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Identification and Evaluation of a Novel Heterocyclic Brominated Flame Retardant Tris(2,3-dibromopropyl) Isocyanurate in Environmental Matrices near a Manufacturing Plant in Southern China

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A brominated flame retardant (BFR), hexabrominated heterocyclic tris-(2,3-dibromopropyl) isocyanurate (TBC), was identified, for the first time, in the natural environment. The chemical was found in river water (2.33−163 ng/L), surface sediments (85.0 ng/g−6.03 μg/g dry weight (dw)), soils (19.6−672 ng/g dw), earthworm (9.75−78.8 ng/g dw), and carp samples (12.0−646 ng/g dw) from a factory-polluted area in southern China. It was found that TBC can strongly adsorb to organic material in sediment, and a trend of decreasing concentration with distance from the source in soil and earthworm samples, combined with calculated K_{ow} (octanol−water partition coefficient) and K_{oa} (octanol−air partition coefficient), suggests its potential ability to undergo regional transportation through dust deposition. Calculated results showed high K_{ow} (log K_{ow} = 7.37) and bioaccumulation factor (BAF) (log BAF = 4.30) of this BFR and indicate that TBC has semivolatile properties and bioaccumulation characteristic in certain biological species. Quantitative structure property relationships (QSPRs) modeling revealed that TBC has K_{oa} (log K_{oa} = 23.68) and K_{aw} (air−water partition coefficient) (log K_{aw} = −16.31) values several orders higher than those of other BFRs. The identification of this chemical additive further reminds us that the production and usage of heterocyclic BFRs may cause potential contamination to the surrounding environment.

Introduction

Over the past decades, halogenated flame retardants have been widely used in large volumes as additive in household products for fire safety reasons due to their excellent capability to reduce flammability (*1*). However, increasing concerns have been raised on the environment problems caused by these flame retardant products, especially for brominated flame retardants (BFRs). Numerous studies showed that these chemicals are persistent, have long distance transport and bioaccumulative abilities, and may potentially harm ecosystems and human health (*2*−*4*). Recently, the usage of pentabrominated diphenyl ethers (penta-BDE) and octa-BDE have been banned in some countries (*5, 6*), and the Stockholm Convention has been considering these two groups of PBDEs as candidates to be added to the list of persistent organic pollutants (POPs) (*7*). With the growing stringent regulations on these flame retardants, it is expected that increasing amounts of substitutes would replace those phased out BFRs in the market. However, these alternative products might also have similar semivolatile properties, and their environment behaviors and underlying toxic effects are still unclear. Several of them have been identified as emerging chemicals that are present in the environment, such as 1,2,5,6,9,10-hexabromocyclododecane (HBCD), Dechlorane Plus and several others have been detected in different environmental matrices (*1, 8*−*17*) and biological samples (*18*).

Tris(2,3-dibromopropyl) isocyanurate (TBC; Figure 2, CAS No. 52434-90-9) is a heterocyclic hexabrominated additive flame retardant, which is resistant to photodegradation, durable, and thermally stable. It is highly effective on glass fiber reinforced plastics and farming polyurethane and is also used widely in polyolefin, polyvinyl chloride, polyphenyl alkenes, acrylonitrile butadiene styrene, unsaturated polyester, synthetic rubber, and fiber (*19*). The concentration range of TBC added in these products is about 5−10% w/w (*19*). The production and usage in China began in the mid-1980s, but only limited output information could be found. The only authentic data, from 1996, shows production in China was no less than 500 tonnes per year (*20*), and the production is still ongoing in certain regions of China.

In this study, a high performance liquid chromatography tandem mass spectrometry (HPLC tandem MS) method was established to identify TBC. Subsequently, the method was applied to determine the existence of TBC in river water, soil, sediment, and biological samples collected near a manufacturing plant. With the combined results obtained from the estimation program interface (EPI) suite models (*21*) and the concentrations measured in different environment matrices, a rudimentary assessment on the environmental fate and behaviors of this heterocyclic BFR in the environment could be presented.

Materials and Methods

Materials. Technical grade TBC (97%) was purchased from Sigma-Aldrich (St. Louis, MO). HPLC grade methanol and pesticide residue grade hexane and dichloromethane (DCM) were obtained from Fisher Scientific (Hampton, NH). Deionized water (18.3 MΩ) was from an ultrapure water purification system (Barnstead International, Dubuque, IA). Silica gel was obtained from Merck (Whitehouse Station, NJ). Oasis HLB solid phase extraction (SPE) cartridges were obtained from Waters (Milford, MA).

Sample Collection. The sampling map and sites are shown in Figure 1. Samples were collected at the upstream watershed of the Liuyang River, which is located southwest of Liuyang, Hunan province, in southern China. The predominant wind direction was mainly northwestern, which is almost parallel with the river flow. Most sampling sites were located downstream of the outlet of a TBC manufacturing plant, which has been producing TBC since 1986 and has a production volume of 200 tonnes per year (*19*), except for two control sampling sites that are several hundred meters upstream of the plant. Water, sediment, and soil sampling

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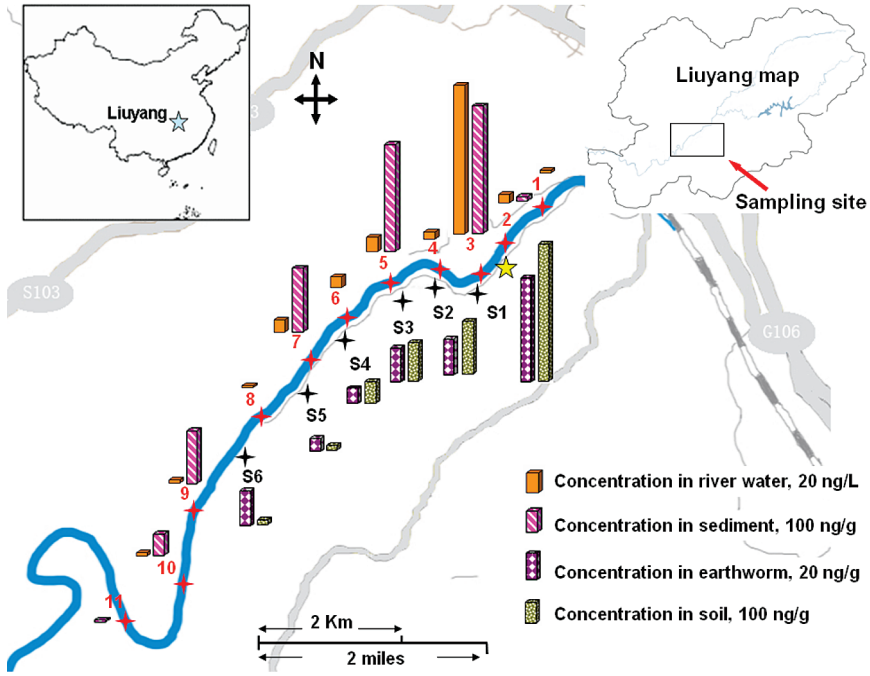

FIGURE 1. The sampling map and the distribution of TBC in water, sediment, soil, and earthworm. (Yellow pentacle, TBC manufacturing plant; red tetragon, sampling sites for river water and sediment samples; black tetragon, sampling sites for soil and earthworm samples. The latitudes of the investigated region ranged from 28°02′26″N to 28°09′54″N and the longitudes from 113°30′59″E to 113°42′35″E.)

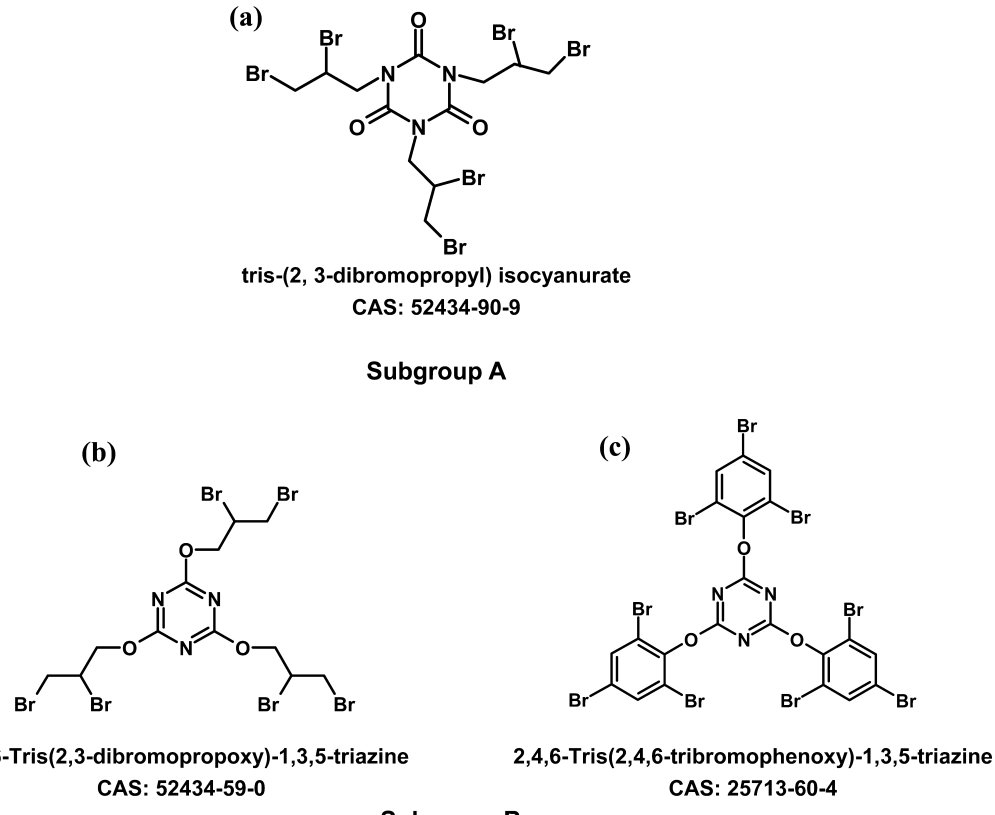

FIGURE 2. Structures of some triazine BFRs: subgroup A, TBC (a); subgroup B, BrTriaz (b) and BrPhTriaz (c).

sites were chosen along the riverside at specific intervals, and common carp samples were obtained nearly 6 km away from the outlet. In total, 12 river water samples, six surface sediments, five soil samples, five earthworm samples, and four common carp were collected.

Before sampling, glass bottles and containers were precleaned with acetone. River water was collected using 500 mL glass bottles to avoid adsorption. The water samples were collected approximately 0.4 m below the water surface, directly carried to the laboratory, and stored at 4 °C until analysis. Soil sampling sites were chosen near farmland and distant from roads. Surface soil samples were collected at ~5 cm depth. Sediment samples were taken at a distance of approximately one-fourth from the riverside with regard to

the river width. The depth of sediment (mostly fine particles) in the river was such that only surface sediment could be collected by a grab sampler (Wildco Ekman Grab, 152 × 152 × 152 mm, Buffalo, NY) (only about 3−5 cm deep). Water in the grab was carefully removed to avoid disturbance. Biological samples were stored in an ice-box after collection, transported back to the laboratory, and kept at −20 °C. All solid samples were packed in aluminum foil in sealed plastic bags to avoid being irradiated by light.

Sample Pretreatment. 300 mL of water sample was prefiltrated through a 0.45 μm filter membrane and loaded onto a 6 CC 200 mg Waters HLB solid phase extraction (SPE) cartridge at the rate of 2−3 mL/min, which was preconditioned with 3 mL of methanol and distilled water. Subsequently, the SPE cartridge was rinsed with 3 mL of distilled water and 40% methanol and then was eluted with 3 × 3 mL of methanol. Finally, the eluent was reduced with a gentle nitrogen flow to 1 mL.

Soils, surface sediments, earthworm, and tissues/organs of carp samples were freeze-dried and homogenized. Soils and sediments were sieved through a stainless steel 100-mesh sieve. Sample preparing procedures for all of these samples were almost the same. Approximately 0.5−1 g of sample mixed with 15 g of anhydrous Na_2SO_4 was extracted with dichloromethane (DCM) at 150 °C and 1500 psi using an accelerated solvent extractor (ASE 300, Dionex Inc.). Acidic silica was added to remove any lipids of biosamples in the extract and the sulfuric acid residue was removed by using an anhydrous Na_2SO_4 column. The extract was thereafter concentrated by rotary evaporation to ∼2 mL and fractioned on an 8 g neutral silica column which was activated at 550 °C for 12 h prior to use. The column was first preconditioned by 50 mL of hexane and eluted by 38 mL of hexane, 50 mL of 50% DCM in hexane, and 40 mL of DCM in sequence. TBC eluted in the third fraction. Finally, TBC was solvent exchanged to 8:2 methanol/water and concentrated to a volume of 1 mL. Recovery results showed that there was little loss of target compound during the solvent exchange step.

Instrument Analysis. An Alliance 2695 model HPLC system (Waters, Milford, MA) equipped with a degasser and a quadruple pump was used for the instrumental analysis. A 150 × 2.1 mm Symmetry Shield 5 μm C18 analytical column (Waters, Milford, MA) was selected for separation. The flow gradient with methanol (A) and water (B) was initiated at a composition of 80:20 (v/v) and increased to 100% A with a flow rate of 0.3 mL/min in 10 min with a linear curve, and the composition was held for 8 min to elute any residues on the column. Before another injection, the column was pre-equilibrated for 7 min. Twenty microliters was injected onto the column and the target analyte eluted within 6 min.

The analyte were detected by a triple-quadrupole mass spectrometer (Quattro Premier XE, Micromass, Manchester, UK). Electrospray ionization was operated in the negative ion mode with a capillary voltage of 3.3 kV. Source and desolvation temperature was selected at 120 and 320 °C, respectively. Desolvation gas flow was 450 L/h and cone gas flow 50 L/h. Argon pressure in the collision cell was kept at 3.3×10^{-3} mbar for MS/MS measurements. For data collection, Q1 and Q3 were operated with unit resolution of 0.50 amu full-width half-maximum. Multiple reaction monitoring (MRM) mode was used for quantification, and dwell time was set to 100 ms for each ion pair. Ion pairs of 727.8 > 81 and 727.8 > 79 ($[M - H]^- > Br^-$) were monitored separately for quantitative and qualitative purpose.

Quality Assurance /Quality Control. Authentic standard of 1000 ng/mL was directly resolved in acetone, and all calibration standards and spiking solutions were prepared by serial dilution in methanol using volumetric flasks. Glassware was thoroughly rinsed with acetone before use. Quality criteria published elsewhere (*15*) were used to ensure the positive identification and quantitative analysis of the target compound: the retention time matched that of the standard within ±3s, while signal-to-noise ratio of 10:1 was a requisite; the isotopic ratios of selected ion pairs were within ±15% of the theoretical value 0.985, which is equivalent to the isotopic abundance of $^{81}Br/^{79}Br$. One method blank of 15 g of solvent-washed anhydrous sodium sulfate was included in each batch of eight samples to avoid cross-contamination during the pretreatment progress. Analyte in all blank samples were under the limit of quantification. Because isotope-labeled TBC standard was unavailable, an external standard method based on peak area measurements was used for quantification. For soils and carp muscle samples ($n = 3$ for each), 100 ng of the TBC standard was spiked and the recoveries ranged from 58−70 and 58−73%, respectively. For water samples, 5 ng of standard was spiked in 300 mL of distilled water and SPE recovery was in the range of 78−83%. Under the conditions used, limits of detection were approximately 1.5 ng/L for the river water, 2.5 ng/g for the soils, 1.5 ng/g for the sediments, and 1.0 ng/g for the biological samples. Limit of quantification (S/N = 10) was estimated to be 20 pg based on the analysis of seven replicates of low-concentration standard solutions, and the linear dynamic range of the method was 20−14 000 pg.

Result and Discussion

Selection of Ionization Mode and Identification of TBC in the Environment. TBC contains six bromine atoms and has a relatively high molecular weight of 728.7 MW. Pure TBC decomposes at 195 °C, while thermal decomposition temperatures vary when technical products of TBC were coated (*19*). Therefore, a softer and more stable ESI negative ionization mode was selected to analyze the target substance. Figure S1 (Supporting Information) shows the cluster of $[M - 1]^-$ molecular ion peaks of TBC. The proportion of these isotope peaks, which is very close to the ideal value (1:6:15:20:15:6:1), affirms the existence of six bromine atoms in the TBC molecule. $m/z = 727.8$ was chosen as the parent ion, and secondary ions were generated from the collision cell. The collision voltage was gradually set up to 70 eV, but no other stable ions were observed except for the bromine atoms ($m/z = 79/81$) and some unstable intermediate-state ions. After optimization, the selected $[M - H]^- > Br^-$ ions gave the strongest response when the collision voltage was set to 11 eV. The generation of only bromine atoms was a result of the ionization mechanism of the ESI mode, as discussed by Tomy (*18*). Only the C−Br bond, the energy of which is relatively lower than that of C−N and C═O in TBC, can be broken down when collided with argon. Thus, the MRM method of monitoring these nondiagnostic $[M - H]^- > Br^-$ ions cannot separate and identify structural or stereoisomers if they coelute in the HPLC column. Nevertheless, in this report, the present method was sufficient to ensure the identification and quantification of TBC in the selected environment matrices.

Concentrations of TBC in Environmental Matrices. TBC was positively detected in almost all water, surface sediment, soil, and earthworm samples. Spatial concentrations of TBC in water samples were in the range of 2.33−163 ng/L (Figure 1). Only the sample collected near the outlet of the manufacturing plant showed comparatively high concentration (163 ng/L), whereas the concentrations of samples located before and after the wastewater outlet of the plant decreased dramatically to a degree 3−4-fold higher than that in distant sampling sites (7.78−16.2 ng/L). Discrete decline of TBC concentration in river water near the plant outlet hinted that rapid distribution of TBC between the water and sedimentary interface might be possible, and a majority of TBC was strongly attached to the sediment. Dilution by tributaries

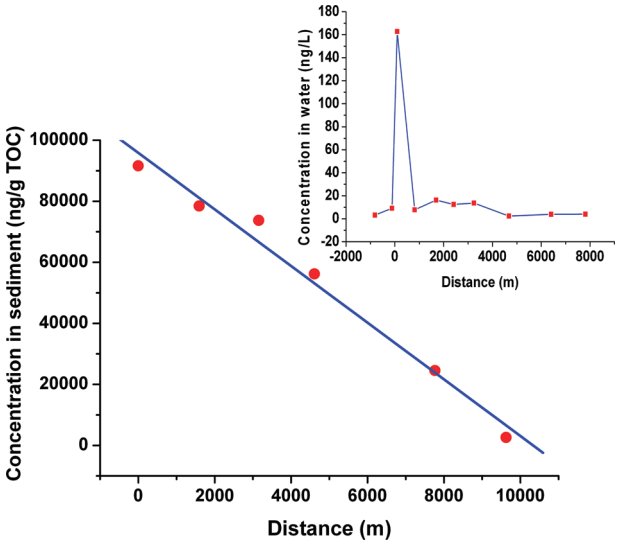

FIGURE 3. TBC concentration in surface sediment vs distance from the manufacturing plant and spatial distribution of TBC in the river of the investigated area (inset).

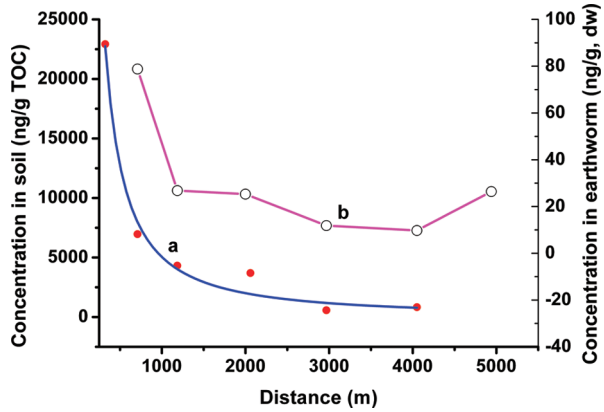

FIGURE 4. TBC concentration vs distance from the outlet: (a) in soil and (b) in earthworms.

could be a possible explanation for the decreased concentrations of distant river water samples several kilometers from the source (nearly 2.3−4.0 ng/L).

The concentrations of TBC in sediments, soil and earthworm samples ranged from 2.62−91.6 μg/g normalized to total organic carbon (TOC), 573 ng/g−22.9 μg/g TOC and 9.75−78.8 ng/g dw, respectively. Significant linear relationship was found between the concentrations of TBC and TOC contents in sediment and soil samples ($R^2 = 0.86$, $P < 0.05$). Similar decreasing trends with distance were found in all of these matrices (Figure 3 and 4). These results strongly indicated that the nearby TBC manufacturing plant should be the main source of TBC released into the surrounding environment. Statistical t test ($P < 0.05$) showed that the order of TBC concentrations in investigated matrices was surface sediment > soil ≈ earthworm > river water. As shown in Figure 3, the trends of the levels of TBC (TOC normalized) in sediment reduced linearly along with the path of the river. A previous work studying the transport of organic compounds into sediments showed that the TOC normalized concentration reduced logarithmically versus distance from the point source for several anthropogenic chemicals with K_{ow} (octanol−water partition coefficient) ranging from 2.7 to 7.2 in Narragansett Bay (*22*). The difference from our result and the reason for this disagreement remains unclear. However, another study discussed that suspended solids such as fulvic acid and humic acid may play important roles in the transportation and deposition of organic chemicals introduced into waters, and a more rapid sedimentation of suspended hydrocarbons near the outfall than further down river was observed in Narragansett Bay (*23*). Thus, it might be possible that the different geographical conditions of the investigated areas, especially in terms of TOC content in sediment and suspended solids in river water and the difference in deposition rate might be responsible for the different concentration patterns as a function of distance from the source. Detectable levels of TBC in sediment sample 10 km away from the plant revealed that the scope of emission from the source outlet exerted a significant influence on the river system. Furthermore, from Figures 3 and 4 an interesting observation could be discerned: TBC concentration in sediment as far as 10 km from the outlet (2.62 μg/g TOC) even exceeded that in soil 4 km away (833 ng/g TOC). The reasons still remain unclear but might indicate that the river ecosystem could be a more contaminated environmental compartment in the investigated area. It is assumed that detection of TBC in remote soil samples was considered to be the result of dust deposition and river water irrigation, while detection in earthworm samples was because of biouptake (Figure 4). We consider that the contamination from particle deposition through atmosphere could be an important factor, since the sharp decreasing trend in soil is in contrast to the relatively parallel concentrations in water samples. Besides, the high K_{oa} (octanol−air partition coefficient) and K_{ow} of TBC suggest that the chemical mainly adsorbs to particles. Figure 4 showed that TBC concentrations dropped by a factor of almost 30 within 4 km from the outlet. Qiu et al. pointed out that concentrations of PCB, PCDD/Fs, and DP decreased dramatically within several kilometers of a major source (*15*), which is analogous with TBC in our work. Further, similar decreasing trends of TBC concentration with distance in earthworm and soil samples implied that earthworm can be used as a bioindicator of TBC contaminant in soil.

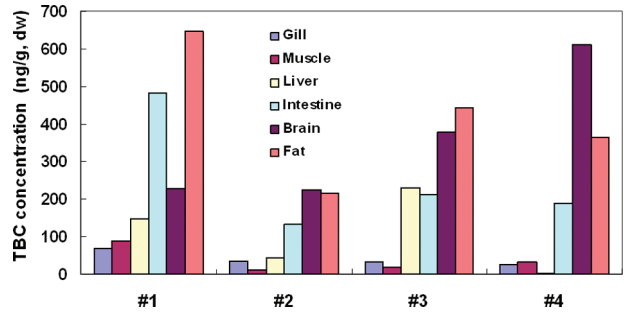

FIGURE 5. Distribution of TBC in different tissues and organs of carp samples.

Distribution of TBC in *Cyprinus carpio*. Four common carp samples with similar length (29.2−32.0 cm) and weight (433.5−618.4 g) were collected from a site distant from the plant. Brain, gill, muscle, liver, intestine, and fat samples of each common carp were analyzed to investigate the distribution of TBC in fish bodies. Two-way ANOVA indicated that there was no significant difference in TBC concentrations among the four individual common carp samples ($P > 0.05$), indicating similar TBC polluted levels. However, as shown in Figure 5, there was an uneven distribution in carp tissues and organs. TBC concentrations in brain were significantly different from those of gill and muscle. TBC concentrations in fat tissue were significantly different from those of gill, muscle, and liver ($P < 0.05$). Although the sample size is small, the distribution patterns indicate that TBC is inclined to be accumulated in the fat-rich organs, such as brain and adipose. Though the concentrations in muscle were only $^1/_{10}$ of that in highly accumulated tissues/organs, the whole amount of TBC in muscle should not be ignored, as muscle contributed almost 60%−70% of the body weight of *C. carpio*. The low

TABLE 1. Physical−Chemical Constants[a] of TBC and Other Flame Retardants of Environmental Concern

name[b]	CAS	S_W[c]	V_P[d]	t_{A0}[e]	log K_{ow}	BCF	log K_{oa}	log K_{aw}
TBC	52434-90-9	1.14×10^{-5}	1.18×10^{-15}	1.629	7.37	1.989×10^{4}	23.68	−16.31
BrTriaz (*31*)	52434-59-0	8.62×10^{-6}	8.85×10^{-12}	0.977	7.52	6074	17.52	−10.00
BrPhTriaz (*31*)	25713-60-4	1.85×10^{-11}	6.97×10^{-19}	7.224	11.46	3	21.46	−10.01
HBCD	3194-55-6	2.00×10^{-5}	1.68×10^{-8}	2.13	7.74	6211	11.8	4.15
DBDPE	84852-53-9	2.60×10^{-12}	3.98×10^{-10}	169.2	13.24	3	19.34	−6.10
DP (*14*)	13560-89-9	6.53×10^{-7}	7.06×10^{-10}	0.468	11.27	3	14.79	−3.52
TBECH (*18*)	3322-93-8	0.06915	1.05×10^{-4}	2.2	5.24	2153	8.01	−2.77
HCDBCO (*8*)	51936-55-1	6.82×10^{-5}	1.07×10^{-7}	0.816	7.91	3633	11.05	−3.14
TBB (*1*)	NA[f]	3.40×10^{-3}	3.43×10^{-8}	0.979	8.75	256	12.34	−3.59
TBPH (*1*)	26040-51-7	1.91×10^{-6}	1.71×10^{-11}	0.49	11.95	3	16.86	−4.91
penta-BDE	32534-81-9	0.0107	1.08×10^{-6}	19.5	7.66	3.69×10^{4}	11.15	−4.31
octa-BDE	32536-52-0	1.11×10^{-8}	1.27×10^{-2}	93.6	10.33	3	15.85	−5.52

[a] Calculated by US EPA EPI Suite V3.20. [b] DP, Dechlorane Plus; TBECH, 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane; HCDBCO, hexachlorocyclopentadienyldibromocyclooctane; TBB, 2-ethylhexyl 2,3,4,5-tetrabromobenzoate; TBPH, 2-ethylhexyl tetrabromophthalate. [c] Water solubility (mg/L). [d] Vapor pressure (mmHg, 25 °C). [e] Atmospheric oxidation half-Life (days). [f] Not available.

concentration of TBC in gill suggested it might not be enriched in the fish blood circulatory system. This enrichment mechanism of TBC is different from that of PBDEs (*24*), which can be taken up by the gill membranes. Moreover, high relative concentrations of TBC observed in the intestine indicate that absorption of TBC from the food chain in the digestive system, rather than by respiratory intake from water, is an important pathway for TBC in carp samples. Interestingly, concentrations in livers varied dramatically with a range of 4.4 and 230 ng/g dw. It can be hypothesized that TBC metabolic processes might exist in the liver, but no conclusions can be made unless confirmed by future experiments monitoring metabolites. High levels of TBC in the brain illustrate that this substance can pass through the blood−brain barrier and accumulate in this target organ.

The bioaccumulation factor (BAF), which is the ratio of the concentration in organism to the concentration in corresponding river water, is often used to estimate the accumulative abilities of pollutants in fish exposed in water bodies. On the basis of the formula for calculating BAF and combining the results obtained in our work, the BAF of TBC was estimated to be about 4700 using the TBC concentration in dry carp muscle and the arithmetic mean value of data in river water samples, excluding the outlier point with the highest concentration (163 ng/L). In general, pollutants with BCF/BAF > 5000 (*9*) are regarded as chemicals having bioaccumulation ability in biota. For example, BFRs such as penta-BDE and HBCDs show a high bioaccumulation property comparable to those of the 12 POPs listed in the Stockholm Convention (Table S1, Supporting Information). Although not all these newly identified alternative BFRs with high K_{ow} values show bioaccumulation behaviors (*25*), TBC could be considered to be, at least to a certain extent, biologically available with high concentration detected in common carp samples, a high calculated BCF of 19 900, and a measured BAF of 4700.

The measured BAF was only about one-fourth of the calculated bioconcentration factor (BCF = 19 900) obtained by BCFWIN, and one possible reason for this disagreement could be regarded as a limitation of the calculation method using investigated data in our work compared with that of the laboratory BCF calculating model (*26*). In the laboratory, BCF is usually calculated with a fixed contaminant exposure concentration. While in our work, taking the arithmetic mean value of TBC concentrations in water in the whole investigation area as the exposure concentration may cause an overestimation. Besides, other environmental factors may also have significant influence. For example, suspended particles can reduce bioavailability and uptake of chemicals by aquatic organisms (*27*), seasonal differences of chemical concentration might exist in aquatic organisms (*28*), BAF/BCF could be affected by the growth dilution rate in different species (*29*), and biotransformation or biological metabolism similar to those found for PCBs and PBDEs (*30*) could be important factors.

Quantitative Structure−Property Relationships (QSPR) and Environmental Fate Prediction. The EPI suite V3.20 (*21*) developed by US EPA, which is widely used as a potential POPs screening method, consists of a suite of stoichiometric models for estimating the physicochemical properties of a chemical by using descriptors such as empirical atom/fragment/group/bond contribution. In this work, the software suite was used to calculate the physicochemical properties of TBC and other halogenated flame retardants (HFRs) of most concern. The predicted data can help one to understand some environmentally relevant behaviors of TCB by comparison with those of other HFRs that have been relatively well studied. High calculated octanol−water partition coefficient (log K_{ow} = 7.37) indicated that TBC prefers to be accumulated in organic materials or fat-rich organisms, which has also been proved in this work. The predicted K_{aw} (air−water partition coefficient) of TBC is nearly 10 orders of magnitude lower than those of the compounds listed in Table 1. It is thus not surprising that a high log K_{oa} of TBC was obtained (log K_{oa} = log K_{ow} − log K_{aw}). The high K_{oa} of TBC hints at its slow respiratory elimination ability and high bioaccumulation potential in respiratory life forms. However, low K_{aw} indicates that the main proportion of TBC is more likely to remain in the water phase when exchange occurs at the boundary of the water−air interface. This characteristic would decrease the potential of human exposure to TBC through atmospheric diffusion to a certain extent.

Further information provided by HENRYWIN V3.1 revealed that the C−N bond in the N−C═O functional group of isocyanurate contributed a main portion to the calculated Henry constant, which has been confirmed by calculated data of triazine-structured chemicals such as 2,4,6-tris(2,3-dibromopropoxy)-1,3,5-triazine (BrTriaz), a structural isomer of TBC, and 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (BrPhTriaz) (Figure 2 and Table 1) (*31*). The structural similarities of these triazine-structured heterocyclic HFRs illustrate that these groups of chemicals have high water−air and octanol−air partition coefficients.

Previous work revealed that chemicals with log K_{oa} > 8 and log K_{ow} > 5 are most likely to adhere to particles (*10*). The physicochemical properties also suggest that TBC might be present in the local area in tree barks and other natural passive air samplers (*32*). The probable particle adherence behavior, possible similar atmospheric transport pattern with some other extensively studied BFRs mentioned above, and the

hydroxyl radical atmospheric oxidation half-life of 1.63 days (Table 1) showed that TBC meets the essential requirements to be regarded as persistent in the environment and undergo long-range transport.

The Presence of HFRs with Triazine Rings in the Environment. Structurally, TBC belongs to the group of heterocyclic flame retardants with a triazine ring, which is different from those previously reported that are mainly alicyclic or aromatic HFRs. Cursorily, these triazine ring structured chemicals can be divided into two subgroups (Figure 2). Subgroup A shows a cyanurate structure; double bonds of carbon to oxygen were formed and nitrogen atoms were linked to brominated branch chains. In subgroup B, oxygen atoms were linked to these brominated branch chains and a triazine ring was formed with conjugated double bonds. Calculated data showed that both TBC and BrTriaz show high K_{ow} and K_{oa}. Compared with TBC, the triazine structure in subgroup B would reduce the negative effect of aromatic nitrogen [N−C(−O)−N] to predicted K_{ow} and contribute less than the cyanurate functional group to the calculated Henry constant.

Some triazine-structured compounds have been proved to be toxic, such as atrazine (*33*) and cyanuric acid (*34*), while information in the literature on the application, usage, and environmental occurrence of halogenated triazines is still very scarce. A previous work reported that a group of halo-derived triazine chemicals is among the list of potential POPs that could be present in the Arctic (*10*). Thus, it is important to monitor this group of HFRs in the environment to properly assess the potential exposure effects on ecosystems and humans.

As a compound in the group of heterocyclic BFRs, TBC has been identified with high concentrations in river water, surface sediment, soil, earthworm, and carp samples in a factory-polluted region in southern China. Measured (4700) and predicted BCF (19 900) indicated the possible bioaccumulation ability of TBC through the food-chain in ecosystems. In general, the ability of TBC to migrate in the environment is similar to penta-BDE and HBCDs (Table 1). Their similar physicochemical properties imply that TBC possess the typical characteristics of a persistent organic pollutant, and high K_{ow} and K_{oa} values further suggest the possible long-range transport ability of this compound. Positive identification of TBC further raises the awareness of the presence of alternative heterocyclic BFRs in the ambient environment. The potential adverse effect to the ecosystems and human health should also be further studied.

Acknowledgments

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Supporting Information Available

Figure S1 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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