Supplementary Materials

Bioaccumulation patterns, trophic transfer characteristics and dietary exposure potential of tetrabromobisphenol A analogs in a coral reef food web of the Xisha Islands, South China Sea

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Contents:

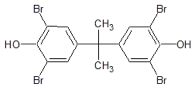
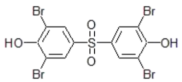
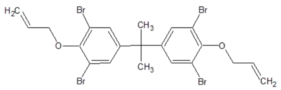
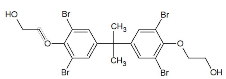
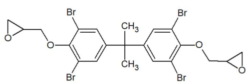
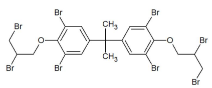
Supplementary Text 1. Analysis procedures of TBBPA analogs in seawater, sediment and biological samples

The seawater, sediment and biological samples were processed using our previously established methods [19, 53] with some modifications. Briefly, seawater samples were filtered through a GF/F glass microfiber filter. Then, 1 L of filtered water sample spiked with 100 ng of TBBPA-d_{10} was extracted with an Oasis HLB column (200 mg, 6 mL; Waters, USA) preconditioned with 10 mL methanol, 10 mL dichloromethane, and 10 mL Milli-Q water. The column was dried under vacuum, and the targets were eluted using 10 mL of dichloromethane and 5 mL of methanol in turn. The elution was evaporated under nitrogen to near dryness and reconstituted in 1 mL of methanol for analysis.

The sediment samples were freeze-dried, 3 g sediments and 1 g copper powder spiked with 100 ng of TBBPA-d_{10} underwent ultrasonic extraction using 20 mL of n-hexane/dichloromethane (1:1, v/v) and 2% formic acid for 20 min and centrifuged at 3000 rpm for 5 min with 2 cycles. Then, the extraction procedure was repeated once with 10 mL of methanol. The extracts were collected and evaporated under a gentle stream of nitrogen, then redissolved in 1 mL of methanol for instrumental analysis.

The freeze-dried biological samples were weighed, homogenized, spiked with 100 ng of TBBPA-d_{10}, and then ultrasonically extracted with 10 mL of n-hexane/dichloromethane (1:1, v/v) and 2% formic acid for 30 min and centrifuged at 3000 rpm for 5 min with 2 cycles. Then, the extraction procedure was repeated once with 5 mL of dichloromethane/methanol (1:1, v/v). All the extracts were merged and purified using 98% H_2SO_4 to remove most of the lipids, and then a silica gel column (5 g, 6 mL, CNW Bond) was used for further cleanup with 25 mL of n-hexane/dichloromethane (1:1, v/v). The solvents were evaporated under nitrogen and redissolved to 1 mL in methanol for analysis.

Supplementary Table 1. Structures and properties of TBBPA analogs

Compounds	Formula	M.W.	Structure	CAS	Solubility (mg/L)	Vapor pressure (mm Hg)	Boiling points (°C)	Melting points (°C)	Predicted *BCF* (L/kg ww)	Log K_{OW}
TBBPA	$C_{15}H_{12}Br_4O_2$	543.87		79-94-7	0.001	$3.46×10^{-11}$	486	206	$1.06×10^4$	7.20
TBBPS	$C_{12}H_6Br_4O_4S$	565.85		39635-79-5	0.037	$1.49×10^{-13}$	545	234	$1.27×10^3$	5.21
TBBPA-DAE	$C_{21}H_{20}Br_4O_2$	624.01		25327-89-3	$3.12×10^{-7}$	$1.99×10^{-9}$	509	217	442	10.0
TBBPA-BHEE	$C_{19}H_{20}Br_4O_4$	631.98		4162-45-2	$1.59×10^{-4}$	$3.93×10^{-14}$	574	247	$7.72×10^3$	6.78
TBBPA-BGE	$C_{21}H_{20}Br_4O_4$	656.01		3072-84-2	$3.26×10^{-5}$	$1.21×10^{-11}$	544	233	$8.43×10^3$	7.40
TBBPA-BDBPE	$C_{21}H_{20}Br_8O_2$	943.62		21850-44-2	$1.16×10^{-10}$	$6.36×10^{-15}$	647	281	81.5	11.5

Note: The data are all estimated by U.S. EPA EPI SUITE V4.1.

Supplementary Table 2. Detailed information on biota samples from coral reef waters of the Xisha Islands, South China Sea

Common name	Species name	Abbreviations	n	Body length (cm)	Body weight (g)	Habitat	Feeding habit
Gold mouth turban	*Turbo chrysostomus*	JKRL	6	9.55 ± 3.29	15.6 ± 5.41	Benthic	Herbivorous
Nerite snail	*Nerita striata*	TYL	3	1.54 ± 0.52	2.16 ± 1.03	Benthic	Herbivorous
Ear-shell	*Haliotis diversicolor*	ZSB	5	8.85 ± 0.64	59.9 ± 12.2	Benthic	Herbivorous
Gear turban	*Trochus sacellum*	ZTMT	5	5.95 ± 1.06	14.7 ± 2.47	Benthic	Herbivorous
Owl-wing conch	*Strombus lentiginosus*	BFL	3	7.50 ± 1.41	8.59 ± 5.11	Benthic	Omnivorous
Bohadschia marmorata	*Bohadschia marmorata*	TWBN	4	14.0 ± 1.13	123 ± 36.8	Benthic	Herbivorous
Sand sifting sea cucumber	*Holothuria hilla*	HYHS	3	13.7 ± 3.32	54.1 ± 20.2	Benthic	Omnivorous
Prickly red sea cucumber	*Thelenota ananas*	JMHS	3	14.4 ± 0.07	232 ± 32.5	Benthic	Omnivorous
Xanthid crab	*Etisus dentatus*	CHMX	5	9.10 ± 2.26	142 ± 28.6	Benthic	Omnivorous (organic debris)
Left-handed	*Calcinus*	TYDQ	6	3.75 ± 1.20	1.02 ± 0.65	Benthic	Omnivorous

hermit crab	*laevimanus*						
Hermit crab	*Clibanarius corallinus*	SHXA	4	6.20 ± 2.24	3.68 ± 2.01	Benthic	Omnivorous
Tricolor parrotfish	*Scarus tricolor*	SS	3	25.8 ± 3.84	435 ± 200	Benthic	Herbivores (plankton)
Darktail parrotfish	*Scarus sordidus*	WS	4	25.5 ± 1.68	418 ± 81.0	Benthic	Herbivores (plankton)
Yellowband parrotfish	*Scarus schlegeli*	XS	3	29.3 ± 2.66	521 ± 111	Benthic	Herbivores (plankton)
Masked rabbitfish	*Siganus puellus*	YD	3	21.5 ± 1.73	191 ± 47.6	Benthic	Herbivores (plankton)
Silver rabbitfish	*Siganus argenteus*	YL	3	44.8 ± 58.1	319 ± 106	Benthic	Herbivores (plankton)
Blue-spotted grouper	*Cephalopholis argus*	BD	3	22.0 ± 1.06	192 ± 21.6	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Blackedge thicklip wrasse	*Hemigymnus melapterus*	CC	3	29.7 ± 1.81	572 ± 88.1	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Red louti grouper	*Variola louti*	CY	4	28.2 ± 4.45	484 ± 226	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Oriental sweetlips	*Plectorhynchus orientalis*	DF	3	483 ± 1105	598 ± 462	Benthic	Carnivorous (shrimp, crab, snail, small fish)

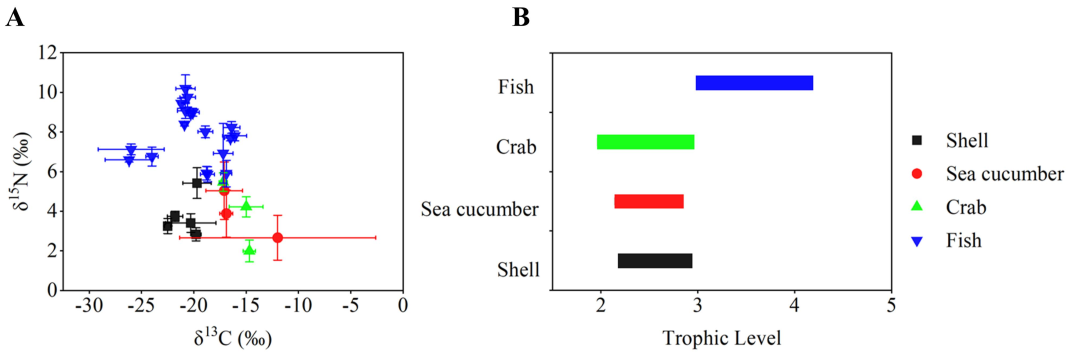
Mottled grouper	*Epinephelus merra*	FC	3	29.6 ± 46.4	72.7 ± 18.4	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Blacktip grouper	*Epinephelus fasciatus*	HB	3	20.8 ± 2.33	154 ± 48.0	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Por's goatfish	*Upeneus sulphureus*	HD	6	23.4 ± 2.12	287 ± 86.1	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Redfin emperor	*Lethrinus rubrioperculatus*	HL	3	24.6 ± 2.86	261 ± 97.1	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Fine-spotted rabbitfish	*Siganus punctatissimus*	HS	3	30.2 ± 2.07	604 ± 55.3	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Clown filefish	*Cantherhines dumerilii*	JW	3	28.2 ± 2.34	493 ± 147	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Doublebar goatfish	*Parupeneus trifasciatus*	SD	6	20.9 ± 3.54	236 ± 143	Benthic	Carnivorous (shrimp, crab, snail, small fish)
Tripletail wrasse	*Cheilinus trilobatus*	SY	3	20.6 ± 1.24	189 ± 46.8	Pelagic	Carnivorous (shrimp, crab, snail, small fish)
Dash-and-dot goatfish	*Parupeneus barberinus*	TB	3	24.5 ± 2.19	305 ± 101	Benthic	Carnivorous (shrimp, crab, snail, small fish)

Supplementary Table 3. Information on scanning ions for TBBPA analogs

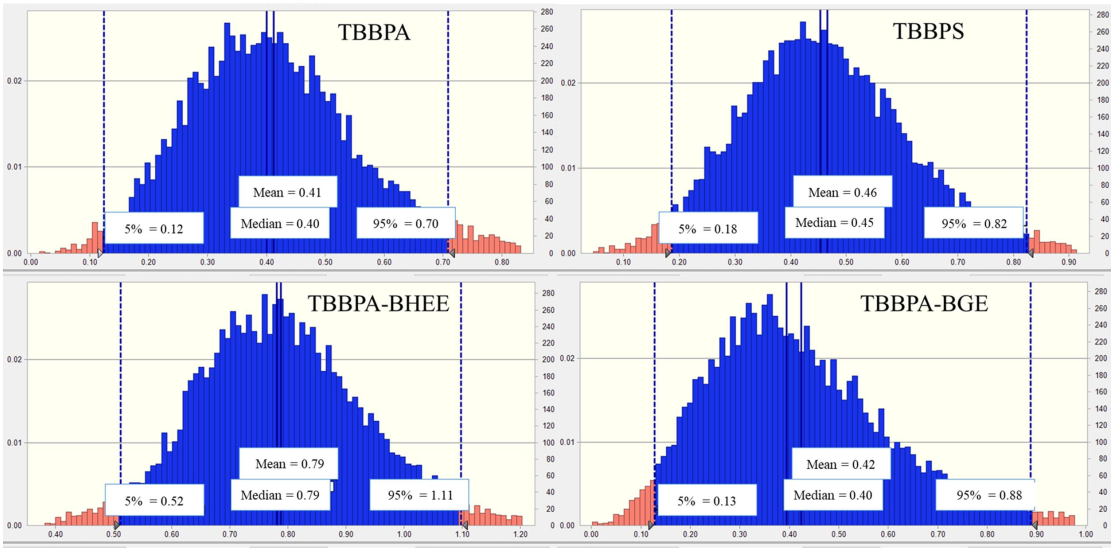
Compounds	Parent ions (m/z)	Fragment energy (V)	Quantitative ions (m/z)	Collision energy (V)	Qualitative ions (m/z)	Collision energy (V)	Retention time (min)
TBBPA	543	150	543→542	0	543→447.8	24	7.152
TBBPS	565	150	565→484.7	20	565→482.7	36	3.372
TBBPA-DAE	583	40	583→526.5	32	583→583	20	8.424
TBBPA-BHEE	587	162	587→526.7	40	587→541.8	28	6.909
TBBPA-BGE	599	144	599→526.7	40	599→541.8	28	7.817
TBBPA-d^{10}	553	150	553→552	10	553→456	48	7.064

Supplementary Table 4. Detailed information on the method detection limit (MDL), method quantitation limit (MQL) and recoveries in the analysis of the samples

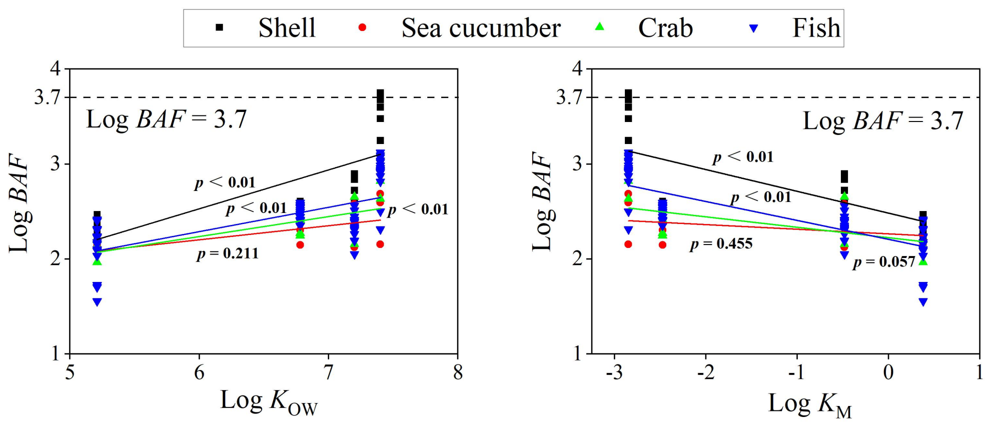
Compounds	Water samples				Sediment samples				Biota samples			
	MDL (ng/L)	MQL (ng/L)	Recoveries (%)	Precision (RSD%)	MDL (ng/g dw)	MQL (ng/g dw)	Recoveries (%)	Precision (RSD%)	MDL (ng/g lw)	MQL (ng/g lw)	Recoveries (%)	Precision (RSD%)
TBBPA	0.016	0.056	92.7-112	6.78	0.004	0.014	75.6-82.1	8.75	0.572	1.89	66.7-73.4	8.14
TBBPS	0.017	0.059	81.2-89.8	9.91	0.007	0.023	71.9-79.5	10.4	0.106	0.327	71.6-84.7	10.0
TBBPA-DAE	0.065	0.215	89.1-92.6	4.57	0.019	0.063	67.2-77.4	3.09	0.302	1.06	69.0-73.4	4.19
TBBPA-BHEE	0.024	0.079	80.3-85.9	11.3	0.012	0.041	69.8-84.6	12.9	0.073	0.241	83.2-90.9	9.21
TBBPA-BGE	0.015	0.051	79.5-94.7	7.92	0.010	0.037	73.7-80.3	5.63	0.164	0.558	91.8-99.1	7.66



Supplementary Figure 1. Relationship between $\delta^{13}C$ and $\delta^{15}N$ values in biota (A) and the distribution of trophic levels in the food web (B).



Supplementary Figure 2. Monte Carlo simulated probability distributions of the *TMF*s for TBBPA analogs (n = 10000).



Supplementary Figure 3. Relationships between Log *BAF*s of TBBPA analogs with Log K_{OW} and Log K_M in biota.