	3.69	15.00	8.40	1.34
MBT	120	15.72	27.45	22.45	1.14
∑BT	120	23.88	44.82	32.60	1.16
Sediment concentration (ng-Sn/g)					
TBT	120	0.46	1.54	1.03	1.30
DBT	120	0.69	3.43	1.56	1.40
MBT	120	2.63	9.59	4.52	1.39
∑BT	120	4.26	14.38	7.18	1.34
Tissue residue (ng-Sn/g)					
TBT	7	0.30	1.94	0.93	2.17
DBT	7	0.51	3.10	1.21	1.95
MBT	7	2.04	6.96	3.66	1.60
∑BT	7	4.33	12.00	6.21	1.46
TBT+DBT	7	1.36	5.04	2.44	1.50
TOC of sediment solid (%)	120	0.048	0.354	0.154	1.53
TOC of suspended matter (%)	-	0.48	3.54	1.54	-

GM, geometric mean; GSD, geometric standard deviation; ∑BT = TBT+DBT+MBT. The surface water and sediment samples were collected from fifteen sites of the JBMA in May, Aug, Oct, and Dec, whereas the biotic samples were collected in May and Sep of the same year. Both the sampling and conservation followed the *Specification for Marine Monitoring of China* (GB 17378-2007), and the chemical analysis was conducted according to Yang et al. [28] and Sousa et al.[29] The tissue residues of the butyltins were analyzed in six species, including *Crassostrea ariakensis*, *Rapana venosa*, *Phalium strigatum*, *Neverita didyma*, *Scapharca subcrenata*, and *Argopecten irradians*. Method blanks (solvent) and spiked samples with the standard (Dr. Ehrenstorfer, Germany) were used for analytical quality control. All experiments were performed in duplicate. The TOC of suspended matter was estimated with that of the sediment solid multiplied by 10, referring Mackay[23].

Table 2 Chemical and environmental relevant parameters cited from references

Chemical	log*Kow*	log*Koc*	Biological half-life (d)	Media	Solid content (g/m^3)	Solid density (kg/m^3)
TBT	4.4[25]	5.11 - 5.46[24]	6 - 245‡	Suspended solid	1.25[23]	1500[23]
DBT	†	4.88 - 5.37[24]	45.1 - 62.5[27]	Sediment solid	4.50E+05[23]	1500[23]
MBT	†	4.65 - 5.11[24]	16.6[27]			

† The log*Kow* of DBT and MBT was estimated based on their log*Koc* given that they have the same linear relationship with that of TBT.[26]

‡ Extracted from the HSDB database.

The ecopath model of the Bohai Sea (Table 3) developed by Tong et al.[30] was used to construct the fugacity-based model. The ecopath model was based on monthly ecological investigations in the Bohai Sea from Mar 1982 to May 1983, which consisted of 1863 stomach contents belonging to 54 fish species and various invertebrate species. The biocommunity of the Bohai Sea comprised thirteen FGs, including detritus phytoplankton, microzooplankton, herbivorous feeders, macrozooplankton, small mollusca, small crustacea, large mollusca, large crustacea, small pelagic fish, demersal fish, benthic feeders, and top pelagic feeders. The key parameters of the model, including average individual volumes, lipid fractions, and growth rates, are listed in Table 4.

Table 3 Food web model in the JBMA (cited from Tong et al.[30])

	Pray	Predator										
		3	4	5	6	7	8	9	10	11	12	13
1	Detritus	0.3	0.55	0.4	0.4	0.4	0.1	0.1	0	0	0.05	0
2	Phytoplankton	0.6	0.3	0.2	0.15	0	0	0.1	0	0	0	0
3	Microzooplankton	0.1	0.15	0.4	0.35	0.4	0.3	0	0.3	0	0	0
4	Herbivorous feeders	0	0	0	0	0	0	0	0	0.1	0	0.15
5	Macrozooplankton	0	0	0	0.05	0	0.05	0.1	0.15	0	0	0
6	Small mollusca	0	0	0	0	0.15	0.3	0.4	0.2	0.35	0.2	0.2
7	Small crustacean	0	0	0	0.05	0.05	0.2	0.2	0.25	0.35	0.4	0
8	Large mollusca	0	0	0	0	0	0	0	0	0	0.05	0.05
9	Large crustacean	0	0	0	0	0	0	0	0	0	0	0.05
10	Small pelagic fish	0	0	0	0	0	0.05	0.1	0.1	0.15	0.15	0.35
11	Demersal fish	0	0	0	0	0	0	0	0	0	0.15	0.15
12	Benthic feeders	0	0	0	0	0	0	0	0	0.05	0	0.05
13	Top pelagic feeders	0	0	0	0	0	0	0	0	0	0	0

Table 4 Organism properties used for the model simulation

Functional Group	*V* † (cm3)	*L* †	*GR* † (1/d)	*Fd*† (1/d)	*Xw*‡	*Xs*‡	*Aw*¶	*Ao*¶
Detritus	2.23E-07	0.005§	5.26E-02	0	1	0	5.30E-08	4
Phytoplankton	2.04E-08	0.015	1.95E-01	0	1	0	5.30E-08	4
Microzooplankton	2.71E-04	0.015	9.86E-02	5.10E-01	1	0	5.30E-08	4

Herbivorous feeders	6.90E+03	0.048	8.22E-03	4.11E-02	1	0	5.30E-08	1.5
Macrozooplankton	1.83E-01	0.015	8.22E-03	3.29E-02	1	0	5.30E-08	3.5
Small mollusca	1.28E-01	0.014	1.88E-02	7.51E-02	0.5	0.5	5.30E-08	3
Small crustacea	2.11E-01	0.018	2.19E-02	8.22E-02	0.6	0.4	5.30E-08	3
Large mollusca	5.19E+00	0.011	5.48E-03	1.92E-02	0.8	0.2	5.30E-08	1.5
Large crustacea	7.22E+01	0.020	4.11E-03	3.18E-02	0.8	0.2	5.30E-08	1.5
Small pelagic fish	1.47E+01	0.048	6.49E-03	2.16E-02	1	0	5.30E-08	1.5
Demersal fish	1.40E+01	0.048	5.75E-03	2.38E-02	1	0	5.30E-08	1.5
Benthic feeders	7.07E+01	0.048	2.19E-03	1.26E-02	0.75	0.25	5.30E-08	1.5
Top pelagic feeders	5.16E+01	0.048	1.26E-03	1.12E-02	1	0	5.30E-08	1.5

V, organism volume; *L*, lipid volume fraction; *GR*, growth rate; *Fd*, feeding rate; *Xw*, fraction of respiration from the water column; *Xs*, fraction of respiration from the porewater; *Aw*, gut absorption efficiency for water; *Ao*, gut absorption efficiency for lipids.

† Cited from Tong et al.[30]

‡ Estimated based on the biomass of different species with associated assemblages used to develop the ecopath model of the Bohai Sea[30-32]

§ Cited from Wilson et al.[33]

¶ Cited from Campfens and Mackay[15].

A Monte Carlo simulation was conducted to estimate the biological residues in the food web based on the distributions of the model parameters because of their variability.[34] To this end, Latin hypercube sampling (n = 10000) was performed to create a parameter matrix. If a parameter involved multiple values following a specific distribution such as a log-normal distribution, it was incorporated into several non-overlapping intervals for random sampling, and if the distribution of the multiple-value parameter was unknown, bootstrap sampling was used instead. Otherwise, if only one value was available, a log-triangular distribution for sampling, with this value ($\log X$) as the mode and $0.5\log X$-$2\log X$ as the range[17], was created. Accordingly, the simulation was implemented by inputting each line of the parametric matrix.

The accuracy of the fugacity-based model was partially verified by the measured values in six fishery species (Table 1).

3. Results and discussion

As illustrated in Fig. 1(a), the 95% confident intervals (CIs) of the estimated tissue levels of TBT, DBT, and MBT in the food web of the JBMA were 0.04-17.09, 0.14-53.54, and 0.27-108.77 ng-Sn/g, respectively. Specifically in each FG, the values generally followed a log-normal distribution, as indicated by the Kolmogorov-Smirnov test, with the 95% CIs being 0.21-11.01, 0.45-23.50, and 1.08-66.24 ng-Sn/g for TBT, DBT, and MBT, respectively, in the small mollusca (G6), which covered the corresponding observed values of 0.30-1.94, 0.51-3.10, and 2.40-6.96 ng-Sn/g (Table 1). The geometric means of the estimated values for the three compounds

in G6 were 1.52, 3.25, and 8.45 ng-Sn/g, with a discrepancy of 2- to 3-fold of the corresponding observed values of 0.93, 1.21, and 3.66 ng-Sn/g (Table 1). There are several possible explanations. Above all, a true food web in an ecosystem is always subject to dynamic changes, whereas the model only represents a simplification for a certain period, which necessarily incorporates uncertainties.[30] Second, the small mollusca samples for verification were just a small part of G6, and the sample size was very limited (Table 1). Additionally, the physicochemical values of butyltins, such as *Kow* and *TOC*, varied with environmental factors such as the pH and temperature.[24] Campfens and Mackay[15] and Nfon and Cousins[16] estimated the distributions of PCBs in the food web of Ontario Lake and the Baltic Sea, respectively, employing a fugacity-based model, with the predicted values differing by a factor of 2-4 and 3, respectively, from the corresponding measured values, which were thus deemed to be well verified. From this point of view, based on the comparisons of the modeled tissue levels with those measured in G6, the estimations in the present study were also reliable. In addition, as illustrated in Fig. 1, the ranking order of the butyltin levels in all FGs was TBT < DBT < MBT, which was identical to that of the measured values in the water, sediment, and six small mollusca (Table 1). Therefore, the estimations agreed well with the observations.

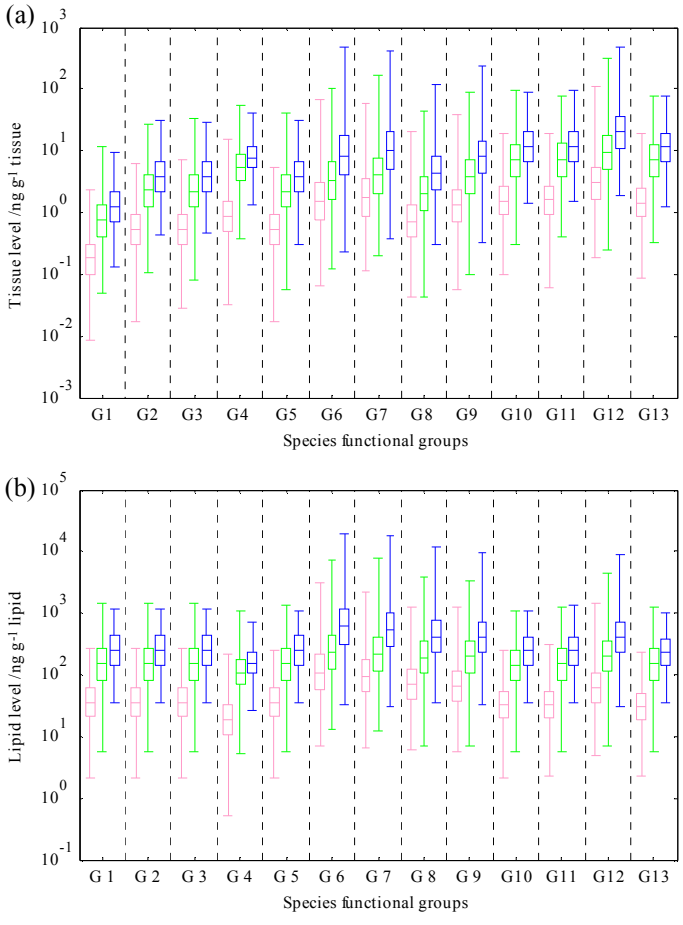


Fig. 1 Tissue levels of butyltins in the JBMA, with the red, green, and blue boxes representing TBT, DBT, and MBT, respectively.

As shown in Fig. 1(a), the detritus (G1) had the lowest tissue residues among all FGs, followed by plankton

(G2, G3, and G5), herbivorous fishes (G4), and large mollusca (G8). The lipid-normalized concentrations in some FGs of high trophic levels (G10, G11, and G13) were comparable or significantly lower than those of the lower trophic levels (G1-3) ($P < 0.05$)(Fig. 1(b)). Therefore, butyltins were not biomagnified up the food web. As reported by Hu et al.[35], the measured tissue levels of TBT, DBT, and MBT were not significantly associated with the trophic levels in phytoplankton, zooplankton, five invertebrate species, and six fish species in the Bohai Bay. Coelho et al.[36] reported that after a 40 d exposure to a steady state, the tissue levels of TBT in the bivalve of *Ruditapes decussatus* were approximately 0.3-fold of those in its algal diet of ^{14}C-TBT-labeled *Isochrysis galbana*. Wang et al.[37] reported that the TBT levels in *T. clavigera* were 0.052- to 0.664-fold of those in its diet (oysters) after a long-term aqueous and dietary exposure. Conclusively, both the field observations and laboratory experiments with different exposure types demonstrated no biomagnification of the butyltins in aquatic food webs. Consequently, in this respect the model predictions were reliable.

In order to explore the discrepancies in the tissue residues between different FGs, the sensitivities of the model parameters were analysized using the standardized regression coefficients (*SRCs*) approach.[38] First, the partial regression coefficients (b) were computed with the least squares method, and then the *SRCs* were calculated accordingly, as follows:

$$y_n = b_0 + \sum_{i=1}^{k} b_i x_{ni} + \varepsilon_n \tag{9}$$

$$SRC_i = b_i \frac{S(x_i)}{S(y)} \tag{10}$$

where y is an output vector as $(y_1,y_2,\ldots,y_n)$, with n being the sample size of the Monte Carlo simulation (n = 10000); x is the parameter matrix as $(x_1,x_2,\ldots,x_k)$, with k being the number of input parameters; ε is the error term; and $S(x_i)$ and $S(y)$ are the standard deviations of x_i and y, respectively. The *SRCs* range from -1 to 1. The larger the $|SRC|$, the more sensitive the parameter. This computation was implemented by editing a Matlab procedure (Box S2).

The *SRCs* of the model parameters are illustrated in Fig. 2. With respect to the total model (Fig. 2(a)), *Kow* was the most sensitive, followed by other physicochemical and environmental parameters, including *Cw*, *Koc*, *Cs*, and *TOC*, whereas the biological parameters were conversely less sensitive. In terms of specific FGs, such as G6 (Fig. 2(b)), the internal butyltin residues were sensitive not only to physicochemical and environmental parameters but also to the biological parameters of *L* and *Xs*. Similar results were also observed for PCBs in the Baltic food web, with *Kow* being the most sensitive parameter[16]. Therefore, the hydrophobicity of butyltins played the primary role in their bioaccumulation in the food web. All the sensitive parameters were inconstant with the

species or environmental situations; for example, the log*Kow* of TBT was changeable from 3.3 to 4.4 with different pHs and salinities[25], and the lipid contents in different species could differ by one order of magnitude.[15, 31, 32] Accordingly, the great differences in the tissue residues between different FGs were explicable.

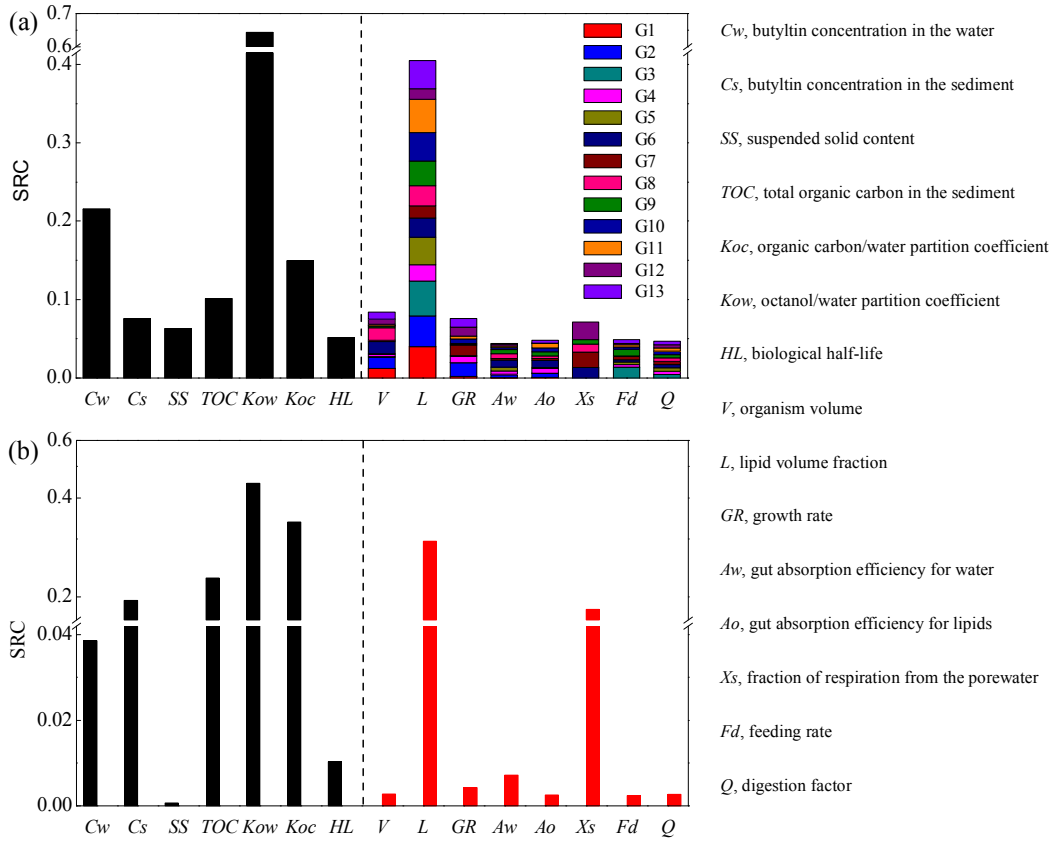
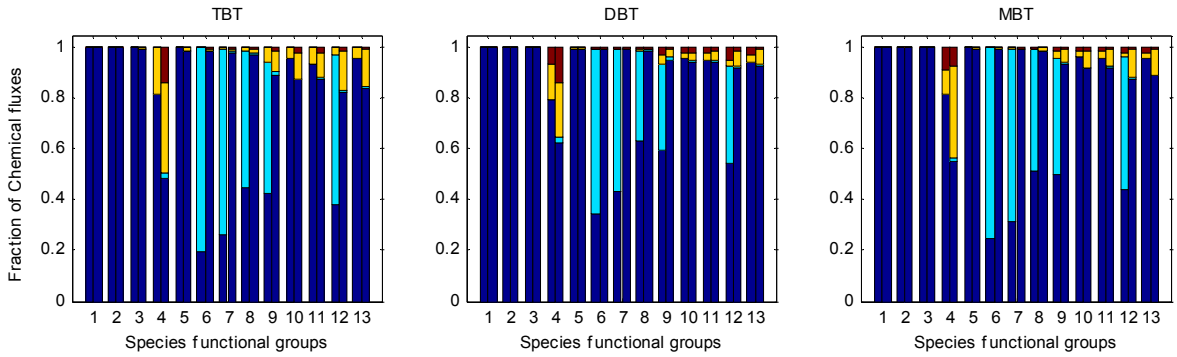


Fig. 2 Parameter *SRCs* of the fugacity-based food web model

Based on the flux equilibrium of butyltins in the food web (Fig. 3), the respiration from water was the predominant exposure route in all FGs, whereas the dietary intake was minor or even negligible. In addition, the biodegradation loss rates in most FGs were higher than the relative dietary intake. For these reasons, butyltins were not biomagnified across a food web. As demonstrated by Mackay[23] and Hu et al.[35], hydrophobicity and biodegradability were the key factors that controlled the biomagnification. Above all, butyltins have a low hydrophobicity, with the log*Kow* less than 5 in seawater (Table 2), and they were consequently demonstrated to be taken up mainly *via* direct aqueous exposure (respiration) by aquatic species.[22] In addition, TBT was readily metabolized to DBT, then to MBT, and further to other chemicals less toxic to the biota[1], with half-lives of 6-245, 45.1-62.5, and 16.6 d, respectively (Table 2), which were much shorter than those of typical persistent organic pollutants, such as DDT and PCB, that can be up to tens of years.[10, 39] In conclusion, the relatively low hydrophobicity and high biodegradability added to the non-biomagnification of butyltins in the aquatic food web.



233

234 **Fig. 3** Flux equilibrium of butyltins in the food web of the JBMA, with the left bars representing the intake fluxes (■respiration
235 from overlying water, ■respiration from porewater, ■dietary intake, ■maternal intake) and the right representing loss fluxes (■loss
236 from respiration, ■egestion, ■metabolism, ■growth dilution)

237 In summary, the predicted values of the biological tissue residues of the butyltins were reliable and explicable.
238 However, the uncertainty of the model predictions was inevitable, which could be attributed to several reasons.
239 Apart from the radically changeable sensitive parameters discussed above, the biotransformation ability of
240 butyltins, which also played a predominate role in their bioaccumulation, varied from species to species due to
241 different metabolic capabilities[40-42]. For example, the half-life (83 d) of TBT in *Thymallus thymallus* was
242 measured to be an order of magnitude greater than that (8.2 d) in *Rudarius ercodes*.[42] Additionally, environmental
243 variation such as the pH, temperature and nutrients could induce strong uncertainty of biotransformation in a
244 specific species[43, 44]. Furthermore, because of the incomplete knowledge of the bioaccumulation mechanism of the
245 butyltins in the food web, considerable uncertainty could be involved for the favourability of model structure.[45]
246 Up to now, two categories of mass balance approaches, the rate constant approach and the fugacity approach, have
247 been reported to quantify bioaccumulation phenomena[46]. Veltman et al.[47] used the rate-constant-based
248 bioaccumulation model to explore the accumulation of organotins in the Western Scheldt food chain, consisting of
249 herbi-detritivores, primary and secondary carnivorous fish, and a piscivorous bird, with elimination of organotins
250 being modeled following two approaches, that were similar to a neutral organic compound and to a metal. The
251 results indicated that the uptake of organotins mainly occurs *via* hydrophobic mechanisms, whereas the
252 elimination may occur *via* metal-like kinetics.[47] However, in this approach, the elimination rate model for
253 organometallic compounds was not chemical-specific, and the deviations of the biota-suspended
254 solids-accumulation ratios between the model predictions and field values generally increased up the food web,
255 which could be up to four orders of magnitude for the top level species. As no consensus mechanistic
256 bioaccumulation model has been reported for organometallic compounds in such a complex food web, in the
257 present study the fugacity approach was used to simulate the bioaccumulation of butyltins in the food web of the

JBMA, where the butyltins were treated as neutral organic compounds. The verified model predictions of the biological tissue concentrations of the butyltins could be further used to conduct an IERA and HHRA in the JBMA, which is presented in the accompanying paper (Part Ⅱ).

4. Conclusions

A fugacity-based food web bioaccumulation model was constructed, and employing this model, the biotic distributions of butyltins in the food web of the JBMA were estimated according to the water and sediment concentrations. The estimations agreed well with the measured values. According to the estimations, butyltins were taken in mainly from direct aqueous exposure rather than diet and thus not biomagnified in the aquatic food web. Based on sensitivity analysis, the hydrophobicity of butyltins played the dominant role in their bioaccumulation phenomena. Furthermore, relatively low hydrophobicity and high biodegradability added to the non-biomagnification of butyltins in the food web.

The estimated biotic tissue concentrations of the butyltins could be further used to conduct an IERA and HHRA in the JBMA. However, the verification was performed partially because of limited measured biological residue data being available. Therefore, further work is needed to improve the fugacity-based bioaccumulation model for organometallic compounds such as butyltins. Specifically, a chemical-specific elimination model based on a supporting experimental study should be developed to be incorporated in the fugacity-based model and more simultaneous field data should be collected to perform sounder validation.

Acknowledgements

This work was supported by the Marine Special Scientific Fund for the Non-profit Public Industry of China (No. 200805031), the Programme of Toxicity and Safety Assessment of Heavy Metals on Mariculture Organisms (No. 2009GG10009044) and the Scientific Research Foundation of Third Institute of Oceanography SOA (No. 2013031).

References

1. B. Antizar-Ladislao, *Environ. Int.*, 2008, **34**, 292-308.
2. V. Axiak, A. J. Vella, D. Micallef, R. Chircop and B. Mintoff, *Mar. Biol.*, 1995, **121**, 685-691.
3. B. Pavoni, E. Centanni, S. Valcanover, M. Fasolato, S. Ceccato and D. Tagliapietra, *Mar. Pollut. Bull.*, 2007, **55**, 505-511.
4. P. Gibbs, G. Bryan, P. Pascoe and G. Burt, *J. Mar. Biol. Assoc. UK.*, 1987, **67**, 507-523.
5. J. Muncke, *The Journal of Steroid Biochemistry and Molecular Biology*, 2011, **127**, 118-127.
6. ESFA, *The EFSA Journal*, 2004, **102**, 1-119.
7. L. D. Thomas, H. Shah, S. A. Green, A. D. Bankhurst and M. M. Whalen, *Toxicology*, 2004, **200**, 221-233.
8. R. Catlin, H. Shah, A. D. Bankhurst and M. M. Whalen, *Environ. Toxicol. Pharmacol.*, 2005, **20**, 395-403.
9. K. R. Solomon, J. Giesy and P. Jones, *Crop Prot.*, 2000, **19**, 649-655
10. K. M. Y. Leung, R. P. Y. Kwong, W. C. Ng, T. Horiguchi, J. W. Qiu, R. Yang, M. Song, G. Jiang, G. J. Zheng and P. K. S. Lam, *Chemosphere*, 2006, **65**, 922-938.

11. Y. Hu, S. Sun, X. Song, J. Ma and S. Ru, *Journal of Ocean University of China*, 2014, **13**, In Press.
12. B. Escher and J. Hermens, *Environ. Sci. Technol.*, 2004, **1**, 455-462.
13. K. G. Sappington, T. S. Bridges, S. P. Bradbury, R. J. Erickson, A. J. Hendriks, R. P. Lanno, J. P. Meador, D. R. Mount, M. H. Salazar and D. J. Spry, *Environ. Assess. Manage.*, 2010, **7**, 116–140.
14. P. F. Landrum, G. R. Lotufo, D. C. Gossiaux, M. L. Gedeon and J.-H. Lee, *Chemosphere*, 2003, **51**, 481-489.
15. J. Campfens and D. Mackay, *Environ. Sci. Technol.*, 1997, **31**, 577-583.
16. E. Nfon and I. T. Cousins, *Environ. Pollut.*, 2007, **148**, 73-82.
17. B. Wang, G. Yu, J. Huang, T. Wang and H. Hu, *Sci. Total Environ.*, 2011, **409**, 495-502.
18. T. Arai, *Ecotoxicology of antifouling biocides*, Springer, Tokyo ; New York, 2009.
19. CCME, *Canadian environmental quality guidelines*, CCME, Hull, Quebec, 2007.
20. UK, Editon edn., 2010, p. 63.
21. J. Su and Q. Tang, eds., *Study on Chinese marine ecosystem dynamics Ⅱ: process of ecosystem dynamics in Bohai Sea*, Science Press, Beijing, 2002.
22. D. Mackay and J. A. Arnot, *J. Chem. Eng. Data*, 2011, **56**, 1348-1355.
23. D. Mackay, *Multimedia environmental models : the fugacity approach*, 2nd edn., Lewis Publishers, Boca Raton ; London, 2001.
24. M. Berg, C. G. Arnold, S. R. Muller, J. Muhlemann and R. P. Schwarzenbach, *Environ. Sci. Technol.*, 2001, **35**, 3151-3157.
25. C. Arnold, S. Haderlein, R. Schwarzenbach, A. Weidenhaupt, M. David, M. Sedlak and S. Muller, *Environ. Sci. Technol.*, 1997, **31**, 2596-2602.
26. R. Seth, J. Munke and D. Mackay, *Environ. Sci. Technol.*, 1999, **33**, 2390-2394.
27. WHO, *Mono- and disubstituted methyltin, butyltin, and octyltin compounds*, World Health Organization, Norfolk, 2006.
28. R. Yang, Q. Zhou, J. Liu and G. Jiang, *Food Chem.*, 2006, **97**, 637-643.
29. A. Sousa, T. Ikemoto, S. Takahashi, C. Barroso and S. Tanabe, *Mar. Pollut. Bull.*, 2009, **58**, 1130-1136.
30. L. Tong, Q. Tang and D. Pauly, *Chinese Journal of Applied Ecology*, 2000, **11**, 435-440.
31. J. Deng, J. Zhu and J. Chen, *Marine Fish Reaseach*, 1988, **9**, 91-120.
32. J. Deng, T. Meng and S. Ren, *Marine Fish Reaseach*, 1988, **9**, 11-90.
33. S. K. Wilson, K. Burns and S. Codi, *Mar. Ecol. Prog. Ser.*, 2001, **222**, 291-296.
34. X. Flores-Alsina, L. Corominas, M. B. Neumann and P. A. Vanrolleghem, *Environ. Modell. Softw.*, 2012, **38**, 50-58.
35. J. Hu, H. Zhen, Y. Wan, J. Gao, W. An, L. An, F. Jin and X. Jin, *Environ. Sci. Technol.*, 2006, **40**, 3142-3147.
36. M. R. Coelho, M. J. Bebianno and W. J. Langston, *Mar. Environ. Res.*, 2002, **54**, 193-207.
37. B. Wang, G. Yu, J. Huang, T. Wang and H. Y. Hu, *ScientificWorldJournal*, 2010, **10**, 1307-1317.
38. A. Saltelli, M. Ratto, S. Tarantola and F. Campolongo, *Chem. Rev.*, 2005, **105**, 2811-2828.
39. D. Mackay, *Handbook of physical-chemical properties and environmental fate for organic chemicals*, 2nd ed edn., CRC Taylor & Francis, Boca Raton, Fla. ; London, 2006.
40. T. G. Luan, J. Jin, S. M. N. Chan, Y. S. Wong and N. F. Y. Tam, *Process Biochemistry*, 2006, **41**, 1560-1565.
41. P. J. Meng, J. T. Wang, L. L. Liu, M. H. Chen and T. C. Hung, *Sci. Total Environ.*, 2005, **349**, 140-149.
42. C. A. Krone and J. E. Stein, *Aquat. Toxicol.*, 1999, **45**, 209-222.
43. J. Jin, L. H. Yang, S. M. N. Chan, T. G. Luan, Y. Li and N. F. Y. Tam, *J. Hazard. Mater.*, 2011, **185**, 1582-1586.
44. A. Sakultantimetha, H. E. Keenan, T. K. Beattie, T. J. Aspray, S. Bangkedphol and A. Songsasen, *International Biodeterioration & Biodegradation*, 2010, **64**, 467-473.
45. J. A. Arnot and F. A. Gobas, *Environ. Toxicol. Chem.*, 2004, **23**, 2343-2355.
46. D. Mackay and A. Fraser, *Environ. Pollut.*, 2000, **110**, 375-391.
47. K. Veltman, M. A. J. Huijbregts, M. J. van den Heuvel-Greve, A. D. Vethaak and A. J. Hendriks, *Mar. Environ.*

339 *Res.*, 2006, **61**, 511-530.