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ABSTRACT: Because investigation on the temporal trends of persistent halogenated compounds (PHCs) is necessary to predict their future impacts on the environment and human health and evaluate the effectiveness of regulations on their production and usage, it is of concern to investigate annual temporal trends of PHCs in biota samples. This study examined the temporal trends of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and perfluorinated compounds (PFCs) in Chinese sturgeon (Acipenser sinensis) eggs over a period of 25 years (1984–2008), and 62 PCBs (19.2–1030 ng/g dw for total PCBs), 16 PBDEs (4.7–572 ng/g dw for total PBDEs), and 14 PFCs (26–46 ng/g dw for total PFCs) were detected. Although a decreasing temporal trend was observed for total PCBs with annual reduction rate of 3.4% ($\rho = 0.005$), a clear break point was observed around 1991, indicating their continuing emission in the 1980s in China. All major PBDEs showed increasing temporal trends, with annual change rates at 3.5–10.2% over the 25 years, but a sharp decreasing trend was observed after 2006, indicating a rapid response to the banning of PBDE usage in China in 2004. The greatest annual rate of increase was observed for BDE-28 (10.2%) followed by BDE-100 (7.7%), which would be due to metabolism input from higher brominated PBDEs. Significantly increasing temporal trends were observed for all PFCs, and the annual rates of increase were 7.9% and 5.9% for total perfluorinated carboxylic acids and perfluorooctanesulfonate (PFOS), respectively. A peak concentration for PFOS was observed in 1989, which may be related to the import history of PFCs in China. The present study is the first report of systematic temporal trends of PHCs in biota samples from China and shows that regulatory policy is needed to reduce their potential health and ecological risk in China considering the increasing temporal trends of PBDEs and PFCs.

INTRODUCTION

Persistent halogenated compounds (PHCs), including polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and perfluorinated compounds (PFCs), are of particular concern due to their environmental persistence, high bioaccumulation potentials, and toxicities. PBDEs have been widely used as flame retardant additives in synthetic textiles in rugs, draperies, and thermoplastics in a variety of consumer products and electronics, and PFCs have been manufactured for >50 years as fire-fighting foams, inks, water repellents, and coatings on paper. Previous studies have reported their global distribution in the environment, biomagnification in foodwebs, and adverse effects on wildlife and humans. Due to these concerns, PCBs and some PBDEs and PFCs have been listed in the Stockholm Convention on Persistent Organic Pollutants (POPs). Despite the ban on their use, these PHCs are still globally detected in sediments, atmosphere, and wildlife due to their environmental persistence and slack regulation and will continuously pose potential ecological and human health risks.

Temporal investigation of pollutants is useful in better understanding their future impacts on both the environment and human health and in evaluating the effectiveness of regulations on the production and usage of chemicals of concern. Previous studies have shown that temporal trends of PHCs in Europe and North America were generally related to the regulatory policy of their production, and decreasing trends of PCBs, PFCs and PBDEs have been observed after their production restriction in these regions. Different from...
North America and Europe, region-specific production history of PHCs was expected in China. PCBs were produced on a large scale in the decade from 1965 to 1975 in China (about 10,000 t (MT)) and were still used as additives to paint and were banned in the 1980s,17 10 years later than the production ban in the U.S. (production history: 1929–1976).18 The production of PBDEs has been reduced since 1980s in Europe but was still increasingly produced in China.19 Although the production of PFOS has been reduced since 2000 in North America,20 regulatory action on PFCs has not been established in China, and the production increased from 30 MT in 2002 to 247 MT in 2006.21 In addition to such region-specific emission history, Asia-Pacific countries offer the largest market demand for PHCs, especially for PBDEs, and it is estimated that nearly half of the total global demand for flame retardants was in Asian countries in 2014.22 Thus, investigation on temporal trends of PHCs is helpful for better evaluating the effectiveness of regulations on the production and usage of PHCs in Asia and understanding their future impacts on the environment. Several papers have documented the increasing trend of PFCs in snow cores from the Tibetan mountains23 and in the annual temporal trends of PCBs and PBDEs in sediment cores from China.24,25 Although these studies provided some information for understanding the temporal variation of PHCs,25,26 some factors such as biomagnification of pollutants in organisms and spatial variation in the environment may lead to different temporal trends of pollutants in biota samples from those in the environment.27 Temporal trends of pollutants in biota samples would be more relevant for ecological risk assessment when samples are available25,26 and thus, systematic investigation on the annual temporal trends of PHCs in biota samples from China is becoming more important.

The Chinese sturgeon (Acipenser sinensis) is listed as a grade I protected animal in China due to its rapidly declining population. The Chinese sturgeon is an excellent sentinel species for monitoring environmental organic contaminants because it is a predatory fish that can live for 40 years or longer and weigh as much as 500 kg.28 Our previous studies have reported the high accumulation of PHCs including PFCs, PBDEs, and PCBs in Chinese sturgeon.29–32 The objective of this study is to measure the concentrations of PFCs, PBDEs, and PCBs in eggs of Chinese sturgeon from 1984 to 2008 and then assess their temporal trends over a period of 25 years.

### MATERIALS AND METHODS

#### Chemicals and Reagents.

Eighteen target PFCs (detailed information is provided in Supporting Information Table S1) and eight stable isotopic labeled standards including $^{13}$C$_2$-PFHxA, $^{13}$C$_2$-PFOA, $^{13}$C$_2$-PFNA, $^{13}$C$_2$-PFDA, $^{13}$C$_2$-PFUnDa, $^{13}$C$_2$-PFDoDa, $^{13}$C$_2$-PFHxS, and $^{13}$C$_2$-PFOS were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Sixteen PBDEs (BDE-7, BDE-11, BDE-25, BDE-28, BDE-75, BDE-71, BDE-47, BDE-66, BDE-77, BDE-100, BDE-119, BDE-99, BDE-154, BDE-153, BDE-138, BDE-183) were selected as target compounds considering their predominance as reported in previous papers, and their standards were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). The mixture of standards of PCBs containing 142 number) were purchased from AccuStandard (New Haven, CT, U.S.A.). Oasis WAX (6 cc, 150 mg, 30 μm) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, U.S.A.). Ammonia solution (28–30%) was from Alfa Aesar Chemical Industries (Ward Hill, MA, U.S.A.). Dichloromethane (DCM), n-hexane, and acetone were pesticide residue grade and were obtained from OmniSolv (EM Science, Lawrence, KS, U.S.A.). Methanol and acetonitrile were all of HPLC grade and were purchased from Fisher Chemical Co. Sodium sulfate, silica gel (100–200 mesh size), and aluminum oxide (neutral, 150 mesh size) were purchased from Beijing Chemical Reagent (Beijing, China).

#### Collection of Chinese Sturgeon Eggs.

The Chinese sturgeon is an anadromous fish. Every June or July, maturing adults leave the ocean and ascend the main channel of the Yangtze River to spawn, and stay in the river for a period of approximately one year before reproducing in middle October to early November, and then they return to the sea for 3 to 5 years before spawning again. Because Chinese sturgeon is listed as a grade I protected animal (the highest level of protection) in China, the capture of Chinese sturgeon (eight to ten every year before 2008) were authorized for scientific purposes by the government of China. After artificial propagation, the live sturgeon must be released into the Yangtze River under the supervision of the local government. Among the more than >100,000 eggs for each female individual, less than 20 eggs were collected for monitoring pollutants. During the reproduction season in the period from 1984 to 2008, eggs of 105 female sturgeon individuals were collected and kept in formalin or at −20°C until analysis. Considering the potential age accumulation, we compared the body length of Chinese sturgeon individuals between different sampling years, because of the good linear relationship between age and body length.30 The body length of Chinese sturgeon individuals used in the present study were similar between different sampling years (ρ = 0.25); therefore, an age accumulation adjustment was not applied in the present paper when assessing temporal trends of target chemicals.

#### Sample Preparation and Analysis of PFCs, PBDEs, and PCBs.

Egg samples were freeze-dried in a freeze-dryer (FDU-200, EYELA, Japan) prior to extraction of chemicals, and the moisture content was 50.6 ± 2.4%, showing minor variation among different egg samples. The details for sample preparation and analysis of chemicals are given in Supporting Information.

#### Instrumental Analysis.

For PFC analysis, aliquots of extracts were analyzed using a Waters ACQUITY UPLC system (Waters, Milford, MA, U.S.A.) with a Waters Micromass Quattro Premier XE (triple-quadrupole) detector operated in electrospray negative mode.31 Separation of PFCs was achieved with a Waters ACQUITY UPLC BEH C18 column (1.7 μm; 2.1 mm × 100 mm), preceded by a Waters ACQUITY UPLC BEH C18 guard column (1.7 μm; 2.1 mm × 50 mm). The guard column displaced the peaks caused by contamination from the HPLC such that they did not interfere with the analytes in the samples. The injection volume was 5 μL. Methanol (A) and 5 mM ammonium acetate (B) were used as the mobile phases.

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Table 1. Concentrations of PCBs and PBDEs\(^a\) in 84 Chinese Sturgeon Eggs from 1984 to 2008

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<tr>
<th></th>
<th>mean ± SD</th>
<th>minimum</th>
<th>maximum</th>
<th>detection %</th>
<th>contribution %(^b)</th>
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<td>PCB178</td>
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<td>63</td>
<td>60</td>
<td>1.8 ± 2.1</td>
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<td>PCB189</td>
<td>23 ± 19</td>
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<td>60</td>
<td>7.0 ± 9.9</td>
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<td>PCB297/117</td>
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<td>0.18 ± 0.18</td>
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<td>PCB128</td>
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<td>3.0 ± 6.7</td>
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<td>12</td>
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<td>PCB115</td>
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<td>76</td>
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<td>PCB25</td>
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<td>PCB47/48/75</td>
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<td>0.3</td>
<td>116</td>
<td>100</td>
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<td>ΣPBDEs</td>
<td>109 ± 90</td>
<td>4.7</td>
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\(^a\)In ng/g dw. \(^b\)Detection frequencies in 84 egg samples.

Initially, 10% A was increased to 65% in 6 min, then increased to 75% at 7 min, a further 75% methanol was increased to 100% over 4 min and kept for 2 min, followed by a decrease to the initial conditions of 10% A and held for 3 min to allow for equilibration. The flow rate was 0.2 mL/min. The column and sample room temperatures were maintained at 40 and 10 °C, respectively. Data were acquired under multiple reaction monitoring (MRM) mode and the optimized parameters were as follows: source temperature, 110 °C; desolvation temperature, 350 °C; capillary voltage, 2.50 kV; desolvation gas flow, 800 L/h; cone gas flow, 50 L/h; multiplier, 650 V.

Identification and quantification of PBDE congeners were performed by a gas chromatography–electron capture negative ionization mass spectrometry system (Shimadzu QP 2010 plus). Chromatographic separation was achieved on a DB-SMS capillary column (30 m × 0.25 mm × 0.1 μm film thickness; J&W Scientific). A splitless injector was used, and the injector was held at 250 °C. The temperature program increased from 80 (4 min) to 160 °C at 20 °C/min, then to 230 °C at 2 °C/min, and then to 300 °C (10 min) at a rate of 30 °C/min. The ion source temperature was maintained at 280 °C. The carrier gas was helium at a constant flow rate of 5 mL/min.

Quality Assurance/Quality Control. While egg samples were collected in a wide period from 1984 to 2008, target chemicals were determined in all samples in 2013 by the same method for each group of chemicals.

As for PFC analysis, all equipment rinses were done with methanol to avoid sample contamination, and procedure blank experiments were performed along with each batch of samples. Standard injections were done among six sample injections, and methanol injections were done after each standard injection to monitor background contamination. As for PFHxA, with detectable blank contamination, the method detection limit (MDL) was defined to be three times the level in the procedure blanks, giving a value of 0.3 ng/g dw. The MDLs for other...
PFCs were defined as three times the noise, and they ranged from 0.1 ng/g for PFNA to 1.5 ng/g for PFHxDA (Supporting Information Table S1). The compound-specific matrix spiking recoveries were determined by spiking standards to the egg samples (n = 3) at about 3−5 fold higher than the concentrations observed in the real egg samples: 0.5 ng/g dw for C5−8 PFCAs, 5 ng/g dw for PFNA, 5 ng/g dw for PFDA, 10 ng/g dw for PFUnDA and PFDoDA, 30 ng/g dw for PFtriDA, 8 ng/g dw for PFTeDA, 20 ng/g dw for PFPeDA, 50 ng/g dw for PFTriDA, 8 ng/g dw for PFTeDA, 20 ng/g dw for PFPeDA, 50 ng/g dw for PFOS, and 1 ng/g dw for other PFSAs. The recoveries in the egg samples ranged from 66% (PFBS) to 109% (PFDoDA). Concentrations of PFPeA, PFHxA, and PFHpA in egg samples were quantified relative to 13C4−PFHxA, PFOA by 13C4−PFOA, PFNA by 13C4−PFNA, PFDA by 13C4−PFDA, PFUnDA by 13C4−PFUnDA, C12−16 PFCAs by 13C4−PFDoDA, and PFSAs by 13C4−PFOS. Average recoveries for 13C4−PFHxA, 13C4−PFOA, 13C4−PFNA, 13C4−PFDA, 13C4−PFUnDA, 13C4−PFDoDA, 13C4−PFHxA, and 13C4−PFOS in all egg samples were 78 ± 9.2%, 109 ± 6.6%, respectively. Three replicate spiked samples and one matrix blank sample were analyzed, and the absolute recoveries were 90.3 ± 14.6% for PBDEs and 107 ± 9.1% for PCBs. The MDLs for PBDEs and PCBs were set to the instrumental minimum detectable amounts with a signal-to-noise ratio of 3. The MDLs of PBDEs and PCBs congeners were between 0.14 to 3.5 ng/g dw and between 0.2 to 6.2 ng/g dw, respectively.

Data Analysis. Statistical analyses were carried out using SPSS 19.0. Values below the MDLs were replaced by MDL/2. After log-transformation, the PHC concentrations were considered normally distributed after being checked with the Shapiro−Wilk test. Log-linear regression was performed to evaluate temporal trends of PHCs in Chinese sturgeon. Differences with ρ < 0.05 were considered significant. To detect the potential break point of total PCBs, a two-segment piecewise model was used as described in previous study. As for PBDE and PCB analysis, all equipment rinses were done with acetone and n-hexane to avoid sample contamination, and a procedural blank was analyzed with every set of 12 samples. To automatically correct for the losses of analytes during extraction or sample preparation, as well as for variations in instrument response from injection to injection, surrogate standards were used in this study. The recoveries of PCB198 and PCB212 in all egg samples were 78 ± 9.2% and 109 ± 6.6%, respectively. Three replicate spiked samples and one matrix blank sample were analyzed, and the absolute recoveries were 90.3 ± 14.6% for PBDEs and 107 ± 9.1% for PCBs. The MDLs for PBDEs and PCBs were set to the instrumental minimum detectable amounts with a signal-to-noise ratio of 3. The MDLs of PBDEs and PCBs congeners were between 0.14 to 3.5 ng/g dw and between 0.2 to 6.2 ng/g dw, respectively.
RESULTS AND DISCUSSION

Concentrations and Temporal Trends of PCBs. Of 142 target PCBs, 62 PCB congeners were detected in the eggs of Chinese sturgeon. Of these PCBs detected, 26 PCB congeners were detected in 60% or more of the 84 egg samples (Table 1) and 36 PCB congeners were detected in less than 60% of the samples (Supporting Information Table S3). PCB-132/153 and -28/31 were detected in all of the 84 egg samples, and PCB-69/52/73, -138/163/164, -101, -146, -118, -180, -187, -90, -84, -47/48/75, and -149 were detected with frequencies ranged from 90.3% to 98.9% (Table 1). The mean concentration of total PCBs (ΣPCBs) was 295 ng/g dw (5th and 95th percentile, 50.1−677.7 ng/g dw) (Table 1), which was comparable to those (40−1047 ng/g dw) in caviar of four wild sturgeon species collected from the Black Sea and the Caspian Sea.36,37 PCB-132/153 was predominant with mean concentration of 65 ng/g dw (5th and 95th percentile, 4.8−140 ng/g dw) (Table 1), which was comparable to those (40−1047 ng/g dw) in caviar of four wild sturgeon species collected from the Black Sea and the Caspian Sea.36,37 PCB-132/153 was predominant with mean concentration of 65 ng/g dw (5th and 95th percentile, 4.8−140 ng/g dw) and accounted for 22 ± 8.2% of total PCBs (ΣPCBs), followed by PCB-189, -138/163/164, -146, -25, -118, -101, and -180, which accounted for 7.0 ± 9.9%, 5.4 ± 1.7%, 4.8 ± 1.8%, 4.2 ± 8.0%, 3.9 ± 1.6%, 3.9 ± 1.2%, and 3.9 ± 2.2% of total PCBs (Table 1, Supporting Information Figure S2), respectively. This profile was in accordance with that in peregrine falcon eggs (Falco peregrinus) from California (1986−2007)38 and our previous results in Chinese sturgeon collected from 2004 to 2006, where PCB-132/153 was the predominant PCB.32

The temporal trends of PCBs were evaluated by a log−linear regression model that has been widely used for evaluating temporal trends of PHCs in previous studies.15,39,40 A significant decreasing trend was observed for ΣPCBs (ρ = 0.005, Figure 1), and also for most PCB congeners, including PCB-132/153 (ρ = 0.007), PCB-105 (ρ = 0.0031), PCB-149 (ρ = 0.031), PCB-90 (ρ = 0.0012), PCB-187 (ρ = 0.0042), PCB-180 (ρ = 0.017), PCB-118 (ρ = 0.000), PCB-146 (ρ = 0.048), PCB-101 (ρ = 0.0051), and PCB-138/163/164 (ρ = 0.0042) (Figure 1 and Supporting Information Figure S1). The temporal change rates of PCB congeners in Chinese sturgeon eggs are listed in Supporting Information Table S4, and PCB-118 showed the highest decrease rate (4.7%/year) during the whole studied period, followed by PCB-132/153 (4.3%/year) (Supporting Information Table S4). The annual reduction rate of ΣPCBs in Chinese sturgeon was 3.4%, similar to that in fish species from Northern Europe (3% per year) during the period from 1967 to 1995.16 The overall reduction of ΣPCBs in Chinese sturgeon from 1984 to 2008 was 57.3%, lower than that in tawny owl eggs (Strix aluco) during a similar period (90.2%).41 Despite the overall decreasing trends of PCBs in Chinese sturgeon eggs, it is interesting to note that clear break points for ΣPCBs and some PCB congeners were observed at year 1991 (Figure 1). Statistical analysis showed that the AIC value of two-segment piecewise model (AIC = −213) when

Figure 2. Temporal trends of ΣPBDE and PBDE congeners in Chinese sturgeon eggs from 1984 to 2008.
setting year 1991 as break point was slightly lower than those of log linear model (AIC = $-207$), indicating breakpoint at year 1991. The concentrations of ΣPCBs showed a slight increase in the early period (1984–1991, $\rho = 0.05$), but decreased significantly in the late period (1991–2008, $\rho < 0.001$) (Supporting Information Table S4), despite the announced banning of production since the 1980s in China. These results were generally different from previous studies in Europe and North America, where consistently decreasing trends were observed since the banning of PCB usage in 1976.16,42 The region-specific increasing trends of PCBs before 1991 indicated continuous release of PCBs to the environment even after the banning of its production in the 1980s in China.

**Concentrations and Temporal Trends of PBDEs.** All 16 tri- to hepta-PBDE congeners (BDE-7, -11, -25, -28, -47, -66, -71, -75, -77, -99, -100, -119, -138, -153, -154, and -183) were detected in Chinese sturgeon eggs. Of the 16 PBDEs, the concentrations of PBDE congeners with detection frequency higher than 60% are listed in Table 1 and those for the rest of the congeners are listed in Supporting Information Table S3. The ΣPBDEs level (4.7–572 ng/g dw) in Chinese sturgeon eggs are among the highest ever found in biota, much higher than those of sturgeons from Azerbaijan (*Huso huso*), Bulgaria (*Acipenser gueldenstaedtii*), and Russia (*Acipenser stellatus*) (0.019–0.51 ng/g dw).35,43 BDE-47 (50 ng/g dw, 5th and 95th percentile, 0–102 ng/g dw), BDE-28 (7.0 ng/g dw, 5th and 95th percentile, 0–27 ng/g dw), BDE-100 (6.4 ng/g dw, 5th and 95th percentile, 0–28 ng/g dw), and BDE-154 (5.4 ng/g dw, 5th and 95th percentile, 0–15 ng/g dw), accounting for 44 ± 20%, 31 ± 23%, 5.7 ± 4.9%, 5.6 ± 10%, 4.4 ± 3.4% of total PBDEs, respectively. This profile of PBDE congeners (Supporting Information Figure S2) in Chinese sturgeon eggs was in agreement with the general BDE-47-dominated pattern reported in biological samples, especially in fish samples.7,29,44

The temporal trends of PBDEs were also evaluated by the log–linear regression model (Figure 2). Different from the decreasing trends of PCB congeners, significantly increasing temporal trends were observed for all major PBDEs, except for BDE-138, in Chinese sturgeon eggs over the whole time period monitored in this study ($\rho$ values ranged from <0.001 to 0.01). An increasing trend for BDE-138 could not be shown ($\rho = 0.10$). The greatest annual increase rate was observed for BDE-28 (10.2%), followed by BDE-100 (7.7%), BDE-154 (6.3%), and BDE-47 (6.3%), and BDE-138 showed the lowest annual increase rate at 3.5% (Supporting Information Table S5). The difference in increase rates among PBDE congeners would lead to changes in PBDE patterns in Chinese sturgeon eggs. The temporal trends of the ratios of PBDEs/ΣPBDEs (PBDEX%) were analyzed, as shown in Figure 3A, and it is interesting to notice that temporal trends of BDE-28% ($\rho = 0.024$) and BDE-100% ($\rho = 0.034$) showed significantly increasing temporal trends, whereas that of BDE-153% ($\rho = 0.012$) significantly decreased over time, and no significant changes were found for BDE-47% ($\rho = 0.24$), BDE-138% ($\rho = 0.19$), and BDE-154% ($\rho = 0.15$). This difference may be due to the congener-specific metabolism of upstream higher brominated PBDEs. It is well accepted that higher brominated PBDEs, such as BDE-209, can be metabolized to form lower-brominated PBDEs.45 According to previous studies, the production of PBDEs from upstream PBDEs was proportional to the metabolism half-life and concentrations of the upstream PBDEs,46 and the typical metabolism routes of PBDEs in Chinese sturgeon are shown in
Concentrations and Temporal Trends of PFCs. The 14 target PFCs were detected in Chinese sturgeon eggs except for the shorter-chain C$_7$–$_8$ PFCAs, and PFOS was detected in all egg samples. The PFCs concentrations in Chinese sturgeon eggs from 1984 to 2008 are listed in Supporting Information Table S6. The mean total concentration of PFCs ($\Sigma$PFCs) was 36 ng/g dw (5th and 95th percentile, 8.4–101 ng/g dw) in the entire study period. Of all PFCs, PFOS was the predominant compound at 14 ng/g dw (5th and 95th percentile, 3.2–44 ng/g dw), which contributed 48 ± 16% to $\Sigma$PFCs. The mean concentration of $\Sigma$PFCs was slightly higher than that of PFOS (19 ng/g dw, 5th and 95th percentile, 2.9–64 ng/g dw), in which PFTriDA was the predominant PFCA (7.8 ng/g dw, 5th and 95th percentile, 0.63–28 ng/g dw) accounting for 18 ± 7.5% to $\Sigma$PFCs and 38 ± 8.0% to $\Sigma$PFCs. This PFTriDA-dominated profile was different from those in other species such as Diporeia (Diporeia hoyi) from the Great Lakes, where PFOA, PFNA, or PFUnDA were generally the most abundant congeners, which may be due to the preferential accumulation of longer-chain PFCs in water-respiring organisms as indicated in our previous study.\textsuperscript{50} Such a species-specific pattern in Chinese sturgeon leads to relatively high ratios of $\Sigma$PFCs to PFOS (1.2 ± 0.87).

Significantly increasing temporal trend ($\rho < 0.01$) was also observed for PFOS (Figure 4), and its increase rate was 5.9% per year during the whole studied period (Supporting Information Table S6). This temporal trend in Chinese sturgeon was different from the decreasing trend observed in North America and Europe, as exemplified by significantly decreasing temporal trends of PFOS in tawny owl from Norway from 1986 to 2009 with 1.6% per year.\textsuperscript{51} To our knowledge, this is the longest study reporting temporal changes of PFOS in biota samples from Asia. Although the temporal decline in PFOS concentrations in North America and Europe has been connected to the production phase-out by the main manufacturers,\textsuperscript{20} the increasing temporal trends of PFOS in Chinese sturgeon observed in the present paper indicated that emission of PFOS is continuously increasing in China, which was accordant with the fact that PFOS production increased from 30 MT in 2002 to 246.88 MT in 2006 in China.\textsuperscript{52}

It should be noted that the annual increase rates of C$_{10-15}$ PFCAs (5.6–11%) were higher than that of PFOS (5.9%) (Supporting Information Table S6). Notably, the annually increasing concentration percentages of C$_{13-15}$ PFCAs (9.1–11%) were higher than those for C$_{9-12}$ PFCAs (0.88–7.7%), which was different from previous studies where all longer-chain PFCAs showed similar temporal trends.\textsuperscript{15,51} The increasing trends of longer-chain PFCAs have been attributed to ongoing exposure source of fluorotelomer-based production after the phase-out of ECF\textsuperscript{53} and this hypothesis has been supported by the detection of FTOHs and polyfluoroalkyl phosphate esters (PAPs) in the environment, as widely documented in previous studies.\textsuperscript{54–57} However, as for Chinese sturgeon, the increasing time trends of PFCAs may be, in part, attributed to the increasing ECF production in China in recent years.\textsuperscript{58}

Although an increasing trend of PFOS was observed throughout the whole period, the concentration of PFOS in 1989 (39.4 ng/g dw) was a breakpoint that was 3-fold higher.
than the mean concentration of the whole period and 1.5 fold higher than that of the late period from 1998 to 2008 (Figure 4). The time when PFOS concentrations reached peak concentrations was reported to be largely dependent on the region. For example, PFOS concentrations peaked in the mid-1990s in U.S. and around 2000 in Sweden. It is interesting to note that a very recent study has also reported a concentration peak of PFOS around 1986 in human blood from Munster in Germany, similar to our present study on Chinese sturgeon. Because most manufacturers of PFCs in China began production after 2000, the change points around 1989 should be due to the import of PFOS from other countries, and further studies are warranted to clarify the potential reason.

Thus, this paper provides the first systematic investigation on annual temporal trends of PCbs, PBDEs, and PFCs in biota samples from China, and region-specific temporal trends were actually observed: (i) although PCBs showed generally decreasing temporal trends, breakpoints were observed around 1991, indicating the continuing emission of PCBs after 1974 when PCBs usage was banned; (ii) increasing temporal trends of PBDEs were observed in Chinese sturgeon while a leveling-off was observed in the 1990s for Europe; (iii) consistently increasing temporal trends were observed for all detected PFCs, obviously different from the decreasing trends in Europe and North America. The region-specific emission history in China could explain most of the temporal trends of PHCs in Chinese sturgeon. However, some unexpected temporal trends could not be explained, especially the breakpoint of PFCs around 1989, which should not be attributed to emission history, and importation may be an alternative explanation as mentioned above.

Overall, our results filled the data gap in annual temporal trends of PCbs, PBDEs, and PFCs in Asia. The study presented here will help in understanding the efficacy of regulatory policy on PHC usage in China. Especially, although contamination by PCBs has been under good control, increasing temporal trends of PFCs and PBDEs indicate that more attention should be paid to their potential health and ecological risks.

## ASSOCIATED CONTENT

### Supporting Information

Text, figures, and tables addressing (1) Analysis of PCBs, PBDEs, and PFCs; (2) method detection limits and recoveries for PFCs; (3) sample size of Chinese sturgeon eggs in each year; (4) concentrations of PCBs and PBDEs in Chinese sturgeon eggs; (5) temporal trends analysis of PCB congeners; (6) temporal change rates of PBDE congeners; (7) mean and 95% confidence interval (CI) of PFC concentrations (ng/g dw) and annual rate of change in the whole period (1984–2008) in Chinese sturgeon eggs; (8) temporal trends of PCB congeners in Chinese sturgeon eggs; and (9) profiles of PCBs and PBDEs. This material is available free of charge via the Internet at http://pubs.acs.org.

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