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Temporal trends of "old" and "new" persistent halogenated organic pollutants in fish from the third largest freshwater lake in China during 2011–2018 and the associated health risks☆

Jinjing Ma [a, b, 1], Xiangnan Li [a, b, 1], Shengtao Ma [b, c], Xiaolan Zhang [a], Guiying Li [b], Yingxin Yu [b, *]

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai, 200444, PR China
[b] Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Guangzhou Key Laboratory Environmental Catalysis and Pollution Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou, 510006, PR China
[c] Synergy Innovation Institute of GDUT, Shantou, 515041, PR China

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ABSTRACT

The study aimed to investigate temporal trends of "old" and "new" persistent halogenated organic pollutants (HOPs) in Taihu Lake, the third largest freshwater lake in China, and the associated health risks. Five fish species were consecutively collected from the lake every year during 2011–2018. HOPs including 37 polychlorinated biphenyls (PCBs), 10 organochlorine pesticides (OCPs), short- and medium-chain chlorinated paraffins (SCCPs and MCCPs), 19 polybrominated diphenyl ethers (PBDEs), and 10 new brominated flame retardants (NBFRs), were measured. The results showed that all the HOPs were detected, with MCCPs and NBFRs showing the highest and lowest concentrations, respectively. The levels of SCCPs and MCCPs were several orders of magnitude higher than those of the other HOPs. There were obvious increasing trends for SCCPs, MCCPs, and hexachlorobenzene, but a decreasing trend for PBDEs. No obvious increasing or decreasing trends were observed for the other HOPs. The present study indicated that the use of NBFRs to replace PBDEs was not yet clearly observed. Fish consumption did not result in non-carcinogenic risks, but posed low carcinogenic risks, with PCBs and DDTs being the highest-risk contaminants because of historical residues. This is the first study for the temporal variations of the HOPs in the lake.

1. Introduction

Persistent halogenated organic pollutants (HOPs) are a type of persistent organic pollutant (POP) containing at least one halogen atom. POPs are of great concern because they persist in the environment, can bioaccumulate and be biomagnified through food chains, and have adverse effects on ecosystems and human health (Ma et al., 2019; Venisseau et al., 2018). To strengthen the management of POPs and reduce the risk caused by them, various multilateral environmental conventions have been reached. The Stockholm Convention, held in 2001, was an international convention on the use and prohibition of POPs, which aimed at global action to protect the environment and humans from POPs. The first 12 POP chemicals addressed by the Convention included organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and unintentional byproducts, such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Later, other POPs, including polybrominated diphenyl ethers (PBDEs), short-chain chlorinated paraffins (SCCPs), and others, were added (Stockholm Convention, 2009a, 2009b; USEPA, 2013; POPRC, 2017). Currently, 31 kinds of POPs have been priority controlled by the Stockholm Convention. Furthermore, when these "old" POPs are banned or restricted, there must be some "new" substitutes, which inevitably create more emerging organic contaminants, such as new brominated flame retardants (NBFRs) as alternatives to brominated flame retardants (BFRs), e.g., PBDEs (Yadav et al., 2019).

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* Corresponding author.
E-mail address: yuyingxin@gdut.edu.cn (Y. Yu).

[1] The authors have equal contribution to this work.

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In the past 40 years, the economy of China has developed rapidly, especially since 2000. The sharp rise in economic development has also led to high usage of products, including PBDEs, chlorinated paraffins (CPs), and others, although some HOPs such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethane (DDT) have been banned since the 1980s in China. For example, the production of CPs grew rapidly from 0.6 million tons in 2007 to 1.05 million tons in 2013, respectively (Wang et al., 2018a; Wei et al., 2016; Zeng et al., 2011). Globally, China has been the largest manufacturer, exporter, and consumer of CPs since 2013 (Li et al., 2019) with Jiangsu Province being the greatest contributor to the environment (approximately 560 and 1290 tons in air and water, respectively) (Zhang et al., 2017). Extensive use of HOPs or products containing these compounds has led to their widespread detection in environmental matrices, organisms, and even human bodies (Dong et al., 2020; de la Torre et al., 2020; Tornkvist et al., 2011; van Mourik et al., 2016; Xu et al., 2019). The wide occurrence of these pollutants has posed potential risks to ecological systems and human health.

Taihu Lake, with an area of 2420 km^2 and a shoreline 393 km long, is the third largest freshwater lake in China. Taihu Lake Basin is located in the Yangtze River Delta, which is one of the fastest-developing regions in China, with a high population density and extremely prosperous industrial and agricultural production. Taihu Lake is a vital place because it not only provides drinking water for the residents in the surrounding regions, but also supports the operation of fisheries (Wang et al., 2016). However, the lake generally acts as a natural sink loaded with a variety of organic pollutants because of the use of toxic chemicals in surrounding regions. For example, many HOPs such as PBDEs, OCPs, and CPs have been detected in the Taihu Lake aquatic ecosystem (Xu et al., 2018; Yu et al., 2012, 2014; Zhang et al., 2019). However, there is not available data on the temporal variations of the "old" and "new" HOPs during the past ten years. Also, there is no long-term environmental data to support the alternative use of "old" by "new" HOPs, such as PBDEs by NBFRs.

In the present study, the authors hypothesized that there were temporal trends of the "old" and "new" HOPs during a long time, for example, up to approximately 10 years, and long-term environmental data can support the alternative use of "old" by "new" HOPs. Also, the changes would lead to fewer health risks via fish consumption. Therefore, the authors prospectively collected five fish species, including bighead carp (*Hypophthalmichthys nolitrix*), silver carp (*Hypophthalmichthys molitrix*), crucian carp (*Carassius carassius*), topmouth culter (*Culter alburnus*), and large icefish (*Protosalanx hyalocranius*), which are the most common commercial species, in Taihu Lake every year from 2011 to 2018. Five types of HOPs, including NBFRs, PBDEs, CPs, PCBs, and OCPs, were analyzed. The temporal variations of the HOPs and possible alternative use of "old" by "new" HOPs were investigated, and the associated human health risks via fish consumption were assessed. This is the first study for the temporal variations of the HOPs in the lake, and the first report on field long-term environmental data for the alternative use of PBDEs by NBFRs.

2. Materials and methods

2.1. Chemicals and reagents

Standards of DDTs (o,p'-DDT, p,p'-DDT, p,p'-DDE, o,p'-DDE, and o,p'-DDD), HCHs (β-HCH, γ-HCH, and δ-HCH), PCBs (PCB5, 8, 28, 52, 49, 38, 44, 37, 47, 74, 70, 66, 60, 101, 99, 87, 110, 77, 82, 118, 114, 123, 153, 105, 179, 138, 158, 126, 160, 187, 183, 128, 156, 180, 169, 170, and 189), and PBDEs (BDE17, 28, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, 197, 203, 196, 208, 207, 206, and 209) were obtained from AccuStandard, Inc. (CT, USA). Standards of medium-chain chlorinated paraffins (MCCPs) and SCCPs (100 ng/mL in cyclohexane) with chlorine contents of 51.5%, 55.5%, and 63% and 47.0%, 52.0%, and 57.0%, respectively, were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). In the present study, NBFR standards (Fig. S1), including allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), pentabromobenzene (PBB), hexabromobenzene (HBB), (2,3-dibromopropyl) (2,4,6-tribromophenyl) ether (DPTE), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), tetrabromocyclooctane (TBCO), tetrabromo-o-chlorotoluene (TBCT), pentabromobenzylacrylate (PBBA), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) (100 μg/mL in toluene), and hexachlorobenzene (HCB) were also bought from AccuStandard, Inc.. Internal standards, $^{13}C_{12}$-PCB208 and non-isotopic-labeled BDE77, were obtained from AccuStandard, Inc., and surrogate standards, $^{13}C_6$-trans chlordane ($^{13}C_6$-TC) and $^{13}C_{12}$-PCB141, were bought from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Acetone (HPLC-grade) came from Mreda Technology Co., Ltd. (USA). HPLC-grade dichloromethane, ethyl acetate, and *n*-hexane were obtained from CNW Technologies GmbH (Germany). Na_2SO_4 came from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Florisil (0.074–0.150 mm, 100–200 mesh, ASTM, residue analysis) and solid-phase extraction cartridges (6 mL, 500 mg) were also supplied by CNW Technologies GmbH (Germany). Silica gel with a size of 80–100 mesh was obtained from Qingdao Chemical Co. Ltd. (Shandong, China).

2.2. Sampling and sample preparation

Fish samples were collected by local commercial fishermen at Guangfu town, Suzhou, Jiangsu Province, who caught fish in Taihu Lake on the second day after the fishing festival that occurred on 1 September every year from 2011 to 2018. In Taihu Lake, fry were released in winter (generally in January) and adult fish were caught in September every year. Therefore, the sampled fish can reflect the pollution of the sampling year (Yu et al., 2012). A total of 203 samples included topmouth culter ($n = 41$), crucian carp ($n = 40$), silver carp ($n = 40$), bighead carp ($n = 41$), and large icefish ($n = 41$) (Table S1). For crucian carp, a sample was generally obtained by combining four to five fish, whereas a sample of large icefish was obtained by combining fish to a weight of approximately 500 g because this kind of fish is too small (approximately 2 g wet weight for an individual). All samples were wrapped with aluminum-foil and transported to the laboratory separately stored in an ice box. After length and weight were measured, the fish muscle (with the whole fish being used for large icefish) was collected, lyophilized, and ground into powder. Finally, the powder was stored at −20 °C until use.

2.3. Analytical protocol

Generally, a 2 g sample spiked with surrogate standards of $^{13}C_6$-TC and $^{13}C_{12}$-PCB141 was Soxhlet-extracted using acetone and *n*-hexane (1:1, *v*:*v*) for 72 h. The extract was concentrated, and the lipid content was measured by gravimetry. Gel permeation chromatography was used to remove the lipids with *n*-hexane and dichloromethane (1:1, *v*:*v*), and a solid-phase extraction cartridge was used to clean up and separate the target compounds. The non-polar fractions were used for further treatment. The details were described in a previous study (Zhuo et al., 2019). Briefly, the fraction containing Florisil and silica gel was purified by a column filled with 3 g sodium sulfate anhydrous, 5 g acid silica gel (1.5% H_2O, ww), 2 g neutral silica gel (1.5%, ww), and 5 g Florisil (1.5% H_2O, ww) from top to bottom. The fractions of 70 mL dichloromethane and *n*-hexane (3:7, *v*:*v*) (for CPs) were collected after 30 mL *n*-hexane (for

the other HOPs) was used to wash the columns. The collection was concentrated and dried with a gentle flow of nitrogen. Finally, after spiking with internal standards (BDE77 and $^{13}C_{12}$-PCB208 for CPs and the other HOPs, respectively) in samples, the sample was stored in 50 μL *n*-hexane at −20 °C until analysis by gas chromatography-mass spectrometry (or an electron capture detector). Detailed information on the instrumental analyses is given in the Supporting Information, and the instrumental monitoring of ions for HOPs are described in Table S2.

2.4. Quality assurance and quality control

To reduce background influence during the experiments, all glassware was heated to 450 °C for more than 4 h, and absorbent cotton was extracted with *n*-hexane by Soxhlet extraction for 48 h before use. One spiked matrix and one procedural blank were conducted for each batch of ten samples. The spiked matrix recoveries of SCCPs was 76.7%–103.4% with standard deviation of 8.7% and the recoveries of MCCPs was 68.5%–97.3% with standard deviation of 6.9%. The recoveries of the other HOPs are shown in Fig. S2. Triplicate samples were randomly selected from every 50 samples, and the relative standard deviation was less than 20% for the target compounds. The surrogate standard ($^{13}C_6$-TC) recoveries of all samples were 64%–110% for SCCPs and MCCPs, and the recoveries of $^{13}C_{12}$-PCB141 were in the range of 78%–114% for the other HOPs. The limits of quantification (LOQs) and limits of detection (LODs) are listed in Table S3. Linear coefficients of determination $R^2 \geq 0.99$ were recorded for OCPs, PCBs, PBDEs, and NBFRs, and $R^2 \geq 0.9$ were obtained for SCCPs and MCCPs. The detail information for calibration curves are shown in Table S4.

2.5. Calculations and statistical analysis

To comprehensively understand whether pollutants pose a threat to the human body through fish consumption, health risks considering non-carcinogenic and carcinogenic effect endpoints were estimated using the hazard quotient (HQ) and the carcinogenic risk (CR), respectively. These were calculated according to the following equations (Cao et al., 2019; Harada et al., 2011):

$$HQ = \frac{EDI}{RfD} \quad (1)$$

$$CR = EDI \times CSF \quad (2)$$

$$EDI = \frac{C \times R}{BW} \quad (3)$$

where EDI (ng/kg-bw/day) is the estimated daily intake of a chemical; RfD (ng/kg-bw/day) is the daily dose for humans that has no known adverse effects on human health; CSF (ng/kg-bw/day) is the cancer slope factor of the chemical for carcinogenic effect; C (ng/g ww) is the chemical concentration in fish; R (g/day) is the fish consumption rate per day; and BW (kg) is body weight. All the related parameters used are given in Table S5. If an HQ value was less than 1, the chemical was considered to pose no obvious non-carcinogenic risks. If a CR value was less than 10^{-6}, the carcinogenic risk posed by the chemical was considered acceptable. Total HQ (CR) was used to evaluate the total non-carcinogenic risk (carcinogenic risk) from multiple contaminants using the addition method (US EPA, 2000; Yu et al., 2014).

SPSS 13 for Windows was used to conduct statistical analyses. The correlations among the variables were evaluated using a linear regression model. A non-parametric Wilcoxon test is used to test the difference between samples. The results were considered to be statistically significant at $p < 0.05$. If the detected concentration was less than the LOD, the value of "not detected" was assigned; if the concentrations of the target substances were greater than the LOD, but less than the LOQ and the detection frequency was >50%, the concentrations of the targets were reported as 1/2 LOQ; if the detection frequency was <50%, the concentrations were reported as 1/4 LOQ (GB 17378.2–2007; Ge et al., 2020). All CP concentrations are shown in ng/g ww (wet weight), and the other target substances are shown in pg/g ww unless otherwise specified.

3. Results and discussion

3.1. HOP concentrations in fish

All the target HOPs, including PBDEs, NBFRs, OCPs, PCBs, and CPs, were detected in all samples (Table 1), suggesting the ubiquitous occurrence of these pollutants. The median total OCP concentrations (including o,p'-DDT, p,p'-DDT, p,p'-DDE, o,p'-DDE, and o,p'-DDD; β-HCH, γ-HCH, and δ-HCH; and HCB) in the five fish species varied from 2.54 to 5.90 ng/g ww, with the concentrations of ΣDDTs, ΣHCHs, and HCB being 2.74–(5.90×10^3), 21.5–84.1, and 33.2–67.5 pg/g ww, respectively. The present OCP contamination levels were lower than those reported in a previous study from the same lake for DDTs ($p < 0.001$), and those from the Qiantang and Yangtze Rivers in China for DDTs and HCHs (Qiantang: $p = 0.012$ for DDTs, $p < 0.001$ for HCHs, Yangtze Rivers: $p = 0.003$ for DDTs, $p < 0.001$ for HCHs) (Table S6). The present OCPs in fish are higher than those in fish from the Kabul River in Pakistan and in most of Africa (except for Kruger National Park), but lower than tilapia from Okinawa Island in Japan ($p < 0.001$) (Tables S6–7) (Aamir et al., 2016; Gerber et al., 2016; Malarvannan et al., 2011). The concentrations of Σ_{37}PCBs ranged from 264 to 1.95×10^3 pg/g ww, with a median of 731 pg/g ww (Table 1). From a global viewpoint, the PCB levels in some parts of Europe are high, followed by the Great Lakes in North America, but they are low in Africa (Table S8). Overall, the OCP and PCB contamination levels in Taihu Lake were moderate compared with those in other regions, although these chemicals have been prohibited in China for over 40 years.

SCCP concentrations were in the range from 4.7 to 504 ng/g ww, with a median of 20.0 ng/g ww, which were lower ($p = 0.012$) than those of MCCPs, with a range of 3.7–(1.40×10^3) ng/g ww (median: 22.2 ng/g ww) (Table 1). The levels of SCCPs in the present study were similar with the Chinese herring in the Pearl River (median: 20 ng/g ww) ($p = 0.065$) (Sun et al., 2016), farmed fish (mean: 40 ng/g ww) and wild fish (mean: 26 ng/g ww) from the Yangtze River (Huang et al., 2019a), and were higher than brook trout (mean: 10 ng/g ww) from Canada (Basconcillo et al., 2015) and fresh water fish (median: 3.6 ng/g ww) ($p < 0.001$) from France (Labadie et al., 2019). The concentration of MCCPs were in the same magnitudes as abalone (mean: 14.9 ng/g ww) from Liaodong Bay (Huang et al., 2017) and fish (mean: 18.5 ng/g ww) from France (Labadie et al., 2019). Compared with trout collected from Canada (Basconcillo et al., 2015), the present levels of MCCPs were much higher. In general, higher SCCP and MCCP concentrations were observed in China than in other countries, which reflect the fact that high CP usage and production have led to serious environmental contamination in China.

Among the detected BFRs, PBDEs occurred at the highest concentrations (Table 1), which was expected given the long-term industrial application of these chemicals. The concentrations of Σ_{19}PBDEs ranged from 3.95 to 5.51×10^3 pg/g ww, with a median of 389 pg/g ww. Among the 19 congeners, BDE47 was predominant, with a median of 114 pg/g ww. The present PBDE concentrations were higher than those in Dianshan Lake ($p < 0.001$) in China, but

Table 1
Concentrations of HOPs in fish collected from Taihu Lake, China during 2011–2018.

	Silver carp				Bighead carp				Crucian carp				Topmouth culter				Large icefish			
	Mean	Median	Range	DF (%)	Mean	Median	Range	DF (%)	Mean	Median	Range	DF (%)	Mean	Median	Range	DF (%)	Mean	Median	Range	DF (%)
OCPs[a]	3.69 × 10^3	3.40 × 10^3	323–1.04 × 10^4	100	4.06 × 10^3	3.66 × 10^3	1.02 × 10^3 –1.17 × 10^4	100	7.57 × 10^3	5.90 × 10^3	265–3.33 × 10^4	100	6.68 × 10^3	4.56 × 10^3	1.95 × 10^3 –2.60 × 10^4	100	2.91 × 10^3	2.54 × 10^3	57.1 –3.36 × 10^4	100
α–HCH	6.79	n.d.	n.d.–94.8	20.5	n.d.	n.d.	n.d.	2.7	3.47	n.d.	n.d. –82.4	8.33	8.67	n.d.	n.d.–49.1	34.3	0.31	n.d.	n.d.–10.4	2.94
β–HCH	18.6	n.d.	n.d.–125	30.8	76.3	43.7	n.d.–676	67.6	91.8	16.8	n.d.–932	58.3	112	79.7	n.d.–433	62.5	76.7	59.4	n.d.–584	79.4
γ–HCH	20.2	n.d.	n.d.–460	30.8	21.2	n.d.	n.d.–496	21.6	9.32	n.d.	n.d.–116	16.7	5.74	n.d.	n.d.–85.0	6.3	14.5	n.d.	n.d.–99.9	47.1
δ–HCH	4.33	n.d.	n.d.–37.2	19.7	6.68	n.d.	n.d.–243	18.9	2.66	n.d.	n.d.–22.3	22.2	6.89	n.d.	n.d.–129	15.6	11.0	n.d.	n.d.–87.6	26.5
ΣHCHs	49.9	21.5	n.d.–477	66.7	104	62.1	n.d. –865	73.0	107	38.7	n.d.–1.01 × 10^3	72.2	134	84.1	n.d.–475	84.4	102	62.1	n.d.–587	97.1
o,p'–DDE	142	97.1	n.d. –567	67.6	115	48.4	n.d.–750	59.4	122	76.1	n.d.–888	53.1	158	116	n.d.–909	75.0	18.3	n.d.	n.d.–195	10.3
p,p'–DDE	2.73 × 10^3	2.55 × 10^3	n.d.–8.48 × 10^3	97.4	3.02 × 10^3	2.72 × 10^3	111–1.10 × 10^4	100	6.55 × 10^3	5.28 × 10^3	n.d.–3.21 × 10^4	97.2	5.54 × 10^3	3.88 × 10^3	1.34 × 10^3 –2.40 × 10^4	100	2.65 × 10^3	2.30 × 10^3	n.d.–1.40 × 10^4	82.4
o,p'–DDD	357	195	n.d.–2.68 × 10^3	94.9	274	223	37.5–2.24 × 10^3	100	363	126	n.d.–4.44 × 10^3	94.4	511	159	39.4–3.66 × 10^3	100	602	96.5	17.0 –3.90 × 10^3	100
o,p'–DDT	379	n.d.	n.d.–3.21 × 10^3	35.9	401	n.d.	n.d.–3.60 × 10^3	32.4	354	n.d.	n.d.–3.71 × 10^3	27.8	829	n.d.	n.d.–7.98 × 10^3	9.4	1240	n.d.	16.7 –9.64 × 10^3	32.4
p,p'–DDT	30.3	19.3	n.d.–183	59.0	35.9	24.8	n.d.–757	64.9	31.0	13.8	n.d.–253	63.9	43.7	28.1	n.d.–263	84.5	889	54.4	n.d.–7.47 × 10^3	91.2
ΣDDTs	3.63 × 10^3	3.28 × 10^3	50.4 –9.97 × 10^3	100	3.93 × 10^3	3.60 × 10^3	983–1.18 × 10^4	100	7.07 × 10^3	5.90 × 10^3	265–3.33 × 10^4	100	7.06 × 10^3	4.99 × 10^3	1.84 × 10^3 –2.56 × 10^4	100	5.40 × 10^3	2.47 × 10^3	54.2 –3.33 × 10^4	100
HCB	96.5	62.3	n.d.–649	92.3	81.1	67.3	n.d.–1000	97.3	107	43.3	n.d.–702	88.9	86.7	67.5	6.0–296	100	57.6	33.2	n.d.–176	85.4
PCBs[a]	847	728	387–1.64 × 10^3	100	676	663	264–1.24 × 10^3	100	846	839	485–1.45 × 10^3	100	957	893	519–1.95 × 10^3	100	595	555	436–1.14 × 10^3	100
Di–CBs	10.8	13.4	n.d.–40.7	87.5	27.2	15.4	n.d.–273	92.5	19.5	15.1	n.d.–64.2	88.6	24.6	19.5	n.d.–74.5	100	15.3	12.8	n.d.–39.6	100
Tri–CBs	54.1	42.9	n.d.–262	97.5	44.1	38.3	18.1–82.9	100	55.0	44.2	25.1–216	100	48.5	47.8	26.4–91.6	100	42.8	43.0	26.8–66.5	100
Tetra–CBs	325	177	70.5 –1.37 × 10^3	100	196	170	42.1–491	100	214	186	90.0–505	100	219	204	110–458	100	131	134	80.5–201	100
Penta–CBs	196	195	n.d.–301	97.5	172	175	79.3–241	100	240	234	137–503	100	279	258	136–657	100	171	158	123–418	100
Hexa–CBs	101	97.4	n.d.–246	97.5	91.9	96.0	n.d.–250	92.5	117	123	21.6–177	100	136	132	36.5–313	100	72.5	71.0	26.8–107	100
Hepta–CBs	80.0	83.8	n.d.–128	97.5	72.8	77.0	37.2–100	100	100	98.8	56.3–195	100	125	112	50.7–362	100	80.7	62.3	54.3–247	100
CPs [b]	105	49.4	9.1–1.65 × 10^3	100	107	31.9	7.9–1.52 × 10^3	100	102	73.9	32.3–515	100	100	38.7	16.4–1.05 × 10^3	100	94.5	36.9	7.2–1.61 × 10^3	100
SCCPs	44.6	60.1	4.7–385	100	30.0	11.9	4.7–413	100	36.1	34.2	13.7–79.5	100	32.3	16.3	4.7–310	100	31.4	17.0	4.7–505	100
MCCPs	20.8	21.6	3.4–1.56 × 10^3	100	76.6	12.8	4.2–1.04 × 10^3	100	65.7	42.3	9.1–482	100	68.0	22.8	5.1–982	100	63.1	20.5	3.4–1.10 × 10^3	100
PBDEs[a]	472	260	4.0–3.21 × 10^3	100	550	274	66.2–4.01 × 10^3	100	660	495	35.9 –5.51 × 10^3	100	815	656	171–2.61 × 10^3	100	396	313	4.0–2.31 × 10^3	100
Tri–BDEs	32	14	n.d.–195	80.6	15.5	13.9	n.d.–70.4	85.0	15.0	13.9	n.d.–52.1	79.4	40.6	35.2	6.1–128	100	19.1	11.9	n.d.–93.6	79.5
Tetra–BDEs	122	83.8	3.9–638	100	99.0	70.4	10.2–345	100	165	144	14.7–408	100	256	192	57.3–632	100	150	113	3.95–610	100
Penta–BDEs	52.4	45.8	n.d.–211	97.2	52.4	39.0	n.d.–147	100	82.5	80.1	11.1–247	100	182	159	21.5–404	100	52.9	54.0	n.d.–134	97.4
Hexa–BDEs	86.0	73.9	7.5–416	100	89.1	53.1	7.6–1.28 × 10^3	100	135	119	7.6–739	100	275	247	81.8–642	100	121	80.4	7.6–1.27 × 10^3	100
Hepta–BDEs	2.0	n.d.	n.d.–22.7	36.1	7.2	n.d.	n.d.–261	20.0	6.7	n.d.	n.d.–139	38.2	1.2	n.d.	n.d.–18.5	24.3	11.4	n.d.	n.d.–226	33.3
Octa–BDEs	13.7	n.d.	n.d.–137	36.1	13.1	n.d.	n.d.–296	30.0	17.9	n.d.	n.d.–211	44.1	11.6	n.d.	n.d.–118	37.8	24.3	n.d.	n.d.–328	33.3
Nona–BDEs	17.3	n.d.	n.d.–502	11.1	23.9	n.d.	n.d.–407	20.0	64.4	n.d.	n.d.–1.23 × 10^3	32.4	8.2	n.d.	n.d.–226	16.2	5.4	n.d.	n.d.–90.3	23.3

Deca−BDE	134	n.d.	n.d.−2.30 × 10^3	16.7	251	n.d.	n.d.−3.67 × 10^3	40.0	174	7.4	n.d.−4.83 × 10^3	55.9	60.0	n.d.	n.d.−1.44 × 10^3	29.7	11.7	n.d.	n.d.−214	15.4
NBFRs[a]	44.1	29.9	2.2−312	100	51.9	26.3	1.8−312	100	65.9	52.4	7.0−343	100	63.5	60.5	19.9−153	100	47.7	34.7	3.7−352	100
ATE	1.6	0.7	n.d.−10.5	69.4	1.0	n.d.	n.d.−10.5	45.0	2.5	1.8	n.d.−9.2	73.5	2.8	1.1	n.d.−9.6	64.9	2.0	0.7	n.d.−24.0	61.5
TBECH	2.0	n.d.	n.d.−31.8	19.4	1.5	n.d.	n.d.−23.9	25.0	2.4	n.d.	n.d.−21.8	23.5	0.8	n.d.	n.d.−13.8	16.2	0.6	n.d.	n.d.−16.3	7.7
BATE	0.2	n.d.	n.d.−4.8	5.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	n.d.−1.2	2.7	0.6	n.d.	n.d.−24.1	2.6
TBCO	1.5	n.d.	n.d.−34.1	8.3	1.5	n.d.	n.d.−15.9	15.0	6.7	4.3	n.d.−20.6	50.0	5.2	n.d.	n.d.−31.5	35.1	4.2	n.d.	n.d.−25.9	43.6
PBB	2.6	n.d.	n.d.−44.9	41.7	5.3	n.d.	n.d.−78.6	42.5	5.8	1.1	n.d.−39.2	50.0	4.1	2.2	n.d.−16.3	59.5	2.9	n.d.	n.d.−36.4	35.9
TBCT	0.5	n.d.	n.d.−9.9	11.1	0.2	n.d.	n.d.−1.2	12.5	1.6	n.d.	n.d.−14.4	23.5	0.3	n.d.	n.d.−5.2	16.2	0.2	n.d.	n.d.−6.7	2.6
DPTE	20.1	17.9	n.d.−91.7	97.2	24.4	19.0	1.8−130	100	28.0	25.7	1.6−103	100	31.9	29.3	14.5−65.5	100	17.8	20.3	2.3−37.4	100
HBB	4.9	3.5	n.d.−29.7	86.1	7.2	4.8	n.d.−39.7	95.0	7.9	7.5	n.d.−37.2	85.3	14.5	11.2	n.d.−29.3	94.6	5.8	5.7	n.d.−28.4	87.2
PBBA	6.3	n.d.	n.d.−138	30.6	5.8	n.d.	n.d.−56.0	20.5	8.0	5.0	n.d.−84.1	55.9	7.1	5.0	n.d.−28.1	75.7	5.0	10.1	n.d.−195	69.2
BTBPE	4.8	n.d.	n.d.−20.8	2.8	5.0	n.d.	n.d.−76.6	12.5	3.0	n.d.	n.d.−49.3	11.8	n.d.	n.d.	n.d.	n.d.	n.d.	3.7	n.d.−72.3	7.7

DF: detection frequency; n.d.: not detected. CPs: chlorinated paraffins; OCPs: organochlorine pesticides; PCBs: polychlorinated biphenyls; DDTs: dichlorodiphenyltrichloroethane; HCHs: hexachlorocyclohexanes; HCB: hexachlorobenzene; PBDEs: polybrominated diphenyl ethers; NBFRs: new brominated flame retardants; SCCPs: short-chain chlorinated paraffins; MCCPs: medium-chain chlorinated paraffins; ATE: including allyl 2,4,6-tribromophenyl ether; BATE: 2-bromoallyl-2,4,6-tribromophenyl ether; PBB: pentabromobenzene; HBB: hexabromobenzene; DPTE: (2,3-dibromopropyl) (2,4,6-tribromophenyl) ether; TBECH: 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane; TBCO: tetrabromocyclooctane; TBCT: tetrabromo-o-chlorotoluene; PBBA: pentabromobenzylacrylate; BTBPE: 1,2-bis (2,4,6-tribromophenoxy) ethane.

[a] The unit was pg/g ww.

[b] The unit was ng/g ww.

lower than those in Greenland, Canada, and the United States (Table S9). Comparatively, much lower NBFR concentrations were detected. The concentration of Σ_{10}NBFRs was in the 1.71−352 pg/g ww range, with a median of 38.9 pg/g ww. DPTE, the most abundant NBFR compound, had a median concentration of 21.4 pg/g ww. Currently, limited data are available for NBFRs in fish. The level of NBFRs in the present study was of the same order of magnitude as in the earlier study in Taihu Lake (Zheng et al., 2018) and in reports from other countries (Poma et al., 2014; Venisseau et al., 2018; Widelka et al., 2016) (Table S10). All the BFRs were several orders of magnitude lower than the SCCPs and MCCPs.

3.2. Composition profiles and sources

Among the OCPs measured, DDTs accounted for 97.1%−99.9% of total OCPs in five fish species, followed by HCHs (0.07%−2.24%) in average. Among the DDTs, p,p'-DDE occurred at the highest concentrations, accounting for 85.8%−96.5% of ΣDDTs (Fig. 1A and S3A). Technical DDT mixtures typically containing 75%, p,p'-DDT, followed by o,p'-DDT (15%), p,p'-DDE (5%), and others (<5%) (Wang et al., 2013). The high percentage of DDE found in the present study demonstrated that the DDTs in fish were mainly historical residues because DDT can be converted to DDD and DDE under anaerobic and aerobic conditions, respectively. Of the HCH isomers, β-HCH accounted for 34.2%−78.6% of the ΣHCHs (Fig. 1A and S3B), which was consistent with previous reports in Taihu Lake (Yuan et al., 2012; Wang et al., 2013). Commercial HCHs include two kinds of products: the pure γ-HCH isomer (lindane) and the technical HCH mixture containing α-, β-, γ-, and δ-HCH at 65%−70%, 5%−5%, 12%−14%, and 6%, respectively (Willett et al., 1998). The high β-HCH concentrations in the fish samples might have been mainly due to isomer conversion of γ-/α-HCH to β-HCH in the environment or in the body of the fish. The higher bioconcentration factor of β-HCH relative to the α-isomer in aquatic organisms is another important factor. Furthermore, β-HCH has more persistent and stable properties than other HCH isomers (Willett et al., 1998). Therefore, HCHs and DDTs in Taihu Lake were mainly attributable to historical residues of commercial products.

Medium-chlorinated PCBs were abundant in the samples, with penta-PCBs (27.9%) being the most abundant congeners, followed by tetra-PCBs (25.0%) and hexa-PCBs (14.9%) (Fig. 1A and S3C). The PCB composition profiles were similar to the technical PCB product Aroclor 1252, which indicated that Aroclor 1252 might be an important source of PCBs in Taihu Lake. Considering the large contribution of tetra- and penta-PCBs in the present result, commercial Aroclor 1242, 1248, and 1254 might also be important sources in the area because tri-to penta-PCBs are the main components in these commercial products. In addition, it should be noted that the abundant medium-chlorinated PCBs in fish can also be a result of biomagnification of these chemicals through food chains because many results have shown that medium-chlorinated PCBs have the highest trophic magnification factor values compared with lower- or higher-chlorinated congeners (Yu et al., 2012; Yuan et al., 2019). Hence, the high contribution of medium-chlorinated PCBs was mainly attributed to the use of technical products and the different magnification properties of PCBs.

The most abundant congeners of CPs were $C_{10}H_{16}Cl_6$ and $C_{10}H_{15}C_7$ for SCCPs and $C_{14}H_{24}Cl_6$ and $C_{14}H_{23}Cl_7$ for MCCPs (Fig. 1C). For SCCPs, C_{10} and C_{11} were found to be the predominant carbon groups, with median percentages of 36.1% and 26.3%, respectively, followed by C_{12} (20.3%) and C_{13} (17.3%). For MCCPs, the congener group C_{14} was observed to be the most abundant, accounting for 52.3%, followed by C_{15} (19.0%) and C_{16} (15.9%). Similar congener group profiles were observed in aquatic foods from 18 provinces of China (Wang et al., 2018b), as well as in composite bivalve and

mollusk samples along the Bohai Sea coast in China (Ma et al., 2014; Yuan et al., 2012). The present profiles were similar to CP42 and CP52, which were most commonly used in commercial products (Yuan et al., 2019), suggesting the commercial products as a possible source.

In the present study, the PBDE patterns in fish followed a sequence of BDE47 and BDE154, which accounted for 32.9% and 24.7% of total PBDEs, respectively (Fig. 1B and S3D), which is consistent with a previous study from the same lake (Yu et al., 2012). The higher contribution of BDE47 rather than BDE99 might be attributed to specific commercial Penta-BDEs that might be consumed in this region (Qiu et al., 2010; Yu et al., 2012). The high-brominated congeners accounted for less than 1% of total PBDEs. BDE 47 is the main congener in commercial Penta-BDEs such as DE-71 and Bromkal 70-5DE (Huang et al., 2019b). A Deca-BDE product with a BDE209 content >98% was the main commercial product being produced and used in China. The results of the present study might have resulted from lower bioaccumulation of BDE209 and higher bioaccumulation of medium-brominated congeners (Yu et al., 2012). Among the NBFRs detected, DPTE accounted for a median of 57.3%, followed by HBB (15.2%) and PBBA (2.3%). Currently, available data on NBFRs are very limited. High DPTE concentrations (470 ng/g ww) have been detected in the blubber of harp seals from Greenland and the Barents Sea (von der Recke and Vetter, 2007), indicating DPTE accumulation in fish. In addition, the high PBBA contribution might be attributed to production of the chemical in the Yangtze River Delta, where Taihu Lake is located. To the authors' best knowledge, currently, there are nine factories that can produce PBBA in China, and four of these are located around the Yangtze River Delta. Therefore, it is not surprising to find a high BPPA contribution in fish from Taihu Lake.

3.3. Temporal trends in HOPs

In the present study, the collected fish reflected the pollution situation every year. The levels and composition profiles of DDTs and HCHs did not change significantly during 2011–2018 (Fig. 2 and S4). Although China has prohibited the usage of DDTs and HCHs since the 1980s, the chemicals are still widely detected because of their long half-lives in the environment. Similar to DDTs and HCHs, NBFRs showed no significant increasing or decreasing trends (Fig. 2A). The highest PBDE concentration was presented in 2012 with a median of 609 pg/g ww, and the lowest was observed in 2018 with a median of 247 pg/g ww (Fig. S4E). The highest NBFR concentrations were observed with a median of 80.3 pg/g ww in 2011 and the lowest in 2012, with a median of 24.7 pg/g ww

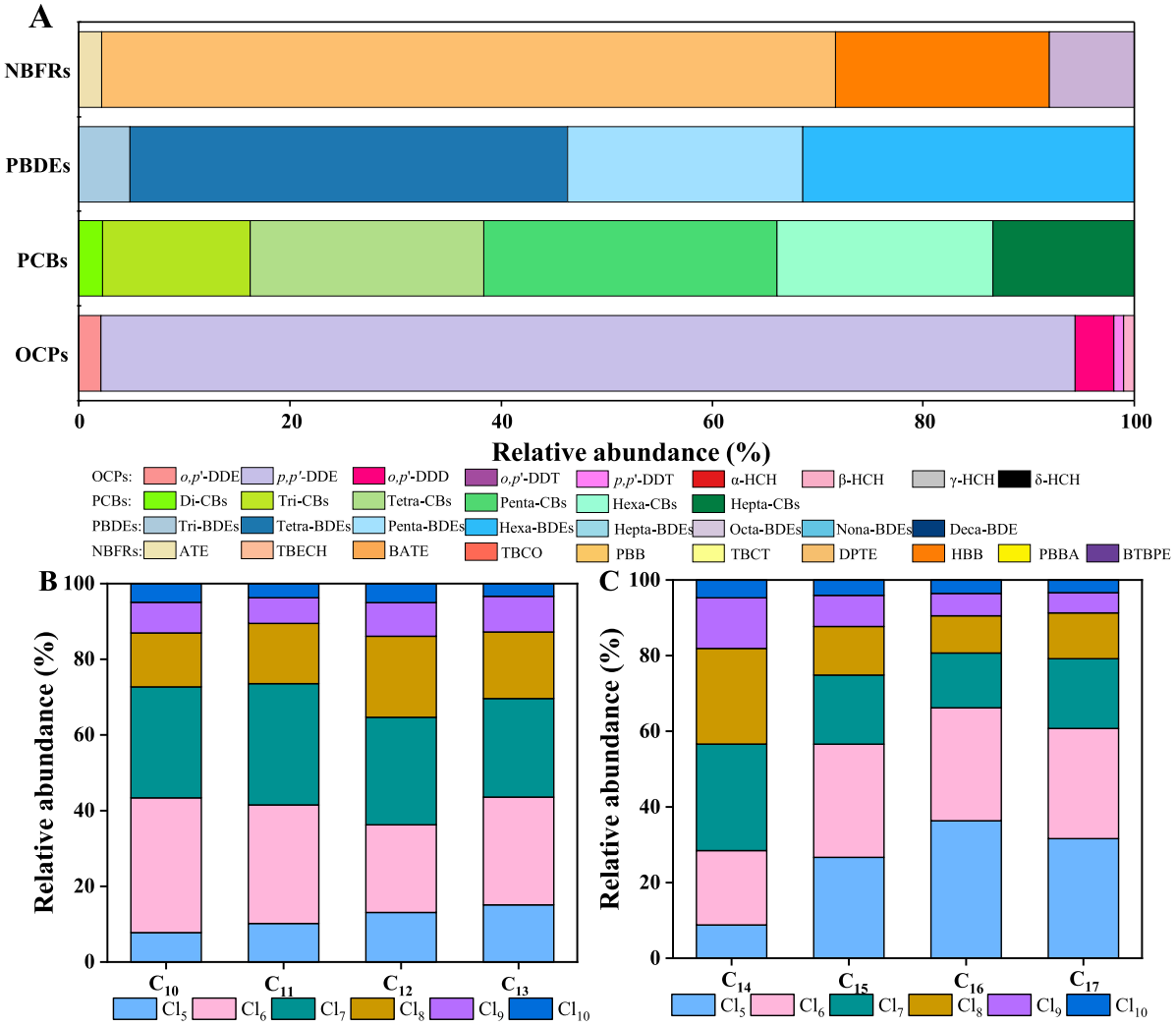

Fig. 1. Composition profiles of HOPs in fish from Taihu Lake (A: OCPs, PCBs, PBDEs, NBFRs; B: SCCPs; C: MCCPs).

(Fig. S4F). With the restriction of PBDEs, other BFRs such as NBFRs might be replacing them. In the present study, the use of NBFRs to replace PBDEs was not yet clearly observed on the basis of the concentration ratios of NBFRs to PBDEs ($p = 0.21$) (Fig. S5). This might have been the case mainly because PBDEs were still the most widely used BFRs, whereas NBFRs were less used in China. On the contrary, the median concentrations of PBDEs showed a significant decreasing trend ($p < 0.01$), which might be because some commercial PBDE products were prohibited in China and the relatively shorter half-lives of PBDEs in the environment compared with DDTs and HCHs. However, for PCBs, a slight increasing trend was observed ($p = 0.13$) (Fig. 2A and S4D), although the chemicals were banned in 1974 in China. These results might be attributed to the long half-lives of PCBs in the environment. For example, PCB153 has an average residence time of approximately 110 years in the environment (Venisseau et al., 2018). Furthermore, a recent report showed considerable unintentional sources of PCB from industries such as pigments and paints, metallurgical industry combustion, and others (Zhao et al., 2020). More studies should be conducted for the possible increasing trend of PCBs and it should deserve further long-term attention.

As for the other HOPs, an obvious increasing trend was observed for HCB from the initial 10.9–108 pg/g ww from 2011 to 2018 (Fig. 2B and S4C). In China, HCB has not been directly used as a pesticide, but has mainly been used in the production of pentachlorophenol, sodium pentachlorophenolate, fireworks, and reagents (Zhang et al., 2012). The usage and production of HCB were significantly reduced beginning in 1983, and the chemical was completely banned in 2004. However, HCB can still be derived from incomplete combustion, from old dump sites, and from pesticides, chlorinated aromatics, and solvents (Zhang et al., 2012). Therefore, the increasing trend of HCB contamination in fish from Taihu Lake might indicate that there are new sources of the chemical, which require further investigation. Similarly, SCCP and MCCP contamination levels showed increasing trends from 2011 to 2018 (Fig. 2B and S4G–H). SCCPs are mainly used as high-pressure additives in metalworking fluid, and MCCPs are widely used as plasticizers in polyvinyl chloride plastics (van Mourik et al., 2016). CP production in China began in the 1950s. In 1978, China's total CP production was only approximately 3.4 kt (Wei et al., 2016). However, it grew rapidly to 0.6 million tons in 2007, and reached 0.8 and 1.05 million tons in 2010 and 2013, respectively (Wang et al., 2018a; Wei et al., 2016; Zeng et al., 2011). At present, China has become the largest producer and exporter of CPs in the world. With SCCPs being listed as priority controlled pollutants in Annex A in 2017 by the Stockholm Convention (Zou et al., 2018), temporal variations of CPs in the environment deserve further long-term attention.

3.4. Human health risks of HOPs through fish consumption

The destruction of the environment by human beings will in turn bring potential risk to human beings. To know whether fish consuming in Taihu Lake poses potential human health risks and which types of HOPs pose the greatest risk, the non-carcinogenic risks of HOPs were estimated using HQ values. Assuming similar toxic endpoints for HOPs, their HQ values were calculated and are shown in Fig. S6. The median HQ values of the HOPs were less than one unit for both adults and children. To consider co-exposure to multiple contaminants through fish consumption, the total non-carcinogenic risks of HOPs were calculated by the addition method using the mathematical sum of HQ values of each chemical (Lei et al., 2015). As a result, the median total HQ values of HOPs through fish consumption were 0.027–0.043 for children and 0.023–0.037 for adults (Fig. 3). In addition, the high exposure was also estimated using the 95th percentile concentrations of HOPs (Table S11). This analysis revealed that the non-carcinogenic risks were in the range of 0.038–0.073 for adults and 0.040–0.083 for children during 2011–2018. All the HQ values were less than one unit, suggesting that there are no obvious non-carcinogenic risks for chemicals through fish consuming in Taihu Lake, although all the HOPs were considered using the addition method.

Among the HOPs, PCBs had the highest HQ value, followed by DDTs, with SCCPs being the lowest. Although CPs were present in much higher concentrations than the other HOPs, the risks were very much lower because of their high RfD value. Comparatively, the highest contributor in median HQ, PCBs, accounted for 67.7%–84.1% of the total risks, followed by DDTs (13.5%–30.1%). Similarly, PCBs showed higher non-carcinogenic risks than DDTs, with the mean contributions of PCBs and DDTs accounting for 16.9% and 8.5% of the totals considering multiple contaminants including POPs and trace elements such as arsenic, cadmium, mercury, and others (Yu et al., 2014). However, DDTs were more harmful than PCBs in terms of carcinogenic risks regardless based on median or 95th percentile concentrations (Fig. 3 and S6), which was consistent with the report by Yu et al. (2014). Furthermore, most HOPs posed no carcinogenic risk through fish consuming in Taihu Lake. The total carcinogenic risks on the basis of the addition method were slightly higher than 10^{-6}, for both adult and children, which meant that fish consuming in Taihu Lake had a low carcinogenic risk. However, the results are based on the lifetime cancer risk. The results demonstrated that DDTs and PCBs were the most important contaminants, resulting in the highest human health risks from fish consuming in

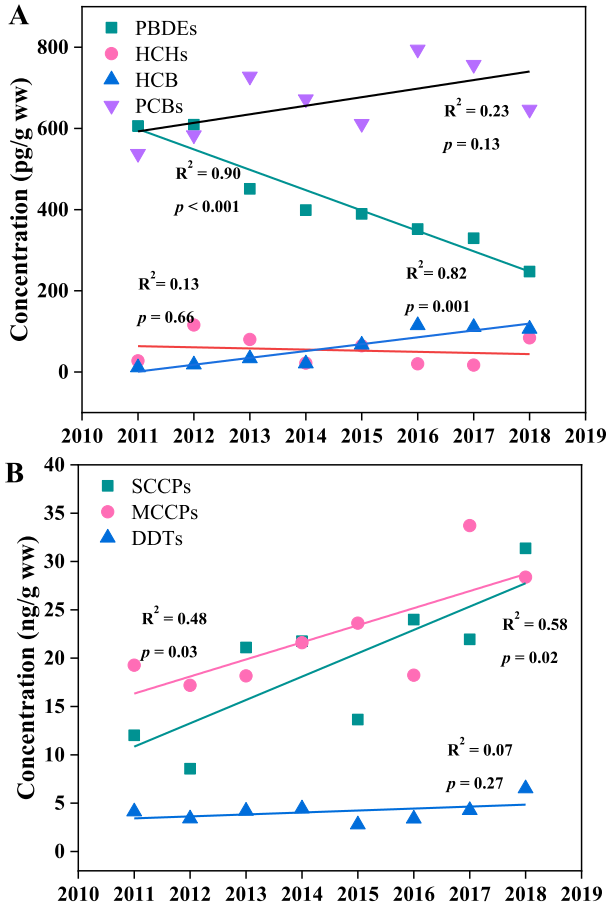

Fig. 2. Temporal trends of HOPs (median concentrations) in fish from Taihu Lake in 2011–2018.

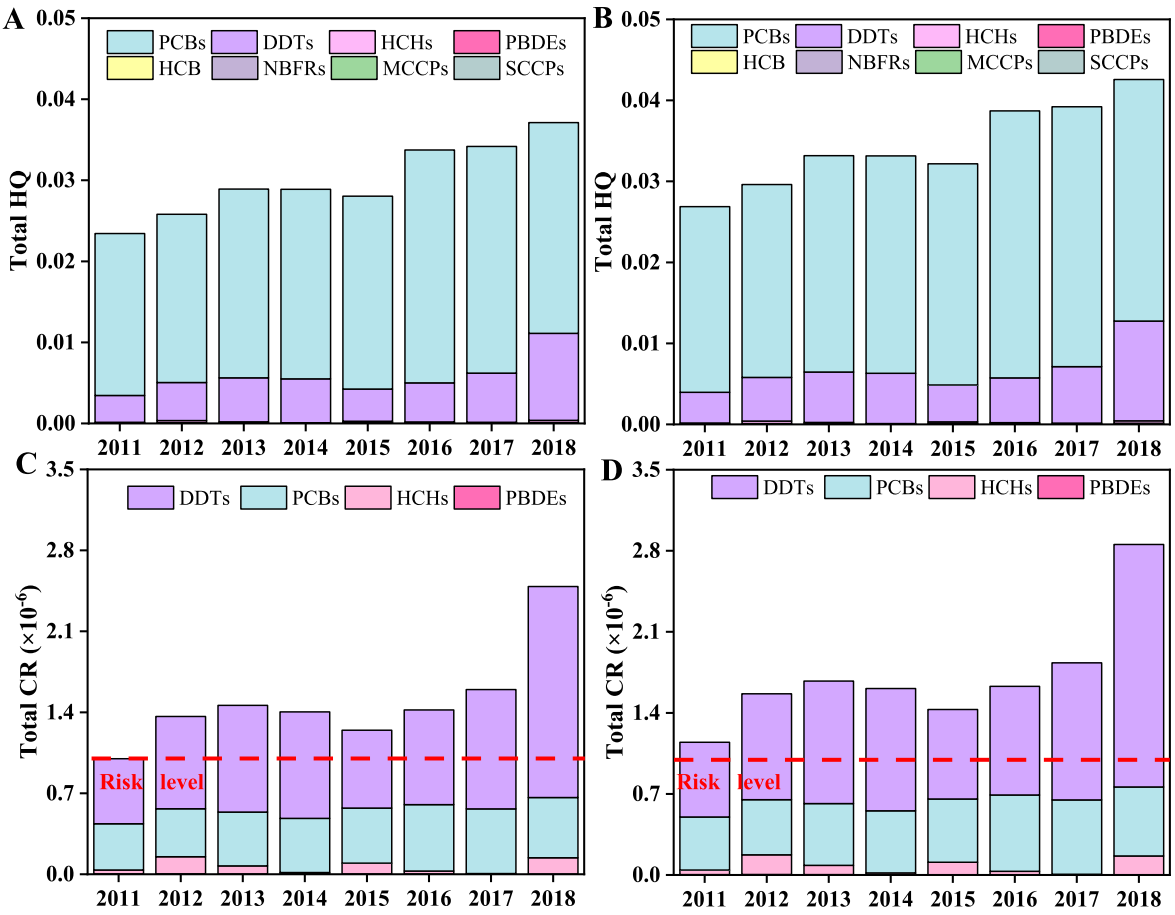

Fig. 3. Human health risks of HOPs by fish consumption by residents (A: Total HQ values of non-carcinogenic risk for adults; B: Total HQ values of non-carcinogenic risk for children; C: Total CR values of carcinogenic risk for adults; D: Total CR values of carcinogenic risk for children).

Taihu Lake, even approximately 10 years later than the previous study, in which the samples were collected in 2009 from the same lake (Yu et al., 2014). In addition, although the non-carcinogenic risks of CPs were generally very much lower and it can be anticipated that over the next several years, CPs will not have an obvious adverse impact on human health, the risks from CPs should be of concern considering the increasing trends in their concentrations and their widespread use in China.

4. Conclusions

HOPs, including PBDEs, NBFRs, CPs, PCBs, and OCPs, in fish from Taihu Lake collected during 2011–2018 were studied. Among the HOPs measured, MCCPs had the highest concentrations and NBFRs the lowest. HOP concentrations were less than or equal to those of other water systems worldwide with the exception of CPs, which were in the same magnitude as at other sites in China, but much higher than in European and American countries. CPs and HCB were found to be significantly increasing, whereas PBDEs were decreasing during 2011–2018. The use of NBFRs to replace PBDEs was not yet clearly observed. Considering the persistence of the HOPs in the environment and the rapid development of new chemicals used in products, longer observations are necessary in the future. There were no obvious non-carcinogenic risks from the chemicals through fish consuming in Taihu Lake, although all the HOPs were considered to be additive. However, there were possible carcinogenic risks from HOPs. DDTs and PCBs were still the most important contaminants that posed the highest human health risks, although usage and production of these chemicals were banned 40 years ago. In addition, considering the high levels and the increasing trends of CPs, the risks from these chemicals should be of concern in the future.

Author statement

Jinjing Ma: Methodology, Formal analysis, and draft preparation. Xiangnan Li: Methodology, Formal analysis, and draft preparation. Shengtao Ma: Methodology. Xiaolan Zhang: Formal analysis. Guiying Li: Formal analysis. Yingxin Yu: Design, writing, reviewing & editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.115497.

References

Aamir, M., Khan, S., Nawab, J., Qamar, Z., Khan, A., 2016. Tissue distribution of HCH and DDT congeners and human health risk associated with consumption of fish collected from Kabul River, Pakistan. Ecotoxicol. Environ. Saf. 125, 128–134. https://doi.org/10.1016/j.ecoenv.2015.12.005.

Basconcillo, L.S., Backus, S.M., McGoldrick, D.J., Zaruk, D., Sverko, E., Muir, D.C.G., 2015. Current status of short- and medium chain polychlorinated n-alkanes in top predatory fish across Canada. Chemosphere 127, 93–100. https://doi.org/10.1016/j.chemosphere.2015.01.016.

Cao, D.D., Gao, W., Wu, J., Lv, K., Xin, S.Z., Wang, Y.W., Jiang, G.B., 2019. Occurrence and human exposure assessment of short- and medium-chain chlorinated paraffins in dusts from plastic sports courts and synthetic turf in Beijing, China. Environ. Sci. Technol. 53, 443–451. https://doi.org/10.1021/acs.est.8b04323.

Stockholm Convention, 2009a. UNEP/POPS/POPRC.4/14 Listing of Hexabromodiphenyl Ether and Heptabromodiphenyl Ether.

Stockholm Convention, 2009b. UNEP/POPS/POPRC.4/18 Listing of Tetrabromodiphenyl Ether and Pentabromodiphenyl Ether.

de la Torre, A., Navarro, I., Sanz, P., Martinez, M.D., 2020. Organophosphate compounds, polybrominated diphenyl ethers and novel brominated flame retardants in European indoor house dust: use, evidence for replacements and assessment of human exposure. J. Hazard Mater. 382, 121009. https://doi.org/10.1016/j.jhazmat.2019.121009.

Dong, S.J., Zhang, S., Li, X.M., Li, T., Fan, M.D., Wang, Y.X., Cheng, J., Wang, R.G., Zou, Y., Wang, S., Suo, D.C., Wang, P.L., Su, X.O., 2020. Short- and medium-chain chlorinated paraffins in plastic animal feed packaging and factors affect their migration into animal feed. J. Hazard Mater. 389, 121836. https://doi.org/10.1016/j.jhazmat.2019.121836.

GB .2-2007, 2007. State Standard of the People's Republic of China. The Specification for Marine Monitoring. Part 2: Data Processing and Quality Control of Analysis.

Ge, X., Ma, S.T., Zhang, X.L., Yang, Y., Li, G.Y., Yu, Y.X., 2020. Halogenated and organophosphorous flame retardants in surface soils from an e-waste dismantling park and its surrounding area: distributions, sources, and human health risks. Environ. Int. 139 https://doi.org/10.1016/j.envint.2020.105741. UNSP 105741.

Gerber, R., Smit, N.J., Van Vuren, J.H.J., Nakayama, S.M.M., Yohannes, Y.B., Ikenaka, Y., Ishizuka, M., Wepener, V., 2016. Bioaccumulation and human health risk assessment of DDT and other organochlorine pesticides in an apex aquatic predator from a premier conservation area. Sci. Total Environ. 550, 522–533. https://doi.org/10.1016/j.scitotenv.2016.01.129.

Harada, K.H., Takasuga, T., Hitomi, T., Wang, P.Y., Matsukami, H., Koizumi, A., 2011. Dietary exposure to short-chain chlorinated paraffins has increased in Beijing, China. Environ. Sci. Technol. 45, 7019–7027. https://doi.org/10.1021/es200576d.

Huang, H.T., Gao, L.R., Xia, D., Qiao, L., 2017. Bioaccumulation and biomagnification of short and medium chain polychlorinated paraffins in different species of fish from Liaodong Bay, North China. Sci Rep-UK 7, 10749. https://doi.org/10.1038/s41598-017-06148-5.

Huang, Y.M., Qing, X., Jiang, G., Chen, L.G., He, Q.S., Meng, X.Z., Gao, B., 2019a. Short-chain chlorinated paraffins in fish from two developed regions of China: occurrence, influencing factors and implication for human exposure via consumption. Chemosphere 236. https://doi.org/10.1016/j.chemosphere.2019.07.048.

Huang, Y.M., Yan, M.T., Nie, H.Y., Wang, W.J., Wang, J., 2019b. Persistent halogenated organic pollutants in follicular fluid of women undergoing in vitro fertilization from China: occurrence, congener profiles, and possible sources. Environ. Pollut. 244, 1–8. https://doi.org/10.1016/j.envpol.2018.09.134.

Labadie, P., Blasi, C., Le Menach, K., Geneste, E., Babut, M., Perceval, O., Budzinski, H., 2019. Evidence for the widespread occurrence of short- and medium-chain chlorinated paraffins in fish collected from the Rhone River basin (France). Chemosphere 223, 232–239. https://doi.org/10.1016/j.chemosphere.2019.02.069.

Lei, B.L., Zhang, K.Q., An, J., Zhang, X.Y., Yu, Y.X., 2015. Human health risk assessment of multiple contaminants due to consumption of animal-based foods available in the markets of Shanghai, China. Environ. Sci. Pollut. Res. 22, 4434–4446. https://doi.org/10.1007/s11356-014-3683-0.

Li, H.J., Li, J.K., Li, H.Z., Yu, H., Yang, L.X., Chen, X.F., Cai, Z.W., 2019. Seasonal variations and inhalation risk assessment of short-chain chlorinated paraffins in PM2.5 of Jinan, China. Environ. Pollut. 245, 325–330. https://doi.org/10.1016/j.envpol.2018.10.133.

Ma, X.D., Chen, C., Zhang, H.J., Wang, Y.Z., Yao, Z.W., Chen, J.P., Chen, J.W., 2014. Congener-specific distribution and bioaccumulation of short-chain chlorinated paraffins in sediments and bivalves of the Bohai Sea, China. Mar. Pollut. Bull. 79, 299–304. https://doi.org/10.1016/j.marpolbul.2013.11.020.

Ma, S.T., Yu, Y.X., Yang, Y., Li, G.Y., An, T.C., 2019. A new advance in the potential exposure to "old" and "new" halogenated flame retardants in the atmospheric environments and biota: from occurrence to transformation products and metabolites. Crit. Rev. Environ. Sci. Technol. 50, 1935–1983. https://doi.org/10.1080/10643389.2019.1681051.

Malarvannan, G., Takahashi, S., Ikemoto, T., Isobe, T., Kunisue, T., Sudaryanto, A., Miyagi, T., Nakamura, M., Yasumura, S., Tanabe, S., 2011. Contamination status and spatial distribution of organochlorine compounds in fishes from Nansei Islands, Japan. Mar. Pollut. Bull. 63, 541–547. https://doi.org/10.1016/j.marpolbul.2011.02.002.

Poma, G., Volta, P., Roscioli, C., Bettinetti, R., Guzzella, L., 2014. Concentrations and trophic interactions of novel brominated flame retardants, HBCD, and PBDEs in zooplankton and fish from Lake Maggiore (Northern Italy). Sci. Total Environ. 481, 401–408. https://doi.org/10.1016/j.scitotenv.2014.02.063.

POPRC, 2017. Recommendation by the Persistent Organic Pollutants Review Committee to List Short-Chain Chlorinated Paraffins in Annex A to the Convention. UNEP/POPS/COP.8/14).

Qiu, X.H., Zhu, T., Hu, J.X., 2010. Polybrominated diphenyl ethers (PBDEs) and other flame retardants in the atmosphere and water from Taihu Lake, East China. Chemosphere 80, 1207–1212. https://doi.org/10.1016/j.chemosphere.2010.06.013.

Sun, R.X., Luo, X.J., Tang, B., Li, Z.R., Huang, L.Q., Wang, T., Mai, B.X., 2016. Short-chain chlorinated paraffins in marine organisms from the Pearl River Estuary in South China: residue levels and interspecies differences. Sci. Total Environ. 553, 196–203. https://doi.org/10.1016/j.scitotenv.2016.02.144.

Tornkvist, A., Glynn, A., Aune, M., Darnerud, P.O., Ankarberg, E.H., 2011. PCDD/F, PCB, PBDE, HBCD and chlorinated pesticides in a Swedish market basket from 2005–Levels and dietary intake estimations. Chemosphere 83, 193–199. https://doi.org/10.1016/j.chemosphere.2010.12.042.

USEPA United States Environmental Protection Agency, 2000. In: Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, EPA 823-B-00-008, November 2000. Volume 2: Risk Assessment and Fish Consumption Limits, third ed. Office of Water, Washington, DC.

USEPA United States Environmental Protection Agency, 2013. EPA Announces Chemicals for Risk Assessment in 2013, Focus on Widely Used Flame Retardants. United States Environmental Protection Agency, Washington, D.C., United States.

van Mourik, L.M., Gaus, C., Leonards, P.E.G., de Boer, J., 2016. Chlorinated paraffins in the environment: a review on their production, fate, levels and trends between 2010 and 2015. Chemosphere 155, 415–428. https://doi.org/10.1016/j.chemosphere.2016.04.037.

Venisseau, A., Bichon, E., Brosseaud, A., Vaccher, V., Lesquin, E., Larvor, F., Durand, S., Dervilly-Pinel, G., Marchand, P., Le Bizec, B., 2018. Occurrence of legacy and novel brominated flame retardants in food and feed in France for the period 2014 to 2016. Chemosphere 207, 497–506. https://doi.org/10.1016/j.chemosphere.2018.05.122.

von der Recke, R., Vetter, W., 2007. Synthesis and characterization of 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and structurally related compounds evidenced in seal blubber and brain. Environ. Sci. Technol. 41, 1590–1595. https://doi.org/10.1021/es062383s.

Wang, D.Q., Yu, Y.X., Zhang, X.Y., Zhang, D.P., Zhang, S.H., Wu, M.H., 2013. Organochlorine pesticides in fish from Taihu Lake, China, and associated human health risk assessment. Ecotoxicol. Environ. Saf. 98, 383–389. https://doi.org/10.1016/j.ecoenv.2013.07.012.

Wang, J.Z., Jia, X.W., Gao, S.T., Zeng, X.Y., Li, H.R., Zhou, Z., Sheng, G.Y., Yu, Z.Q., 2016. Levels and distributions of polybrominated diphenyl ethers, hexabromocyclododecane, and tetrabromobisphenol A in sediments from Taihu Lake, China. Environ. Sci. Pollut. Res. 23, 10361–10370. https://doi.org/10.1007/s11356015-5511-6.

Wang, P.W., Zhao, N., Cui, Y., Jiang, W., Wang, L.N., Wang, Z.H., Chen, X.F., Jiang, L., Ding, L., 2018a. Short-chain chlorinated paraffin (SCCP) pollution from a CP production plant in China: dispersion, congener patterns and health risk assessment. Chemosphere 211, 456–464. https://doi.org/10.1016/j.chemosphere.2018.07.136.

Wang, R.H., Gao, L.R., Zheng, M.H., Tian, Y.L., Li, J.G., Zhang, L., Wu, Y.N., Huang, H.T., Qiao, L., Liu, W.B., Su, G.J., Liu, G.R., Liu, Y., 2018b. Short- and medium- chain chlorinated paraffins in aquatic foods from 18 Chinese provinces: occurrence, spatial distributions, and risk assessment. Sci. Total Environ. 615, 1199–1206. https://doi.org/10.1016/j.scitotenv.2017.09.327.

Wei, G.L., Liang, X.L., Li, D.Q., Zhuo, M.N., Zhang, S.Y., Huang, Q.X., Liao, Y.S., Xie, Z.Y., Guo, T.L., Yuan, Z.J., 2016. Occurrence, fate and ecological risk of chlorinated paraffins in Asia: a review. Environ. Int. 92–93, 373–387. https://doi.org/10.1016/j.envint.2016.04.002.

Widelka, M., Lydy, M.J., Wu, Y., Chen, D., 2016. Statewide surveillance of halogenated flame retardants in fish in Illinois, USA. Environ. Pollut. 214, 627–634. https://doi.org/10.1016/j.envpol.2016.04.063.

Willett, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ. Sci. Technol. 32, 2197–2207. https://doi.org/10.1021/es9708530.

Xu, Z.A., Li, T., Bi, J., Wang, C., 2018. Spatiotemporal heterogeneity of antibiotic pollution and ecological risk assessment in Taihu Lake Basin, China. Sci. Total Environ. 643, 12–20. https://doi.org/10.1016/j.scitotenv.2018.06.175.

Xu, C., Gao, L.R., Zheng, M.H., Qiao, L., Cui, L.L., Wang, K.R., Huang, D., 2019. Short- and medium-chain chlorinated paraffins in commercial rubber track products and raw materials. J. Hazard Mater. 380, 120854. https://doi.org/10.1016/j.jhazmat.2019.120854.

Yadav, I.C., Devi, N.L., Singh, V.K., Li, J., Zhang, G., 2019. Measurement of legacy and

emerging flame retardants in indoor dust from a rural village (Kopawa) in Nepal: implication for source apportionment and health risk assessment. Ecotoxicol. Environ. Saf. 168, 304–314. https://doi.org/10.1016/j.ecoenv.2018.10.089.

Yu, Y.X., Zhang, S.H., Huang, N.B., Li, J.L., Pang, Y.P., Zhang, X.Y., Yu, Z.Q., Xu, Z.G., 2012. Polybrominated diphenyl ethers and polychlorinated biphenyls in freshwater fish from Taihu Lake, China: their levels and the factors that influence biomagnification. Environ. Toxicol. Chem. 31, 542–549. https://doi.org/10.1002/etc.1722.

Yu, Y.X., Wang, X.X., Yang, D., Lei, B.L., Zhang, X.L., Zhang, X.Y., 2014. Evaluation of human health risks posed by carcinogenic and non-carcinogenic multiple contaminants associated with consumption of fish from Taihu Lake, China. Food Chem. Toxicol. 69, 86–93. https://doi.org/10.1016/j.fct.2014.04.001.

Yuan, B., Wang, T., Zhu, N.L., Zhang, K.G., Zeng, L.X., Fu, J.J., Wang, Y.W., Jiang, G.B., 2012. Short chain chlorinated paraffins in mollusks from coastal waters in the Chinese Bohai Sea. Environ. Sci. Technol. 46, 6489–6496. https://doi.org/10.1021/es203839h.

Yuan, B., Vorkamp, K., Roos, A.M., Faxneld, S., Sonne, C., Garbus, S.E., Lind, Y., Eulaers, I., Hellstrom, P., Dietz, R., Persson, S., Bossi, R., de Wit, C.A., 2019. Accumulation of short-, medium-, and long-chain chlorinated paraffins in marine and terrestrial animals from Scandinavia. Environ. Sci. Technol. 53, 3526–3537. https://doi.org/10.1021/acs.est.8b06518.

Zeng, L.X., Wang, T., Wang, P., Liu, Q., Han, S.L., Yuan, B., Zhu, N.L., Wang, Y.W., Jiang, G.B., 2011. Distribution and trophic transfer of short-chain chlorinated paraffins in an aquatic ecosystem receiving effluents from a sewage treatment plant. Environ. Sci. Technol. 45, 5529–5535. https://doi.org/10.1021/es200895b.

Zhang, D.P., Zhang, X.Y., Yu, Y.X., Li, J.L., Yu, Z.Q., Wang, D.Q., Wu, M.H., Sheng, G.Y., Fu, J.M., 2012. Intakes of omega-3 polyunsaturated fatty acids, polybrominated diphenyl ethers and polychlorinated biphenyls via consumption of fish from Taihu Lake, China: a risk-benefit assessment. Food Chem. 132, 975–981. https://doi.org/10.1016/j.foodchem.2011.11.082.

Zhang, B.Y., Zhao, B., Xu, C., Zhang, J.B., 2017. Emission inventory and provincial distribution of short-chain chlorinated paraffins in China. Sci. Total Environ. 581, 582–588. https://doi.org/10.1016/j.sdtotenv.2016.12.167.

Zhang, C.X., Chang, H., Wang, H.P., Zhu, Y.R., Zhao, X.L., He, Y., Sun, F.H., Wu, F.C., 2019. Spatial and temporal distributions of short-, medium-, and long-chain chlorinated paraffins in sediment cores from nine lakes in China. Environ. Sci. Technol. 53, 9462–9471. https://doi.org/10.1021/acs.est.8b07296.

Zhao, S.Z., Jones, K.C., Li, J., Sweetman, A.J., Liu, X., Xu, Y., Wang, Y., Lin, T., Mao, S.D., Li, K.C., Tang, J., Zhang, G., 2020. Evidence for major contributions of unintentionally produced PCBs in the air of China: implications for the national source inventory. Environ. Sci. Technol. 45, 2163–2171. https://doi.org/10.1021/acs.est.9b06051.

Zheng, G.M., Wan, Y., Shi, S.N., Zhao, H.Q., Gao, S.X., Zhang, S.Y., An, L.H., Zhang, Z.B., 2018. Trophodynamics of emerging brominated flame retardants in the aquatic food web of Lake Taihu: relationship with organism metabolism across trophic levels. Environ. Sci. Technol. 52, 4632–4640. https://doi.org/10.1021/acs.est.7b06588.

Zhuo, M.H., Ma, S.T., Li, G.Y., Yu, Y.X., An, T.C., 2019. Chlorinated paraffins in the indoor and outdoor atmospheric particles from the Pearl River Delta: characteristics, sources, and human exposure risks. Sci. Total Environ. 650, 1041–1049. https://doi.org/10.1016/j.scitotenv.2018.09.107.

Zou, Y., Niu, S., Dong, L., Hamada, N., Hashi, Y., Yang, W.L., Xu, P.J., Arakawa, K., Nagata, J., 2018. Determination of short-chain chlorinated paraffins using comprehensive two–dimensional gas chromatography coupled with low resolution mass spectrometry. J. Chromatogr. A 1581, 135–143. https://doi.org/10.1016/j.chroma.2018.11.004, 2018.