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Tissue Distribution, Maternal Transfer, and Age-Related Accumulation of Dechloranes in Chinese Sturgeon

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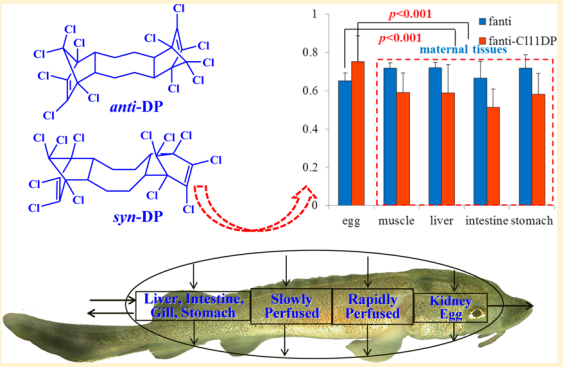
Supporting Information

ABSTRACT: While dechloranes have been detected in environmental media and wildlife, limited information was available on their tissue distribution in wildlife. *Syn*-dechlorane plus (*syn*-DP), *anti*-DP, *syn*-undecachloropentacyclooctadecadiene (*syn*-Cl_{11}DP), *anti*-Cl_{11}DP, dechlorane 602, dechlorane 603 and mirex were measured in 13 organs of 17 female Chinese sturgeon (*Acipenser sinensis*). Dechloranes were detected in all tissues and the highest concentrations of total dechloranes were detected in heart (87 pg/g ww, 4.5−645 pg/g ww), followed by adipose (61 pg/g ww, 14−531 pg/g ww) and eggs (57 pg/g ww, 13−261 pg/g ww). The tissue distribution of DP was mainly determined by lipid partition, while Dec 602 and Dec 603 preferred to accumulate in the intestine and stomach. The values of f_{anti} (the concentration of anti-DP relative to the sum concentration of DP) in maternal tissues (0.72 ± 0.03 in muscle) were significantly higher than those found in eggs (0.65 ± 0.04) ($p < 0.001$), while $f_{anti\text{-}Cl11DP}$ (the concentration of anti-Cl_{11}DP relative to the sum concentration of Cl_{11}DP) in maternal tissues (0.59 ± 0.10 in muscle) was significantly lower than that in eggs (0.75 ± 0.13) ($p < 0.05$). High maternal transfer efficiencies of dechloranes were observed in eggs, which accounted for 49% of the total body burden, and the ratios of concentrations in eggs to maternal tissues (EMR) for mirex, Dec 602, Dec 603, *syn*-Cl_{11}DP, *anti*-Cl_{11}DP, *syn*-DP, and *anti*-DP were 18, 8.8, 5.2, 2.6, 5.2, 5.5 and 3.7, respectively, which are dependent on their K_{OW} values ($r = -0.66$, $p < 0.01$). Negative age-related trends were observed for mirex, Dec 603, *syn*-Cl_{11}DP and *anti*-Cl_{11}DP in eggs ($R^2 = 0.28-0.38$, $p = 0.02-0.05$), which were possibly due to their high transfer efficiencies to eggs from maternal body (49%).



INTRODUCTION

Dechloranes including mirex, dechlorane plus (DP), Dechlorane 602 (Dec 602) and Dechlorane 603 (Dec 603) are a group of highly chlorinated flame retardants (HFRs) and have been used in coatings, plastic materials and other polymeric systems.[1] Of these, DP has been classified as a high-production-volume chemical by the United States Environmental Protection Agency (EPA).[2] It has been reported that DP elicited biomagnification in the aquatic food web,[3,4] despite predicted low bioaccumulation potentials due to relatively high molecular mass (654 Da) and log K_{OW} (ca. 9.3).[3] Dec 602 and Dec 603 have been manufactured by the same manufacturer as DP since the late 1960s and 1970s.[1] Recent field investigations[5,6] and experimental exposure data on Atlantic salmon[7] both indicated their high bioaccumulation potential compared with DP, partly due to their relatively low K_{OW} values (8.05 for Dec 602).[6] While there is exceedingly little toxicology information on dechloranes, the toxicological effects on fish reported in one document submitted to the voluntary EPA HPV Challenge Program (OxyChem, Niagara Falls, NY)[2] indicated the potential ecological risk of dechloranes.

Since the first report on environmental occurrence of DP in the Great Lakes Basin in 2006,[8] several studies have reported their wide occurrence in environmental matrices including the atmosphere,[8] surface water,[9] and sediments.[9] Besides their ubiquitous occurrence in environmental matrices, DP have also been detected in wildlife such as benthic organisms, fish and high-trophic birds.[5,6,10] While most previous studies focused on the occurrence of DP, several recent studies have detected reductive dechlorinated metabolites of DP (undecachloropentacyclooctadecadiene, Cl_{11}DP) in human sera,[11] sediment[12] and wildlife.[13] Environmental occurrence of Dec 602 and Dec 603 was reported very recently in lake trout and sediments from the Great Lakes,[6] and subsequent investigations further confirmed their occurrence in water, aquatic organisms and birds.[5,10] Overall, these studies revealed the bioaccumulation of dechloranes in wildlife, however, previous information on the concentrations of dechloranes was limited to muscle,[3−6] and only one study investigated DP and Cl_{11}DP concentrations in the brain, liver, and muscle of fish.[13] To better understand the toxicokinetics and potential risk of dechloranes, tissue

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distribution is critical for contaminant-mediated effects as a function of tissue in organisms, which could help clarify the tissue concentration and maternal transfer of these dechloranes in organisms and help identify possible target organs to guide monitoring and studies of toxicity. Especially, maternal transfer of pollutants is of particular concern for oviparous/egg-producing organisms such as fish and birds since organisms during embryonic development usually exhibit high sensitivity to pollutant exposure.[14] In addition, study on maternal transfer can also help to understand age-related accumulation trends of pollutants [15] which is useful for risk assessment of potential adverse effects of dechloranes on wildlife.

Chinese sturgeon (*Acipenser sinensis*) is listed as a grade I protected animal in China,[16] and is predatory fish feeding on benthic organisms as their food.[17] Chinese sturgeon is an excellent sentinel species for monitoring environmental organic contaminants since it is a predatory fish that can live for 40 years or longer and weigh as much as 500 kg.[17] In this study, concentrations of seven dechloranes including mirex, Dec 602, Dec 603, *syn*-DP, *anti*-DP, *syn*-Cl_{11}DP, and *anti*-Cl_{11}DP were measured in 13 organs (egg, gonad, adipose, liver, heart, muscle, intestine, stomach, gill, kidney, pancreas, gallbladder, and spleen) from 17 Chinese sturgeons. Then the tissue distributions, maternal transfer, and age-related accumulation trends of the target dechloranes were investigated.

MATERIALS AND METHODS

Chemicals and Reagents. Dechlorane standards (DP, *anti*-Cl_{11}DP, Dec 602, Dec 603, and mirex) were obtained from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Dichloromethane (DCM), *n*-hexane, methyl *tert*-butyl ether (MTBE), acetonitrile, and methanol were pesticide residue grade obtained from OmniSolv (EM Science, Lawrence, KS, U.S.). Sodium sulfate, silica gel (60−100 mesh size), aluminum oxide (neutral, 150 mesh size), potassium hydroxide (KOH), and hydrochloric acid (HCl) were purchased from Sigma-Aldrich (St. Louis, MO, U.S.). For biochemical analyses, the fluorescence kit was obtained from Genmed Scientific Inc. (U.S.), and sodium phosphate dibasic (Na_2HPO_4), sodium phosphate monobasic (NaH_2PO_4), potassium chloride, resorufin, ethylenediaminetetraacetic acid (EDTA), dithiothreitol (DTT), and all other biochemical reagents including NADPH were obtained from Sigma-Aldrich (St. Louis, MO, U.S.).

Sample Collection. Chinese sturgeon is an anadromous fish. They live in the sea (e.g., East Sea and Yellow Sea) until the initial reproduction of fish at an average age of 14.3 years as shown in Supporting Information, SI, Figure S1. 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.[17] Between 2003 and 2006, a limited number of Chinese sturgeon were allowed to be captured in Yangtze River by roller hook for propagation and scientific study. Organs and eggs were collected for artificial spawning while other organs were collected from individuals who died. Samples were kept at −20 °C until analysis. Ages of sturgeon were estimated by growth layers in the cleithrum, as described in previous research.[18]

In Vitro Microsomal Incubation. Microsomes were isolated from cultured two-year-old Chinese sturgeon, according to the method improved by Benedict et al.[19] and dithiothreitol (DTT) was included in the homogenization, wash, and resuspension buffers to preserve the catalytic activity of reductases. Protein concentrations were determined using the Bradford method with bovine serum albumin as standard. Ethoxyresorufin *O*-deethylase (EROD) activity was determined by use of a fluorescence kit (Genmed Scientific Inc. U.S.). The final reaction volume was 250 μL which contained 50 μL of the microsomal preparation and 3 μL of exposure chemicals. The concentration of *syn*-DP and *anti*-DP in the incubation mixture was 50 ng/mL. The protein concentration in the reaction vial was 2.4 mg/mL and the CYP1A1-catalyzed EROD activity was 4.6 pmol/mg/min. Reactions were performed at 37 °C for 24 h with constant agitation. Incubations without chemicals and without microsomes were used as negative controls to assess background contaminants and the possibility of nonenzyme-mediated changes in chemical structure. After the incubation, the samples were extracted by *n*-hexane immediately for chemical analysis.

Quantification of Dechloranes and Quality Assurance/Quality Control. Identifying and quantifying dechloranes were carried out according to the method reported in a previous paper.[20] Tissues were freeze-dried, and then approximately 1−3 g dry weight (dw) subsamples were spiked with ^{13}C-labeled polychlorinated biphenyl ($^{13}C_{12}$−PCB180), and extracted by accelerated solvent extraction (Dionex ASE-200, Sunnyvale, CA). The extraction employed two 10 min cycles: the first cycle was performed with *n*-hexane/DCM (1:1) at 100 °C and 1500 psi, followed by a second cycle with *n*-hexane/MTBE (1:1) at 60 °C and pressure of 1000 psi. The two extraction fractions were combined and rotary evaporated to near dryness. The extract was then transferred to 15 mL glass tubes with 8 mL *n*-hexane, and 4 mL 0.5 M KOH in 50% ethanol was added. The aqueous layer (KOH) was extracted with 8 mL of *n*-hexane three times (neutral fraction). The neutral fraction was concentrated to approximately 2 mL and loaded onto a column of 1 g Na_2SO_4 and 8 g acidified silica (48% Na_2SO_4) and eluted with 15 mL of *n*-hexane and 10 mL of DCM. The eluate was further purified on a neutral alumina column (4 g of sodium sulfate, 4 g of neutral alumina, 4 g of sodium sulfate). The first fraction eluted from the alumina column with 20 mL of *n*-hexane was discarded. The second fraction, which contained the target dechloranes, was obtained by elution with 25 mL of 60% DCM in *n*-hexane. The eluate was evaporated to dryness under a gentle stream of nitrogen, and then 40 μL *n*-hexane was added for analysis.

Concentrations of all dechloranes in sample extracts were quantified relative to $^{13}C_{12}$−PCB180. The recoveries of dechloranes ranged from 85 to 123%, and the recovery of $^{13}C_{12}$−PCB180 was 85 ± 19% (Table S1 of the SI). All equipment rinses were carried out with acetone and *n*-hexane to avoid sample contamination. A laboratory blank was incorporated in the analytical procedures for every batch of 12 samples. The method detection limits (MDLs) for dechloranes were set to the instrumental minimum detectable amounts with a signal-to-noise ratio of 3. The MDLs were 0.1−0.5 pg/g ww (Table S1 of the SI).

Identification and quantification of dechloranes were performed using a gas chromatography-electron capture negative ionization mass spectrometer (GC-ENCI-MS) (Shimadzu QP 2010 plus, Japan). Chromatographic separation was achieved on a VF-5MS capillary column (15 cm ×0.25 mm ×0.1 μm film thickness; J&W Scientific, U.S.). A splitless injector was used, and the injector was held at 290 °C. The temperature program was from 110 °C (2 min) to 300 °C (5

min) at a rate of 30 °C/min. The transferline temperature and the ion source temperature were maintained at 285 and 220 °C, respectively. The carrier gas was helium at a constant flow rate of 5 mL/min. Data acquisition was conducted in selected ion monitoring mode.

Data Analysis. The ratios between concentrations of dechloranes in eggs to those in maternal tissues (EMR) were calculated by the following equation:

$$\mathrm{EMR} = C_{\mathrm{egg}}/C_{\mathrm{tissue}} \quad (1)$$

where C_{egg} is the concentration of a dechlorane in eggs; C_{tissue} is the weighted concentrations of a dechlorane in maternal tissues, which was calculated by eq 2:

$$C_{\mathrm{tissue}} = \sum C_i \times \mathrm{weight}_i/\mathrm{BW} \quad (2)$$

where C_i is the concentration of a dechlorane in the i^{th} tissue, weight_i is the weight of the i^{th} tissue, and BW was the body weight of the Chinese sturgeon. Weights of different tissues were derived from two sturgeon individuals as shown in Table 1. Weight of eggs was derived from 29 sturgeon individuals.

For those results lower than the MDL, half of the MDL was assigned to avoid missing values in the statistical analyses. All data analyses such as linear regression were performed with SPSS 15.0. Statistical significance was defined as $p < 0.05$.

RESULTS AND DISCUSSION

Concentrations of Dechloranes among Tissues. All target dechloranes including mirex, Dec 602, Dec 603, *syn*-DP, and *anti*-DP were detected in all tissues from the 17 Chinese sturgeons (Table 1). The median concentration of total DP (ΣDP) in Chinese sturgeon was 0.15 ng/g lipid weight (lw) (0.05−0.21 ng/g lw) in muscle, which was similar to concentration in lake trout from the Great Lakes (0.2 ng/g lw)[6] but much lower than in oysters from Northern China (250 ± 50 ng/g lw).[5] The median concentrations of Dec 602 and Dec 603 in muscle were 29 pg/g lw (15−53 pg/g lw) and 1.1 pg/g lw (ND-3.2 pg/g lw), respectively, lower than those (470−34 000 pg/g lw for Dec 602 and 14−500 pg/g lw for Dec 603) in fish muscles from the Great Lakes.[6] All dechloranes were preferentially accumulated in organs with high lipid contents such as adipose tissue (61 pg/g ww, 14−531 pg/g ww) and liver (44 pg/g ww, 4.8−244 pg/g ww) [Figure 1(a)], which was similar to organochlorine compounds[18] and polybrominated diphenyl ethers (PBDEs)[20] in the same individual sturgeon. While dechloranes have been detected in the muscles of fish,[3,6] only one study investigated the occurrence of DP and dechlorinated DP in the liver, brain, and muscles of mud carp (*Cirrhinus molitorella*) and northern snakehead (*Channa argus*).[13] In that study, the concentrations of DP and dechlorinated DP in liver were found to be about 10-fold higher than in muscles,[13] which is similar to Chinese sturgeon. The concentrations of dechloranes in heart tissues (87 pg/g ww, 4.5−645 pg/g ww) of Chinese sturgeon were unexpectedly high even though the lipid content of the heart (4.4%) was much lower than adipose tissue (66%) and liver (13%); this phenomenon was also observed for highly chlorinated PCBs in fur seals (*Callorhinus ursinus*).[21] It should be noted that high concentrations of dechloranes were found in eggs (57 pg/g ww, 13−261 pg/g ww), 10-fold higher than in muscles (8.4 pg/g ww, 5.7−16 pg/g ww). Considering the fact that organisms during embryonic development usually exhibit greater sensitivity to pollutant exposure,[14] such high accumu-

Table 1. Concentrations (pg/g ww) of Dechloranes in Chinese Sturgeon

	lipid	weight[a]		mirex	Dec 602	Dec 603	*syn*-Cl_{11}DP	*anti*-Cl_{11}DP[b]	*syn*-DP	*anti*-DP
egg (n = 14)	0.35	18 ± 6.4	median range	112 (ND[d]-213)	5.5 (0.4−17)	0.2 (ND-1.0)	1.0 (ND-7.8)	2.3 (1.2−7.8)	2.2 (0.4−9.9)	4.1 (0.7−13)
gonad (n = 5)	0.13	0.1 ± 0.0	median range	15 (9.3−79)	1.4 (1.1−7.2)	0.1 (ND-0.1)	0.4 (ND-7.3)	0.9 (0.7−2.8)	1.6 (1.1−3.7)	4.0 (2.1−6.9)
adipose (n = 5)	0.04	/[c]	median range	62 (22−398)	6.6 (ND-1.6)	0.7 (ND-1.6)	2.7 (ND-7.1)	6.6 (ND-9.9)	3.0 (ND-32)	6.4 (ND-34)
liver (n = 7)	0.66	1.7 ± 0.2	median range	15 (1.2−142)	9.7 (0.2−68)	0.4 (0.1−0.6)	1.8 (ND-61)	1.9 (0.5−22)	3.3 (ND-25)	5.5 (1.5−62)
heart (n = 5)	0.04	0.1 ± 0.0	median range	82 (ND-551)	10 (ND-56)	0.4 (ND-1.1)	2.5 (0.3−6.7)	2.5 (0.4−15)	6.3 (0.4−15)	7.2 (2.4−15)
muscle (n = 7)	0.02	77 ± 6.4	median range	5.4 (1.5−11)	0.4 (0.2−1.3)	0.1 (ND-0.1)	0.3 (ND-1.1)	0.5 (ND-1.5)	0.6 (0.4−0.8)	1.4 (1.1−2.2)
intestine (n = 7)	0.03	1.1 ± 0.1	median range	4.5 (ND-9.6)	0.6 (ND-1.4)	/ ND-0.1	0.1 (ND-2.6)	0.3 (ND-2.9)	0.9 (0.4−4.5)	2.5 (0.8−11)
stomach (n = 5)	0.01	0.5 ± 0.2	median range	/ ND-35	1.7 (ND-3.0)	/ ND-0.1	1.0 (0.1−3.6)	1.6 (0.3−2.8)	1.0 (0.2−2.4)	3.2 (0.8−8.4)
gill (n = 6)	0.02		median range	5.9 (1.3−62)	1.3 (ND-6.8)	0.1 (ND-0.2)	/ ND-0.4	/ ND-1.5	1.7 (0.5−2.3)	2.7 (1.1−19)
pancreas (n = 2)	0.07		minimum	21	3.9	ND	ND	ND	1.4	1.5
			maximum	39	4.4	0.1	ND	0.9	2.9	4.8
gallbladder (n = 1)	0.23	0.1 ± 0.0		10	8.0	0.8	3.9	ND	4.6	9.0
spleen (n = 1)	0.03	0.3 ± 0.1		14	1.3	0.2	ND	1.3	1.7	3.1
kidney (n = 1)	0.32			30	5.1	0.5	3.4	3.9	4.7	3.1

[a]The values of weights for different tissues are the proportions of body weight (%). [b]Calculated with the relative response factor of anti-Cl_{11}DP.[26] [c]Not determined. [d]ND indicated not detected.

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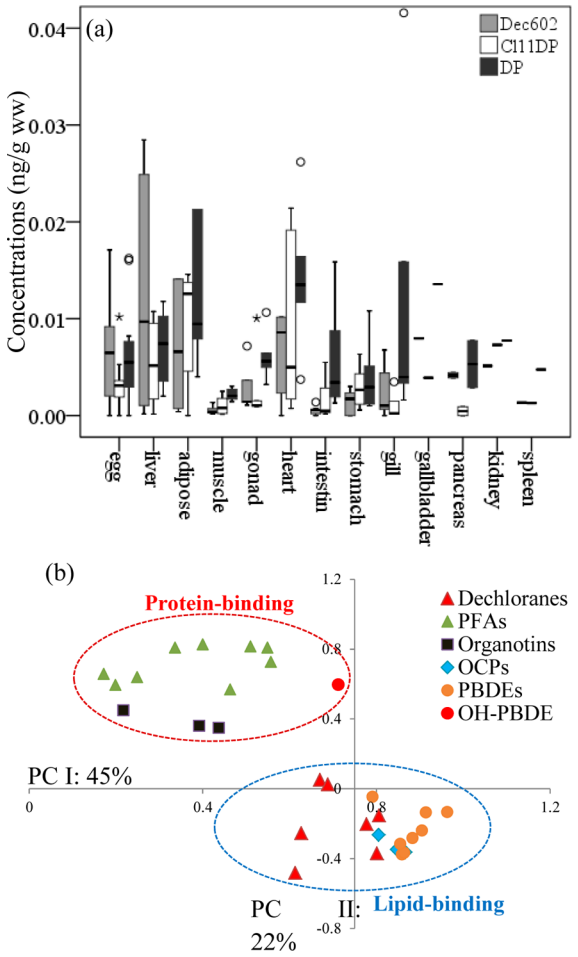

Figure 1. Tissue distributions of dechlorane concentrations (a) and the loading factor scores of different pollutants using principal components analysis (b).

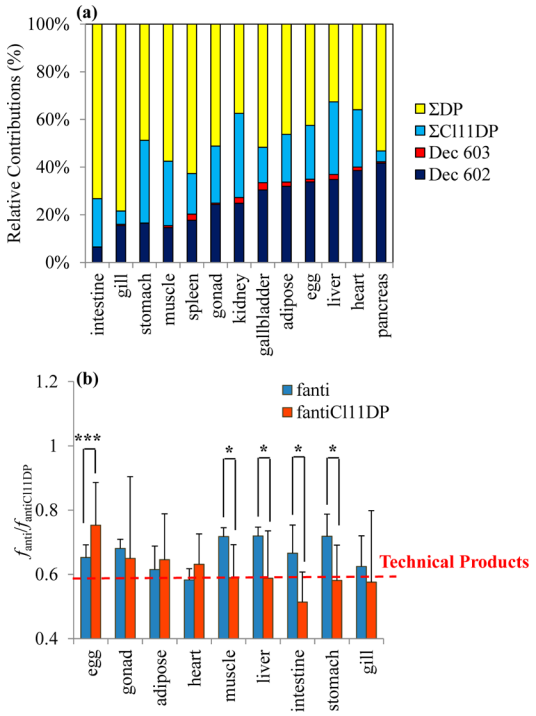

Figure 2. Relative contributions of dechloranes in different tissues (a) and tissue distribution of f_{anti} and $f_{antiCl11DP}$ in Chinese sturgeon (b). f_{anti} = concentrations of *anti*-DP/(concentrations of *anti*-DP+ concentrations of *syn*-DP), $f_{antiCl11DP}$ = concentrations of *anti*-Cl_{11}DP/concentrations of *anti*-DP. * indicates $p < 0.05$; *** indicates $p < 0.001$. The number of samples has been listed in Table 1.

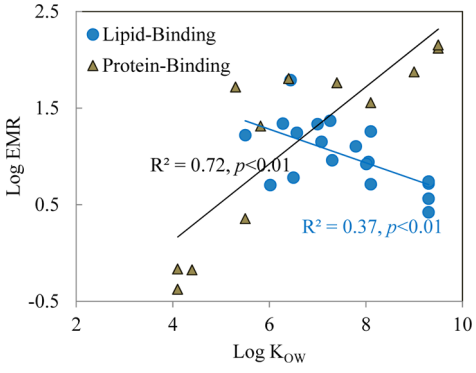

Figure 3. Correlations between eggs to maternal tissues (EMRs) and K_{OW} values of dechloranes and comparison with other pollutants. K_{OW} values for organochlorine compounds, PBDEs, organotins, OH-PBDEs, and MeO-PBDEs and PFCs are from refs 36−41. K_{OW} values of dechlorinated DP were unavailable and were assumed to be the same as DP, considering their similar retention time during GC analysis.

lation of dechloranes in eggs should be paid particular attention.

Previous investigations on the concentrations of perfluorinated compounds (PFCs),[22] organotins,[14] PBDEs,[20] and organochlorine compounds[18] in the same sturgeon individuals provide an opportunity to compare the tissue distribution among different compounds. Principle component analysis (PCA) clearly showed that the cluster of dechloranes separated from PFCs, organotins and OH-PBDEs along PC II and PC I [Figure 1 (b)], reflecting their different partition mechanism. Previous mechanism studies have suggested that PFCs, organotins and OH-PBDEs all bind to protein (albumin or transthyretin) within the body,[23−25] and therefore these chemicals are here defined as "protein-binding" pollutants, while the tissue distribution of PBDEs and DDTs were driven by the partition ability to lipid (here defined as "lipid-binding" compounds). Thus, dechloranes were clearly categorized as "lipid-binding" compounds. In addition, by comparing lipid-normalized concentrations between liver and adipose tissue, lipid-normalized concentrations of dechloranes in liver were all higher than in adipose tissue by 1.7 fold for mirex to 4.9 fold for Dec 602, showing hepatic sequestration of dechloranes in Chinese sturgeon.

Two isomers of dechlorinated DP (Cl_{11}DP) were detected in all tissues and the highest concentrations of *syn*-Cl_{11}DP and *anti*-Cl_{11}DP were both detected in adipose (the median concentrations were 2.7 pg/g ww for *syn*-Cl_{11}DP and 6.6 pg/g ww for *anti*-Cl_{11}DP), followed by heart (the median concentrations were 2.5 pg/g ww for *syn*-Cl_{11}DP and 2.5 pg/g ww for *anti*-Cl_{11}DP) (Table 1). The presence of dechlorinated DP has been reported in several terrestrial passerine bird species from South China, fish and peregrine falcon (*Falco peregrinus*).[10,13,26] It should be noted that the ratio between ΣCl_{11}DP and ΣDP (ranging from 0.24 in gill to 1.2 in intestine) was much higher than previously reported values in wildlife, such as northern snakehead (0.07), mud carp (0.02), and peregrine falcon (*Falco peregrinus*) (0.07 ± 0.08).[10,13] The

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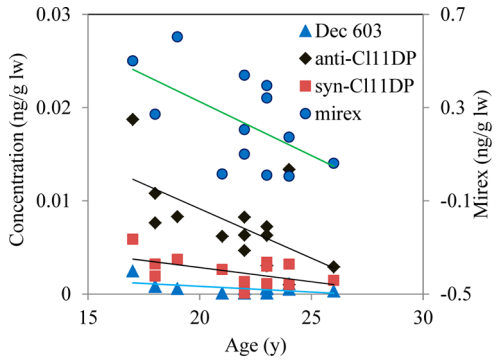

Figure 4. Age related accumulation trends of dechloranes in eggs. $Conc_{mirex} = -0.046 \times age + 1.25$, $R^2 = 0.34$, $p = 0.04$; $conc_{anti\text{-}Cl11DP} = -0.0011 \times age + 0.03$, $R^2 = 0.38$, $p = 0.02$; $conc_{anti\text{-}Cl11DP} = -0.0003 \times age + 0.0089$, $R^2 = 0.29$, $p = 0.04$; $conc_{Dec603} = -0.0001 \times age + 0.0033$, $R^2 = 0.28$, $p = 0.05$.

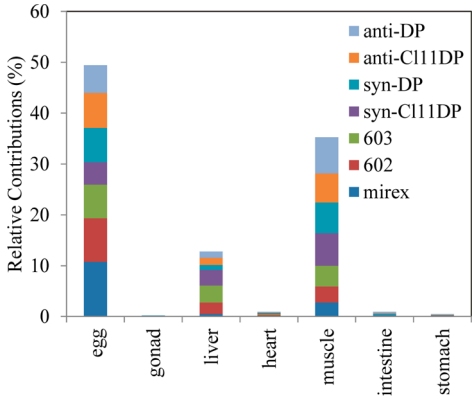

Figure 5. Relative contributions of different tissues to total body burden of dechloranes. The number of samples has been listed in Table 1.

source of dechlorinated DP in biota remains unknown, although previous studies suggested that metabolism from DP may be responsible for dechlorinated DP in humans[11] or wildlife.[13] Since there is no evidence of DP dechlorination in these organisms, in vitro studies of DP were conducted in microsomal fractions of Chinese sturgeon liver to better understand the potential biotransformation of DP in Chinese sturgeon. However, dechlorinated DP could not be observed after a 24-h exposure, indicating that the metabolism rates of DP were very low in Chinese sturgeon. The results suggested that metabolism of DP should not be the source of dechlorinated DP in Chinese sturgeon. Considering the occurrence of dechlorinated DP in sediments from Lake Ontario,[12] and experimental evidence of DP dechlorination in sediment,[12] accumulation from sediments may be an alternative source for dechlorinated DP in Chinese Sturgeon.

Relative Contributions of Dechloranes among Tissues. Of all dechloranes, mirex was the predominant dechlorane in all tissues, and the relative contributions ranged from 28% in gallbladder to 83% in eggs. The predominance of mirex in Chinese sturgeon was partly due to its higher bioaccumulation potentials than other dechloranes, which is also found in most previous studies.[6,10] Mirex is used as a termicide for termite control in China. It has been reported that China started to produce mirex in the 1960s and then ceased in 1975, and the production of mirex resumed in 1997 after a termite disaster in southern China and continued until 2002.[5] When mirex was excluded, Dec 602 was the most abundant compound in liver (39%) and heart (35%), while DP were the predominant dechloranes in other tissues [Figure 2(a)]. The relative contribution pattern of dechloranes in muscle was *anti*-DP > *syn*-DP > Dec 602 > Dec 603, which is similar to results in sediment and oysters collected from Northern China,[5] but different from those of lake trout (U.S.) and peregrine falcon (*Falco peregrinus*)[6,13] in which Dec 602 and Dec 603 often showed higher concentrations than DP. The similar profiles of dechloranes between Chinese sturgeon and sediments or benthic organisms may be due to the fact that Chinese sturgeon mainly take benthic organisms as their food.[20] While the patterns of relative concentrations were similar among tissues, the contributions of Dec 602 and Dec 603 to total dechloranes in intestine (6.4% for Dec 602 and 0.1% for Dec 603), stomach (16% for Dec 602 and 0.2% for Dec 603), and gill (15% for Dec 602 and 0.5% for Dec 603) were relatively low compared with other organs [Figure 2(a)]. These organs were the major absorptive organs of fish for pollutants from water or diet, and chemicals with high K_{OW} values and molecular size could be sequestered by these tissues' walls.[27]

Among DP and their dechlorinated compounds, *anti*-DP was the predominant compound in all tissues except for kidney, accounting for 53% in intestine, 49% in muscle and 46% in gonad (Figure S2 of the SI). Isomer compositions of DP in different tissues within the body would be important to well understand their isomer-specific pharmacokinetics. Tf_{anti} (concentration of *anti*-DP relative to the sum concentration of DP) 0.72±0.03), stomach (0.72±0.06) and liver 0.72±0.03), gonad 0.68±0.03), intestine 0.67±0.08) and egg 0.65±0.04), which were all significantly higher than the technical DP produced in China (0.59)[28] [Figure 2(b)]. Such results were different from those reported in other fish in which f_{anti} was often lower than the commercial products.[3,4] Previous studies have reported similar preferential accumulation of *anti*-DP in benthic organisms (0.70 and 0.77 for diporeia (*Diporeia hoyi*) and mysis (*Mysis relicta*) from Lake Ontario),[6] and therefore the species-specific accumulation of *anti*-DP in Chinese sturgeon may be due to the fact that Chinese sturgeon mainly take benthic organisms as their food.[20] It should be noted that f_{anti} values in eggs and heart (0.58 ± 0.03) were significantly lower than those in muscle and liver ($p < 0.001$). Heart was a richly perfused organ with relatively high blood flow rates,[29] and the low values of f_{anti} in heart tissue indicated that *anti*-DP would be more difficult to pass through the tissue walls of muscle or liver into the bloodstream, and therefore leading to the relatively low f_{anti} values in eggs which was delivery from maternal transmission via the bloodstream. Similar sequestration of *anti*-DP during the penetration through tissue wall has been observed in the intestine of rainbow trout, and then caused relatively low absorption rates.[30] In contrast to DP, dechlorinated DP showed different tissue distribution patterns and $f_{antiCl11DP}$ values in maternal tissues including muscle ($p = 0.003$), liver ($p = 0.007$), intestine ($p < 0.001$), and stomach ($p = 0.014$) were found to be significantly lower than those of eggs as shown in Figure 2(b). The inverse trends between eggs and maternal tissues for f_{anti} and $f_{antiCl11DP}$ indicated that the tissue distribution pattern of dechloranes would be dependent on their transfer from maternal tissue to eggs.

Maternal Transfer to Eggs. The ratios of the concentrations of chemicals in eggs to those in maternal tissues (EMR) were used to assess their maternal transfer efficiencies. EMRs for mirex, Dec 602, Dec 603, *syn*-Cl_{11}DP, *anti*-Cl_{11}DP,

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syn-DP, and *anti*-DP were calculated to be 18, 8.8, 5.2, 2.6, 5.2, 5.5, and 3.7, respectively. It should be noted the EMR value of *syn*-DP was higher than *anti*-DP, but *anti*-Cl_{11}DP EMR was greater than *syn*-Cl_{11}DP. The EMR values of dechloranes, especially for those with high K_{OW} values such as DP and dechlorinated DP, were similar to those of highly brominated PBDEs (from 4.2 to 14), but lower than those of lowly brominated PBDEs (from 18 to 23) and hexachlorobenzene (17) in the same sturgeon individuals.[18,20] To assess the potential effects of the physicochemical properties of pollutants on their maternal transfer efficiencies, we made an attempt to correlate the EMR values of different pollutants in the same individual sturgeon and their K_{OW} values. As shown in Figure 3(b), significant negative correlations between EMR values of "lipid-binding" compounds and K_{OW} values ($r = -0.66$, $p < 0.01$) were observed. However, it is interesting to find that a positive correlation between EMR and K_{OW} was observed for "protein-binding" compounds ($r = 0.85$, $p < 0.01$). Although previous maternal transfer models have suggested that lipid-normalized maternal transfer ratios should be close to 1 independent of their K_{OW},[31] our study provided the first observation of different correlation trends between maternal transfer efficiencies and K_{OW} values for different chemicals. Such different trends for "lipid-binding" and "protein-binding" pollutants may be due to their different mechanism of maternal transfer: as for "lipid-binding" pollutants, diffusion between maternal tissues and eggs was driven by the partition between lipid pools,[31] and transfer of pollutants with high K_{OW} to eggs may be hindered by their high molecular weights; however, as for "protein-binding" pollutants, the maternal transfer to eggs was mediated by active transport by lipoproteins or other proteins,[32] and pollutants with high K_{OW} values often exerted high binding affinities to protein.[33]

Age Related Accumulation Trends of Dechloranes in Eggs. High maternal transfer of dechloranes to eggs may have influence on the lifetime accumulation of dechloranes in female Chinese sturgeon. Since Chinese sturgeon is listed as a grade I protected animal in China, only female sturgeons were captured for scientific purposes. The concentrations of dechloranes in eggs represent the levels in female sturgeon, and regression analysis was conducted to investigate the age related accumulation trends of the pollutants. Significant negative age-related accumulation trends were found for mirex ($R^2 = 0.34$, $p = 0.04$), Dec 603 ($R^2 = 0.28$, $p = 0.05$), *syn*-Cl_{11}DP ($R^2 = 0.29$, $p = 0.048$), and *anti*-Cl_{11}DP ($R^2 = 0.38$, $p = 0.02$) in eggs (Figure 4), while other dechloranes showed a generally negative relationship with age but without statistical significance ($R^2 = 0.02-0.12$, $p = 0.22-0.60$) (Figure S3 of the SI). This is the first report on the age-related accumulation trends of dechloranes, while such decreasing concentration trends with age have also been found for PBDEs and some PFCs in the same sturgeon individuals.[20,22]

To evaluate the potential influence of maternal transfer on age-related decreasing concentration trends, the relative contributions of dechloranes in eggs to total body burden were calculated. Egg was the predominant accumulation organ, which contributed 49% of total body burden, much higher than liver (13%) and muscle (35%) and also other organs (<1%) (Figure 5). Such maternal transfer efficiencies of pollutants in Chinese sturgeon were much greater than other reported halogenated compounds in mammals [34] and birds,[35] not only due to the highly accumulated dechlorane concentrations in eggs but also the great weight of eggs in Chinese sturgeon. The high level of dechloranes in eggs indicated that maternal transfer could be responsible for the age-related decreasing trends of dechlorane concentrations in female Chinese sturgeon.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures and tables addressing (1) recoveries and method detection limits of dechloranes; (2) the habitat of Chinese sturgeon; (3) relative contributions of dechlorane plus (DP) and dechlorinated DP in different tissues from Chinese sturgeon; (4) age related accumulation trends of Dec 602, *syn*-DP and *anti*-DP in eggs from Chinese sturgeon. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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