Science of the Total Environment 554–555 (2016) 320–328

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Extensive organohalogen contamination in wildlife from a site in the Yangtze River Delta☆

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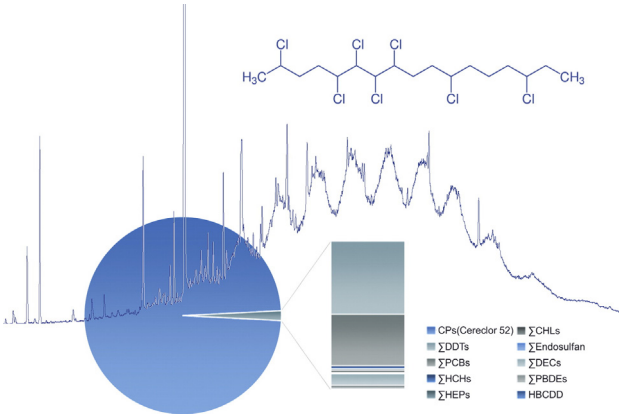
HIGHLIGHTS

- Six wildlife species of amphibians, fish and birds were sampled and screened for organohalogen contaminants (OHCs) in a paddy field in Yangtze River Delta, China.
- High contaminations of chlorinated paraffins were found particularly in terrestrial species.
- A novel pattern of PCBs with relatively high contribution from octa-CBs to decaCB was observed.
- A new group of OHCs, with 5–8 chlorines, were found but are not yet structurally confirmed.
- DDTs was the major organochlorine pesticide contaminant in wildlife; HBCDD level in wildlife was comparable to PBDEs in the present study.
- The results show an extensive contamination of OHCs in wildlife in Yangtze River Delta, calling for further (eco)toxicology study and environmental monitoring.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 December 2015
Received in revised form 6 February 2016
Accepted 25 February 2016
Available online xxxx

Editor: Adrian Covaci

ABSTRACT

The environmental and human health concerns for organohalogen contaminants (OHCs) extend beyond the 23 persistent organic pollutants (POPs) regulated by the Stockholm Convention. The current, intense industrial production and use of chemicals in China and their bioaccumulation makes Chinese wildlife highly suitable for the assessment of legacy, novel and emerging environmental pollutants. In the present study, six species of amphibians, fish and birds were sampled from paddy fields in the Yangtze River Delta (YRD) were screened for OHCs. Some extensive contamination was found, both regarding number and concentrations of the analytes, among the species assessed. High concentrations of chlorinated paraffins were found in the snake, Short-tailed mamushi

☆ The authors declare no competing financial interest

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http://dx.doi.org/10.1016/j.scitotenv.2016.02.176

Keywords:
Wildlife
Chlorinated paraffins (CPs)
Persistent organic pollutants (POPs)
Emerging contaminants
Yangtze River Delta

(range of 200–340 μg g^{-1} lw), Peregrine falcon (8–59 μg g^{-1} lw) and Asiatic toad (97 μg g^{-1} lw). Novel contaminants and patterns were observed; octaCBs to decaCB made up 20% of the total polychlorinated biphenyls (PCBs) content in the samples and new OHCs, substituted with 5–8 chlorines, were found but are not yet structurally confirmed. In addition, Dechlorane 602 (DDC-DBF) and numerous other OHCs (DDTs, hexachlorocyclohexanes (HCHs), polybrominated diphenyl ethers (PBDEs), hexbromocyclododecane (HBCDD), chlordane, heptachlor, endosulfan and Mirex) were found in all species analyzed. These data show extensive chemical contamination of wildlife in the YRD with a suite of OHCs with both known and unknown toxicities, calling for further in-depth studies.

1. Introduction

Exposure to persistent organic pollutants (POPs) is a risk for human health and wildlife and has led to the Stockholm Convention which today regulates 26 POPs (Stockholm Convention, 2015a). However, numerous other chemicals are identified as both persistent (Green and Bergman, 2005) and bioaccumulative in humans and wildlife although their toxicological and ecotoxicological impacts are not yet well established. There is worldwide occurrence of such persistent and bioaccumulative chemicals, particularly in intense chemical production and application areas, i.e. fast growing economies like China. These chemicals, appearing as organohalogen contaminants (OHCs), are originally from the manufacturing of well-established chemicals, but also of new chemicals (Chen et al., 2009a; Ruan et al., 2015; Shi et al., 2009; Sun et al., 2012a), including byproducts and impurities (Qiu et al., 2005), all of which undergo biotic and abiotic transformations once released into the environment. In the past, China produced approximately 0.4 and 4.9 million metric tons (MTs) of technical dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs) from the 1950s to 1983 (Zhang et al., 2002), and an estimated 10,000 MTs of polychlorinated biphenyls (PCBs) between 1965 and1974 (Chen et al., 2009b). From 1988 to 2002, an additional 54,000 MTs of DDT was used to manufacture dicofol for mite control, resulting in an estimated amount of almost 9000 MTs of DDTs as an impurity in commercial dicofol and its release to the environment (Qiu et al., 2005). Decabromodiphenyl ethane (DBDPE), dechlorane plus (DDC-CO) and chlorinated paraffins (CPs) have been produced in China as emerging flame retardants in addition to polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDD), and detected in various environmental compartments (Newton et al., 2015; Vorkamp et al., 2015; Zheng et al., 2015). Commercial CP mixtures include short chain CPs (SCCPs) with a chain length of 10–13 carbons and 30–70% relative chlorine content by weight; they are currently under review for inclusion in the Stockholm Convention (Stockholm Convention, 2015b) and are on the candidate list of substances of very high concern within the European Chemical Agency (ECHA, 2008).

China started their CP production at the end of the 1950s (Zeng et al., 2013) and has become the world's largest CP producer (Wang et al., 2013). The production volume had grown to about 1 million MTs in 2009 (Wu et al., 2013). Most manufacturing and usage occurred in the coastal regions of China, and CPs in marine sediments have recently been found to be more abundant in nearshore areas of East China Sea compared to outer shelf, suggesting a direct influence of riverine inputs and the proximity to land-based sources (Zeng et al., 2013). CP-42, CP-52 and CP-70 are the main commercial CP products in China with almost 80% of national production as CP-52 (Zhang et al., 2013a). The applications of CPs in China are disperse, including use as flame retardant, plasticizer, rubbers, sealant, paint and lubrication (Zeng et al., 2015).

Numerous researchers have reported contamination of OHCs in the Chinese environment, primarily in abiotic media (i.e., air, water, soil and sediment), but the studies are not even distributed on a national scale and limited for wildlife in Yangtze River Delta (YRD). Still, exposure data have been published for birds (Chen et al., 2007, 2009b; Dong et al., 2004; Gao et al., 2009; Lam et al., 2008; Luo et al., 2009; Sun et al., 2012a, 2013; Zhang et al., 2011a, 2011b), fishes (Hu et al., 2010; Sun et al., 2015; Yang et al., 2010), amphibians (Wu et al., 2009, 2012b), and other species (Yin et al., 2015). In China, studies on OHCs in birds began about 10 years ago, focusing on Pearl River Delta (Liu et al., 2010; Luo et al., 2009; Shi et al., 2009; Sun et al., 2012a, 2012b, 2012c, 2013; Zhang et al., 2011a, 2011b) and north China (Chen et al., 2007, 2009b; Gao et al., 2009; Yu et al., 2011, 2013). Of the OHCs measured, 4,4′-DDE had the highest concentrations (Chen et al., 2009b; Gao et al., 2009), BDE-209 was the most abundant PBDE (Chen et al., 2007) and many POPs and some emerging pollutants were detected in birds in China (He et al., 2010; Luo et al., 2009; Shi et al., 2009; Sun et al., 2012a; Sun et al., 2012b; Sun et al., 2013; Zhang et al., 2011a). In addition to birds, frogs collected from an Electronic-waste (E-waste) site in Pearl River Delta had a unique PBDE congener profile that was intermediate between aquatic and terrestrial species (Wu et al., 2009). However, there is a major lack of information regarding the situation of such compounds in wildlife from YRD.

The YRD is an important area of economic growth in China. It supports extensive industrial activities, business, trade, transportation, agriculture and aquaculture, contributing 20% of the Chinese Gross domestic production in 2014 (China NBS, 2014). With rapid economic development and high energy consumption, the regional environment is deteriorating (Shao et al., 2006; Zhang et al., 2013c). A recent report showed high concentrations of OHCs in YRD air (Suzhou, Wuxi, Nantong) (Zhang et al., 2013c). Total discharges of chlorinated compounds, aromatic hydrocarbons, phenols, and polycyclic aromatic hydrocarbons in Yangtze River water, were estimated to range between 500 and 3500 kg d^{-1} (Müller et al., 2008) and represent a threat to wildlife and humans. The YRD is well known as “a town of rice and fish” in China. Rice is one of the most common staple food for Chinese, especially in South of China and paddy field is the typical feature of rice farming in many Asian countries. The paddy field environments are complex ecosystems including both aquatic and terrestrial environments (Tojo, 2014).

The aim of the present study is to screen for OHCs in wildlife from paddy field environments in the YRD and to quantify selected OHCs in order to establish a baseline for future environmental monitoring efforts.

2. Materials and methods

2.1. Samples

Two amphibian, two bird, one fish and one reptile species were collected from paddy fields in YRD, China, located in the junction between Jinshan District in Shanghai and Jiaxing City in Zhejiang province, close to Hangzhou Bay (Supplemental Material (SM), Fig. S1). The sampling site is also adjacent to Jianshan second industrial park. Hence, it may be impacted by both agriculture and industrial activities. The amphibian species were Dark-spotted frog (*Pelophylax nigromaculatus*, n = 5 in pool) and Asiatic toad (*Bufo gargarizans*, n = 8 in pool); the two bird species were Chinese pond heron (*Ardeola bacchus*, n = 3) and Peregrine falcon (*Falco peregrinus*, n = 3); the fish species was Rice field eel (*Monopterus albus*, n = 5 in pool) and the reptile species was

Short-tailed mamushi snake (*Gloydius brevicaudus*, n = 3). All of them are common species in the paddy fields of YRD and samples were collected with the help of local farmers. Dead birds were received after they accidently flew into nets protecting some paddy fields. The samples were stored in a freezer at −70 °C prior to dissection. After dissection, the pectoral muscle tissues of birds and whole muscle tissues of other species were freeze-dried, homogenized into powder in liquid nitrogen and stored at −20 °C until extraction.

2.2. Chemicals and standards

All chemicals and authentic reference standards used in the present study are presented in Table S1 (SM).

2.3. Analysis strategy

The present study was composed of qualitative analysis and quantitative analysis. For qualitative analysis, one pooled sample was analyzed for each species. Qualitative analysis of all the compounds was performed by gas chromatography–mass spectrometry (GC–MS) using electron capture negative ionization (ECNI) in full scan mode. The contaminants identified from qualitative analysis were summarized in Table S2.

Once the reference standard is available, the contaminants go for quantitative analysis. The samples used for quantitative analysis were described in Section (2.1). The quantification of the chlorinated compounds was achieved by gas chromatography with electron capture detection (GC-ECD). Quantification of the brominated compounds was performed by GC–MS using ECNI and selected ion monitoring mode measuring the bromide ions *m/z* 79 and 81. The methods are further described in the SM.

2.4. Extraction and cleanup

The samples were extracted according to Jensen et al. (2009) with some minor modifications. Separation of chlorinated paraffin was done using a silica gel (deactivated by 3% water) column to enable separation of the analytes prior to quantification. 2,2′,3,3′,4,5,6,6′-octachlorinated biphenyl (CB-200) for quantification of OCPs and PCBs, 1,2,3,4,5,6,7,8,12,12,13,13-Dodecachloro-1,4,4a,5,8,8a,9,9a,10,10a-decahydro-1,4:5,8:9,10-Trimethanoanthracene (DDC-Ant) for quantification of HCHs and decloranes and 2,2′,3,4,4′,5′-hexabrominated diphenyl ether (BDE-138) for quantification of brominated flame retardants (BFRs) were spiked into the samples prior to extraction as surrogate standards. Satisfactory results were obtained for separation of CPs from other OHCs (Fig. 1). Detailed chemicals information, extraction, lipid determination and cleanup procedures are presented in the SM.

2.5. QA/QC analysis

One procedure blank was run for each batch of six samples. Except for 4,4′-DDE (0.25 ng), no analytes were present in the blank. Baltic Sea herring (*Clupea harengus*, BSH) was analyzed together with the samples as a working lab standard. The range of recoveries (mean ± SD) for surrogate standards CB-200, DDC-Ant and BDE-138 were 62.7–104% (73.7% ± 5.91%), 56.6–118% (93.0% ± 11.7%) and 91.7–110% (101% ± 5.06%), respectively. The limit of detection (LOD) and limit of quantification (LOQ) were defined as three and ten times the baseline noise in the chromatogram, respectively. If the blank samples were contaminated, the LOQ was defined as three times the average amount found in the blanks. LOQ for CPs was estimated from the lowest concentration in the calibration curve (e.g., for CP S52, 8 μg mL^{-1}).

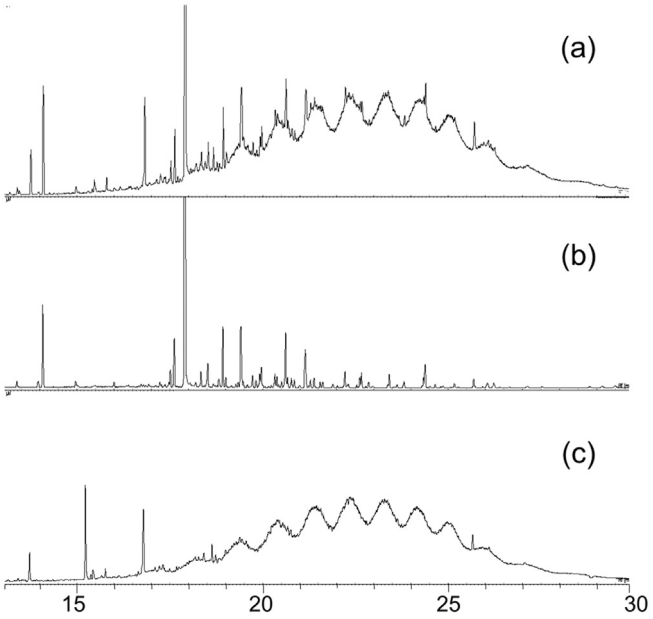

Fig. 1. GC-ECD chromatogram of (a) unfractionated Peregrine falcon (*Falco peregrinus*) sample, (b) fraction 1: PCBs and unipolar pesticides, (c) fraction 2: chlorinated paraffins and polar pesticides. The silica gel fractionation is described in Supplementary Material (SM).

3. Results and discussion

The results from qualitative analysis are presented in Table S2 and the chromatogram of heron was shown in Fig. S3. Overall, more than one hundred compounds (CPs not included) were identified in the wildlife falling into 12 chemical classes. The numbers of compounds identified in each class, halogen numbers, occurrence and the origin of the OHCs are presented in the same table (Table S2). PCBs, DDTs, CHLs, HCHs, DECs, PBDEs and MeO-PBDEs were commonly found among species. PCDEs, MeO-PCDEs and unknown series (c.f. 3.6) was only identified in heron.

The concentrations of CPs, OCPs, PCBs and BFRs in muscle tissue from the six species analyzed from the YRD are presented in Table 1. The results and discussion is based on the compound groups and ordered by the perceived scientific importance of the findings.

3.1. Chlorinated paraffins

CPs were detected in all species analyzed, except for the frog (Table 1). The snakes showed the highest concentrations of CPs (200 000–340,000 ng g^{-1} lw, i.e. as high as 0.2–0.3‰ in extracted fat, followed with CP levels of 97,000 ng g^{-1} lw in the toad and in the falcon, 8000–130,000 ng g^{-1} lw (Table 1). Among all quantified halogenated compounds, CPs were by far the most abundant contaminant, contributing over 90% of the total OHCs in snake, toad, falcon, respectively (Fig. S2 and S4). Concentrations of CPs were higher in terrestrial species (the falcon, snake and toad (8000–340,000 ng g^{-1} lw)) than in the species relating to the aquatic environment (heron, eel and frog <LOD to 9300 ng g^{-1} lw) (Table 1).

The present study has found high concentrations of CPs and this underscores the importance for further studies of CPs in the YRD region and elsewhere in China. Some of the CP concentrations in this study are comparable to those reported for invertebrates (4800–54,000 ng g^{-1} lw) and fish (9700–33,000 ng g^{-1} lw) in Liaodong Bay, North China (Ma et al., 2014). The concentrations in the YRD wildlife are about two orders of magnitude higher than SCCPs and medium chain chlorinated paraffins (MCCPs) in Greenland shark (430 ng g^{-1} lw) (Strid et al., 2013), Kittiwake (82–1100 ng g^{-1} lw)

Table 1
Concentrations of chlorinated paraffins (CPs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and flame retardants (ng g^{-1} lw) in muscle of wildlife from the Yangtze River Delta, China. Sum concentrations are in bold. The species are: Chinese pond heron (*Ardeola bacchus*, CPH), Peregrine falcon (*Falco peregrinus*, PF), Short-tailed mamushi snake (*Gloydius brevicaudus*, STM), Asiatic toad (*Bufo gargarizans*, AT), Dark-spotted frog (*Pelophylax nigromaculatus*, DSF) and Rice field eel (*Monopterus albus*, RFE).

	CPH			PF			STM			AT	DSF	RFE
N	3[a]			3[a]			3[a]			1[b] (8)[c]	1[b](5)[c]	1[b](5)[c]
CPs (Cereclor S52)[m]	**830**	**5000**	**9300**	**8000**	**130000**	**59000**	**340000**	**220000**	**200000**	**97000**	**nd**	**7000**
β-HCH	0.53	93	3.4	7.3	48	5.7	91	270	53	69	160	29
∑ HCHs[d]	**1.0**	**93**	**4.1**	**8.0**	**49**	**6.0**	**91**	**270**	**53**	**69**	**160**	**30**
∑ HEPs[e]	**nd [f]**	**8.4**	**3.4**	**5.2**	**27**	**0.22**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**
trans-Nonachlor	0.47	9.7	9.7	5.4	27	1.6	1.6	3.2	1.3	0.66	0.12	0.34
∑ CHLs[g]	**0.47**	**12**	**11**	**9.7**	**33**	**2.6**	**1.6**	**8.2**	**1.3**	**0.66**	**0.12**	**0.34**
∑ Endosulfan[h]	**7.7**	**32**	**180**	**17**	**6.7**	**7.6**	**1.9**	**11**	**4.5**	**3.6**	**0.44**	**0.74**
4,4′-DDT	25	28	130	14	8.1	4.7	27	55	31	68	29	37
4,4′-DDD	6.8	6.3	79	5.8	11	2.8	3.8	7.0	11	15	8.5	140
4,4′-DDE	390	1600	17000	180	1200	130	210	330	430	590	23	760
∑ DDTs[i]	**430**	**1700**	**17000**	**210**	**1200**	**150**	**260**	**410**	**490**	**680**	**61**	**970**
Mirex	29	120	420	21	77	35	32	20	9.4	12	0.35	3.4
HCB	0.02	3.2	0.09	0.08	3.0	0.19	9.0	3.4	0.90	9.9	1.1	0.05
∑ OCPs[j]	460	1900	18000	270	1400	200	400	720	560	780	230	1000
CB-118	11	47	280	25	32	9.9	3.0	18	7.1	5.7	0.75	2.9
CB-138	38	190	790	71	120	36	4.9	29	15	8.4	1.4	6.1
CB-153	31	80	480	63	83	36	7.6	36	18	15	1.9	7.8
CB-180	20	71	340	32	60	24	1.7	12	4.2	6.1	0.71	2.1
CB-202	13	48	230	21	27	13	2.7	13	4.6	4.1	0.38	2.7
CB-206	4.4	6.8	26	5.4	7.2	6.1	nd	2.7	0.69	1.2	nd	Nd
CB-209	4.2	6.4	26	4.1	4.8	9.7	1.1	5.2	0.99	2.2	0.64	0.59
∑ PCBs (7)[k]	100	390	1900	190	300	110	23	96	48	36	6.9	20
∑ PCBs (30)[l]	**210**	**690**	**3300**	**350**	**520**	**230**	**59**	**180**	**82**	**73**	**10**	**37**
DDC-DBF	3.0	72	80	29	37	25	0.18	1.6	0.60	1.9	nd	0.69
∑ Decloranes[o]	**3.5**	**75**	**87**	**30**	**37**	**25**	**0.18**	**1.6**	**0.60**	**1.9**	**nd**	**0.69**
BDE-47	0.77	0.57	2.1	1.7	1.1	4.7	0.28	0.12	0.12	0.38	0.22	1.9
BDE-99	0.80	0.99	1.0	2.4	2.5	5.2	0.32	0.44	0.30	0.44	0.29	1.28
BDE-154	5.3	10	40	2.0	2.1	2.8	0.47	1.8	2.4	1.9	0.10	2.1
BDE-153	6.1	16	60	5.9	7.9	5.8	1.5	4.6	2.9	2.3	0.20	1.2
BDE-209	0.48	0.83	1.0	1.7	0.25	0.64	12	2.5	4.0	6.3	5.1	5.0
∑ PBDEs (23)[n]	**29**	**52**	**210**	**28**	**22**	**30**	**27**	**22**	**36**	**24**	**8.1**	**34**
HBCDD	**39**	**68**	**330**	**4.8**	**3.7**	**12**	**1.2**	**230**	**9.8**	**14**	**3.1**	**16**

[a] Individual sample.
[b] Pool sample.
[c] Number of individual sample in one pool.
[d] ∑ HCHs: sum of α-HCH, β-HCH, γ-HCH, δ-HCH and ε-HCH.
[e] ∑ HEPs: sum of heptachlor, cis-heptachlorepoxide and trans-heptachlorepoxide.
[f] nd: not detected.
[g] ∑ CHLs: sum of trans-nonachlor, oxy-chlordan, trans-chlordan and cis-chlordan.
[h] ∑ Endosulfan: sum of α-Endosulfan and β-Endosulfan.
[i] ∑ DDTs: sum of 2,4′-DDE, 2,4′-DDD, 2,4′-DDT, 4,4′-DDE, 4,4′-DDD and 4,4′-DDT.
[j] ∑ OCPs: sum of ∑ HCHs, ∑ HEPs, ∑ CHLS, ∑ Endosulfan, ∑ DDTs, Mirex, HCB, aldrin and endrin.
[k] ∑ PCBs (7): sum of CB-28, 52, 101, 118, 138, 153 and 180.
[l] ∑ PCBs (30): sum of CB-28, 52, 101, 105, 118, 128, 138, 146, 150, 153, 170, 180, 183, 187, 189, 194-199 and 201-209.
[m] CPs are calculated based on standard Cereclor S52
[n] ∑ PBDEs (23): sum of BDE-28, 47, 99, 100, 153, 154, 183 and 194-209.
[o] ∑ DECs: sum of DDC-DBF, HCTBPH, *syn*-DDC-CO, *anti*-DDC-CO and aCl_{10}DDC-CO.

(Reth et al., 2006), Little auk (690–4600 ng g^{-1} lw) (Reth et al., 2006), Arctic char (200–2100 ng g^{-} lw) (Reth et al., 2006) and Cod (46–236 ng g^{-1} lw) (Reth et al., 2006) from outside of China. The YRD wildlife concentrations of CPs are also far higher than the highest average values measured in aquatic species from Lake Ontario and northern Lake Michigan (Slimy sculpin, 730 and 2800 ng g^{-1} lw, respectively) (Houde et al., 2008), and UK human milk (max 1100 ng g^{-1} lw) (Thomas et al., 2006). The results from the current study indicate that wildlife contamination of CPs is more severe in China than in other parts of the world.

3.2. Organochlorine pesticides

4,4′-DDE was the most abundant organochlorine pesticide contaminant in the YRD wildlife and ΣDDT concentrations were up to 17,000 ng g^{-1} lw in the heron (Table 1). ΣDDT in the six species represented 50–70% of the OHCs in the wildlife when CPs were excluded from the calculation. This result is consistent with those reported in other studies in China (Table S4). 4,4′-DDE was detected in all samples and contributed between 79% and 98% of ΣDDTs in all species but the frog (Table 1, Fig. S5). The knowledge of organochlorine pesticides in this frog is limited, but the data show it is exposed to 4,4′-DDT albeit at low concentrations. Further, the ratio of 4,4′-DDT/ΣDDTs was up to 0.48 in frog but between 0.007 and 0.13 for the other five species from the YRD, indicating the input of new DDT was limited.

Among the other organochlorine pesticides, β-HCH was detected in all samples and its concentrations ranged from 0.53 to 270 ng g^{-1} lw (Table 1), dominating the HCH isomers in the YRD wildlife. The percentage of β-HCH and α-HCH in all six species ranged from 96 to 100% and 0 to 1.2%, respectively, of ΣHCHs (Fig. S5). The results confirm that β-HCH had the highest bioaccumulation potential of the HCH isomers (Buser and Mueller, 1995) and do not indicate any recent use of Lindane (γ-HCH). The frequent occurrence of 4,4′-DDE and β-HCH at high concentrations and the low levels of 4,4′-DDT and α-HCH suggest that residues

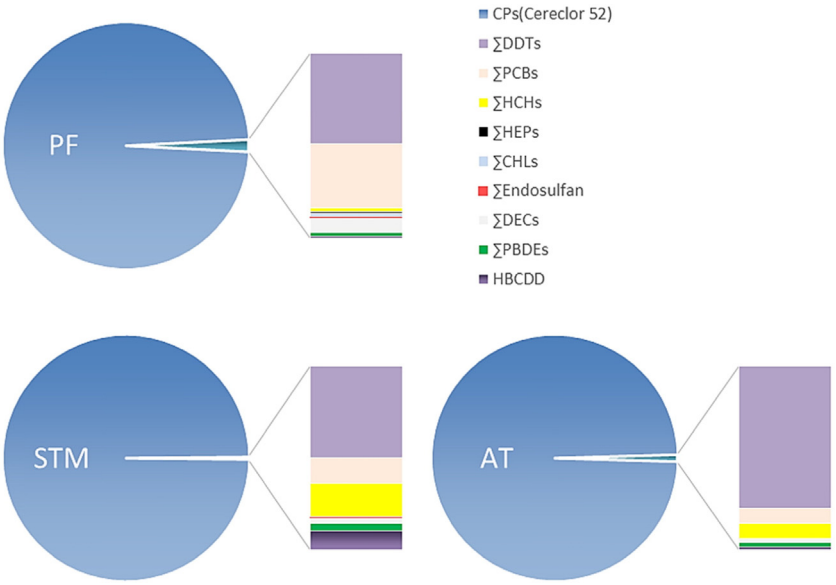

Fig. 2. Contribution of chlorinated paraffins (CPs) and other halogenated persistent bioaccumulating compounds in Peregrine falcon (*Falco peregrinus*, PF), Short-tailed mamushi (*Gloydius brevicaudus*, STM) and Asiatic toad (*Bufo gargarizans*, AT). In addition to the CPs, the compound/classes of compounds shown are: dichlorodiphenyltrichloroethanes (DDTs), polychlorinated biphenyls (PCBs), hexa-chlorocyclohexanes (HCHs), heptachlor and related compounds (HEPs), chlordane and related compounds (CHLs), Endodulfan, dechlorane and related compounds (DECs), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecanes (HBCDD).

of DDTs and HCHs in the samples were largely derived from historical uses/discharges.

Mirex was the third most abundant organochlorine pesticide with concentrations from 0.35 to 420 ng g^{-1} lw (Table 1). Mirex concentrations in two bird species averaged 118 ng g^{-1} lw, one and two orders of magnitude greater than those determined in Great blue heron eggs from St. Lawrence River (Canada) (Champoux et al., 2006) and coastal British Columbia (Canada) (Harris et al., 2003) and Grey heron eggs from Limpopo Province of South Africa (Bouwman et al., 2013). Mirex has rarely been reported in the Asia-Pacific region and there is a lack of data on this compound in China. However, oyster samples collected from the Bohai and Huanghai Sea of northern China were 100 ng g^{-1} lw of Mirex (Jia et al., 2011). Mirex concentrations in Chinese pond heron eggs from Mai Po Village and Ho Sheung Heung (Hong Kong, China) were 255 and 126 ng g^{-1} lw, respectively, (Wang et al., 2011), slightly higher than or in the same range as our results. The present results and those of previous studies show Mirex to be a compound of concern in China. It is known that Mirex has been used as termiticide in China (Wang et al., 2010a) and the consumption is known to be relatively high in the southeast provinces of China (Wang et al., 2010a). Most of the Mirex manufacturers are today located in Jiangsu Province, which lies in the downstream area of the Yangtze River (Wang et al., 2010a). The production, together with application in southeastern China, are reasonable sources of Mirex found in the YRD wildlife in this study.

As shown in Table 1, *trans*-nonachlor and hexachlorobenzene (HCB) were present in all the species analyzed from the YRD. However, the concentrations were lower than the three most abundant organochlorine pesticides discussed above. HCB was mainly used to produce pentachlorophenol in China. The HCB might also be a trace contaminant in other pesticides and/or a byproduct from industrial processes and incineration activities.

Polychlorinated diphenyl ethers (PCDEs) and methoxylated polychlorinated diphenyl ethers (MeO-PCDEs) were identified in the heron samples but not quantified. However, the observation led to a separate more in-depth study that for which the results will be reported elsewhere. The PCDEs and polychlorophenoxyphenols (PCPPs) are impurities from pentachlorophenol commercial products (Becker et al., 1991; Holt et al., 2008; Koistinen et al., 1997; Persson et al., 2007) while the MeO-PCDEs may be methylated PCPPs.

3.3. Polychlorinated biphenyls

The concentrations of ΣPCBs (30 congeners) were 10–3300 ng g^{-1} lw and those of ΣPCBs (7 congeners) ranged from 6.9–1900 ng g^{-1} lw in the samples from the YRD, with the highest concentrations (210–3300 ng g^{-1} lw) in the heron, followed by the falcon (230–520 ng g^{-1} lw) (Table 1). However, these concentrations are lower than those in muscle of birds from the Qingyuan E-waste recycling site (960–1,400,000 ng g^{-1} lw) and from the Beijing Raptor Rescue Center (40–28,000 ng g^{-1} lw), China (Table S4). The levels of PCBs in birds (210–3300 ng g^{-1} lw) presented herein are still higher than those in fish, amphibians and snake (10–180 ng g^{-1} lw), and confirm that the accumulation of PCBs in YRD wildlife is related to their trophic level.

The penta-, hexa-, and hepta-CBs were predominant, contributing 76–80% of the ΣPCBs in all YRD wildlife (Fig. S6), which is consistent with results from Pearl River Delta in China (Luo et al., 2009). Among them, the PCB congeners, CB-118, -138, -153 and -180 constituted 48–60% of ∑ PCBs.

A novel result from the present study is the detection of highly chlorinated biphenyl congeners (octaCBs–decaCB) in relatively high concentrations (Fig. S6 and S3). These highly chlorinated biphenyl (Cl_{8-10}) congeners constituted 18–24% of the ∑ PCBs in five of the species from the YRD, while frog showed a lower abundance of these CB homologues (9.9%) (Fig. S6). Also, all of the Cl_{8-10} PCB congeners, except for CB-200, were present in all samples (Fig. S6). This is an intriguing result indicating a hitherto overlooked sources of PCBs and/or novel production of highly chlorinated biphenyls. This is similar to a previous study on bird eggs from East Tai Lake in YRD (Zhou et al., 2015; Zhou et al., in press).

Commercial PCB mixtures produced and used in China have congener patterns similar to those of Aroclor 1242 and Aroclor 1254 (Jiang et al., 1997). However, even commercial PCB mixtures of Aroclor 1260 contain very low, or even negligible, amounts of Cl_{8-10} PCB congeners. Results of the current study indicate the production and/or use of unknown PCB mixtures with a high degree of chlorination. In support of our results, surface sediments from the Wuhan River, China show the presence of Cl_{8-10} PCBs (Yang et al., 2009). Similarly, in the Qingyuan E-waste recycling area CB-209 was reported in 47% of the wildlife

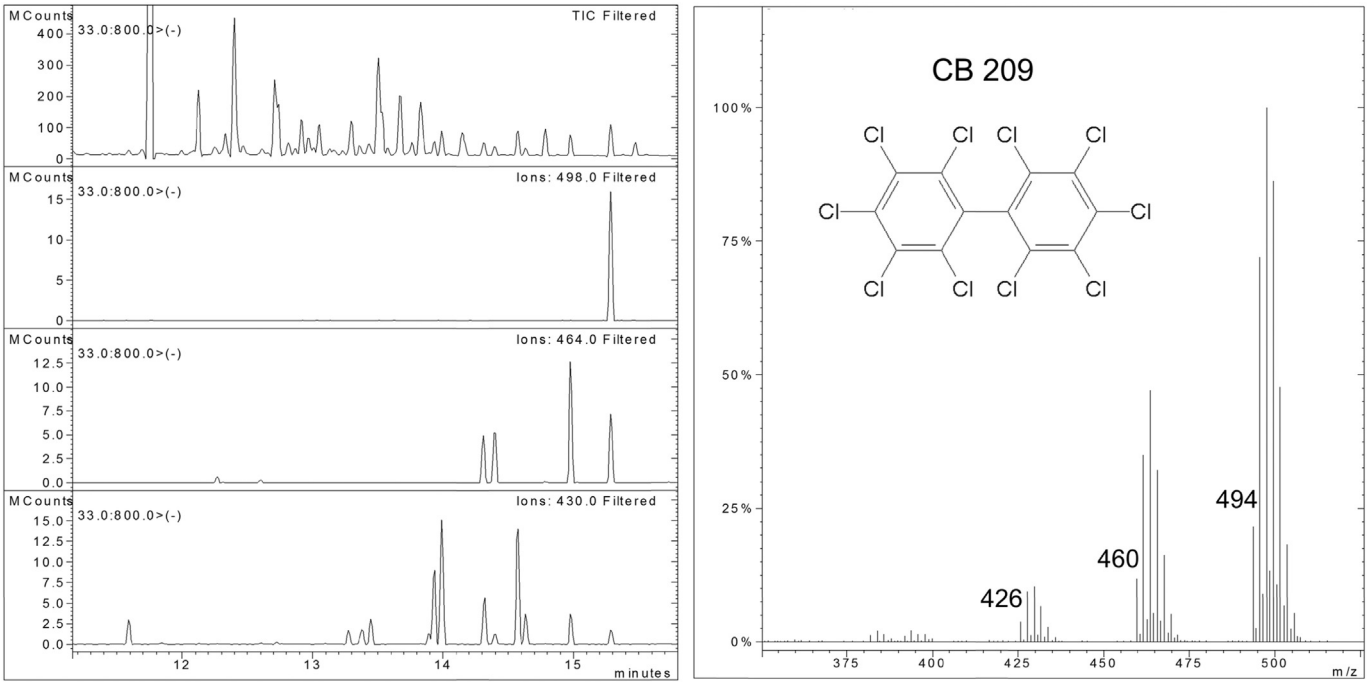

Fig. 3. Ion chromatograms of octa-, nona- and deca-PCBs in Chinese pond-heron (*Ardeola bacchus*), to the left, and the mass spectrum of the decachlorinated biphenyl (CB-209), to the right.

samples, with concentrations ranging from 0.2 to 16 ng g^{-1} ww (Wu et al., 2008). Aroclor 1268, 1270 and 1271 all contain higher percentages of CB-206 and/or CB-209 (Hartmann et al., 2004; Kannan et al., 1997, 1998; Maruya and Lee, 1998) and these or similar PCB products produced in China, may be a source of the highly chlorinated biphenyls. This conclusion is supported by comparing the CB-209/CB-206 ratios in Aroclor 1260, 1268, 1270 and 1271 of 0.19, 0.28, 17 and 60, respectively (Hartmann et al., 2004) with those in the YRD wildlife of 1.0–1.9. It is surprising that Cl_{8-10} have not been reported more frequently in other studies in China.

3.4. Dechloranes

Dechlorane 602 (DDC-DBF), Dechlorane 604 (HCTBPH), and Dechlorane Plus (DDC-CO) (abbreviations according to Bergman and coauthors (Bergman et al., 2012), cf. Table S1) were analyzed in the present study. DDC-DBF showed the highest abundance in the wildlife from YRD except for frog (Table 1). *Syn*-DDC-CO and *anti*-DDC-CO were only detected in the heron and falcon, respectively, and DDC-Ant and HCTBPH were not detectable in any of the samples. In contrast, fish from Lake Ontario contain all of these dechloranes (DDC-DBF > DDC-CO > HCTBPH > DDC-Ant) and the concentrations of DDC-DBF were 15–80 times greater than the others, suggesting that DDC-DBF is present at higher environmental concentrations and/or more bioavailable to fish than DDC-CO and the other related compounds (Shen et al., 2009). Concentrations of DDC-DBF in the bird species (3.0–80 ng g^{-1} lw in heron and 25–37 ng g^{-1} lw in falcon) were comparable to those reported by Guerra et al. (2011). They reported mean concentrations of DDC-DBF in Peregrine falcon eggs in the Canadian Great Lakes basin that ranged from 27.4 to 89.2 ng g^{-1} lw, likely an effect of the manufacturing of dechloranes in Niagara Falls (NY, USA) (Guerra et al., 2011). There is a DDC-CO manufacturer in east China and dechloranes were also detected in water, soil, and air nearby (Wang et al., 2010b), and their products are similar to those of Oxychem (NY, USA) (Zhang et al., 2013b) The comparable levels of DDC-DBF detected in birds from Canada and the present study, together with the relatively low bioavailability of dechloranes, suggests that the source of dechloranes in the YRD wildlife is the nearby manufacture and use of DDC-CO.

3.5. Brominated flame retardants

The concentrations of ΣPBDEs (23 congeners) in the six wildlife species from the YRD ranged from 8.1–210 ng g^{-1} lw, with the heron having the highest concentrations (29–210 ng g^{-1} lw). In addition to ΣPBDEs (23 congeners), concentrations of four individual congeners are reported in Table 1. Our results are consistent with those reported by Luo et al. (2009), who also found Chinese pond-heron to contain the highest PBDE concentrations of five water-bird species all occupying higher trophic levels (Luo et al., 2009), and indicates that the heron readily accumulates PBDEs. The concentrations of ΣPBDEs (23 congeners) in heron were comparable to those in eggs of black-crowned night heron from urban sites of Xiamen (120 ng g^{-1} lw) and Quanzhou (320 ng g^{-1} lw) in South China (Lam et al., 2008), but lower than levels in muscle of heron from an *E*-waste recycling site in South China (530–2500 ng g^{-1} lw) (Luo et al., 2009). In the latter case it is most likely an effect of heavy contamination due to the handling of E-waste. Similarly, PBDEs in the frog (*Rana limnocharis*) and water snake (*Enhydris chinensis*) from an E-waste recycling site in South China were reported at 96–1200 and 190,000 ng g^{-1} lw, respectively (Wu et al., 2009, 2008), which is two orders of magnitude higher than those of similar species analyzed from the YRD as part of the current study.

Contrary to PCBs, the congener profiles of PBDEs differed between the species studied (Fig. S6). Wu and coworkers reviewed PBDEs profile in wildlife from Chinese environment, showing that most aquatic organisms accumulate more of the lower brominated PBDE congeners when compared to terrestrial species; frogs seemed to show an intermediate congener profile (Wu et al., 2012a). For example, BDE-47 and BDE-99 were the major congeners in aquatic species, whereas the terrestrial species accumulated more BDE-153. For amphibian species such as frog, the PBDE pattern is dominated by BDE-99 and BDE-153 (Wu et al., 2012a). The eel, showed the highest proportions of BDE-47, followed by the frog, falcon, toad, snake and heron, while BDE-153 levels were contrasting this picture (Fig. S6). Drouillard and coworkers examined dietary retention during the posthatch-to-fledgling life

stage (0–36 d) in America kestrel (*Falco sparverius*) via daily gavage dosing and observed that BDE-47 had the lowest accumulation and dietary retention among BDE-47, 99, 100 and 153, while BDE-153 showed highest retention factor (Drouillard et al., 2007), and these results support the patterns observed in Chinese bird species. The concentration of BDE-209 ranged from 0.25–12 ng g^{-1} lw among all six species reported on in the present study. Further, the occurrence of all 3 nonaBDE congeners together with BDE-209 in the samples indicates the use and discharges of decaBDE in YRD.

HBCDD was detected in all YRD samples at concentrations (1.2–330 ng g^{-1} lw; Table 1) that are comparable to their levels of ΣPBDEs. Concentrations of HBCDD in the heron in the current study were higher than those of most bird species from China (Table S4). The present results indicate that the HBCDD contamination in YRD is as much as that of a hotspot for this chemical in E-waste recycling sites. Lam et al. (2009) found that HBCDD in humpback dolphins from Hong Kong watershed significantly increased from 1997 to 2007, with an estimated annual rate of 5%, and assumed the rate of usage of HBCDD remains. Comparison of PBDE and HBCDD concentrations in species from the YRD with those of wildlife from the Pearl River Delta implies that these two BFRs are equally important for environmental monitoring programs.

3.6. Emerging OHCs

A series of hitherto unidentified polychlorinated OHCs, all with similar chromatographic and mass spectrometric behavior, was found in YRD wildlife. It has not been possible to confirm the structures of these substances with the formula $C_{14}H_xCl_y$ with $x + y = 12$; with the mass spectrum example of $C_{14}H_4Cl_8$ being shown in Fig. 4, pointing out the molecular ion at *m/z*: 452 Da, and fragments ions (*m/z*) at 418, 382 and 348 Da. These spectra fit with one octa-, three hepta-, and several hexachlorinated substances and most likely also a pentachlorinated congener. All of these not yet structurally defined OHCs are found in all of the individual heron samples (Fig. 4). Unfortunately, the amounts of these OHCs were too low to allow any further mass spectrometric analysis, i.e. Electron Ionization. However, two possible structures are proposed; one suggestion is a stilbene backbone structure and the other is a DDE-like compound with an additional number of chlorine atoms attached to the phenyl rings. To identify these novel compounds, one stilbene congener with five chlorines was synthesized in house. However, the retention time and/or fragmentation pattern did not match any of the peaks in the samples. Nevertheless, a stilbene structure must not be excluded and more effort is warranted to identify this novel class of compounds. The spectrum of the "unknowns" show similarities with compounds reported in blubber from the Atlantic common dolphin (*Delphinus delphis*), which included two hepta- and one hexachlorinated compounds(Hoh et al., 2012). These authors suggested that the "unknowns" are polychlorobisdiphenyl ethenes, i.e. more highly chlorinated compounds than DDE itself. Since this was not confirmed by comparison to any authentic reference standards it is just a suggestion, like ours above. Results of the current study clearly show that an emerging class of polychlorinated OHCs has been identified in higher-trophic-level wildlife, and we recommend further studies of this group of compounds in other regions and species to improve our understanding of its pervasiveness.

3.7. Species for environmental monitoring

In the YRD, terrestrial biota (the snake, falcon and the toad) had much higher concentrations of total OHCs (primarily CPs) than the aquatic wildlife (the heron, eel and frog). This indicated that species feeding primarily on terrestrial species might be good bioindicators for CPs monitoring. However, heron had the highest concentrations of ΣDDTs, ΣPCBs, ΣPBDEs, ΣChlordanes (CHLs), ΣDechloranes, Mirex and HBCDD of all species. Bird and bird eggs have been widely used for environmental monitoring purpose, due to the high trophic level, high and stable fat content and often wide geographic distribution (Bignert and Helander, 2015; Miller et al., 2014). Hence, heron is suggested to be utilized to monitor temporal and geographical trend of OHCs in YRD.

4. Conclusion

In conclusion, the present study on wildlife in the YRD found: *i*: extensive contamination by CPs; *ii*: a novel pattern of PCB contamination, with octaCBs to decaCB at relatively high concentrations (i.e., making up

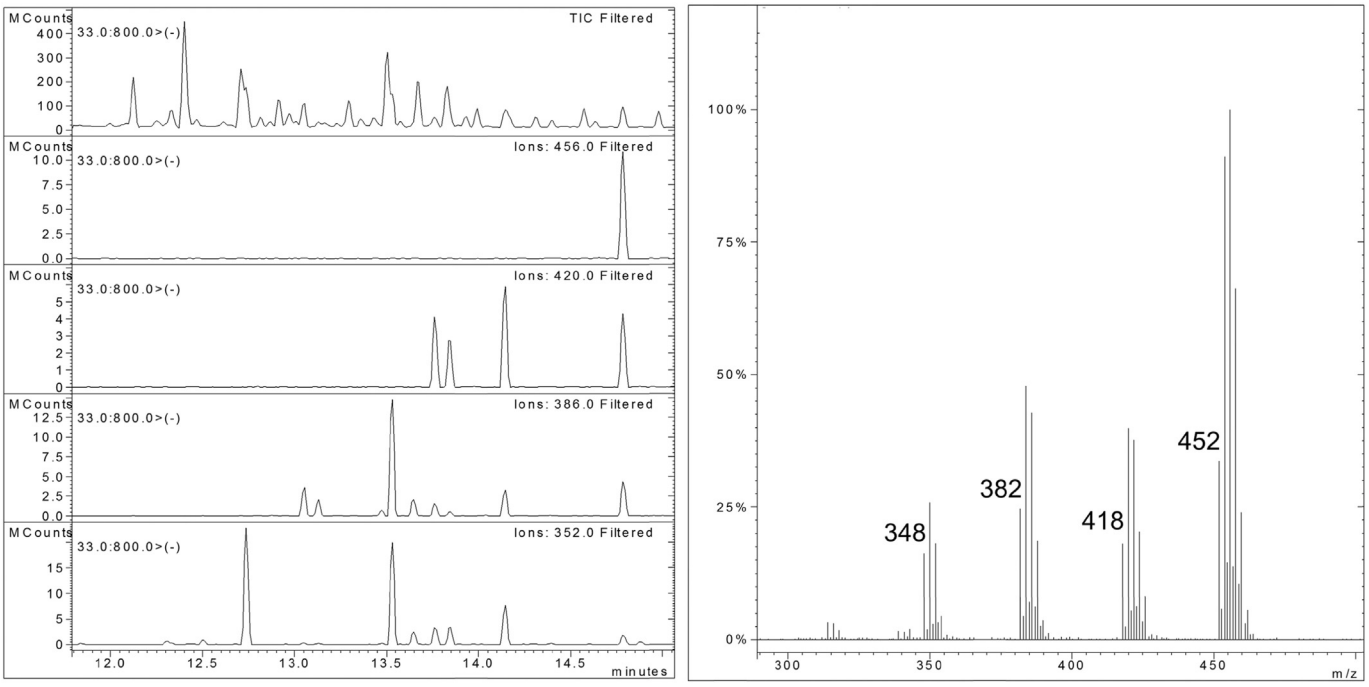

Fig. 4. Ion chromatograms of penta-, hexa, hepta and octachlorinated congeners of a novel set of environmental pollutants present in Chinese pond-heron (*Ardeola bacchus*), to the left. A full mass spectrum of one of the novel compounds is shown, indicating substitution of 8 chlorine atoms.

20% of ΣPCBs content in the samples) and *iii*: an emerging class of polychlorinated OHCs, including polychlorinated congeners with 5–8 chlorines, not yet structurally confirmed. In addition to these novel findings, the study showed how complicated and extensive the OHCs contamination of wildlife is in the YRD, a relatively small area of China, and emphasizes the importance of structured research monitoring efforts in YRD but also all of China because of the ongoing industrial growth.

Further, it is worthwhile highlighting that the HBCDD concentrations in several species of YRD wildlife were higher than the sum of their 23 PBDE congeners (Table 1). HBCDD is listed as a new POPs according to Stockholm Convention in 2013, again calling for further environmental monitoring in the YRD and other regions of China, exploration of the sources of the contamination and comparison with electric and electronic recycling hot spots in, e.g., the Pearl River Delta. Apart from CPs, DDE was the predominant contaminants in most species, calling for concern about ecotoxicological effects, particularly in the aquatic environments.

The present study increases the collective knowledge on OHCs in wildlife in YRD. The contamination we observed raises the question of the effects that the chemicals are having on the health of these and other species in the YRD. Of particular concern are the CPs, especially the SCCPs are known to be toxic to aquatic species (WHO, 1996); assessments of their effects are strongly recommended. Overall, the results presented herein are a call for action regarding the pollution of the YRD, as industrial development in this region is continuing to expand.

Acknowledgments

We sincerely thank Andreas Ryden for synthesising the pentachlorostilbene. Dr. Karen Kidd from University of New Brunswick, Canada, is appreciated for her kind help on language polishing and useful comments. The study was funded by the Swedish Research Council (No. 639-2013-6913); the Swedish Toxicology Sciences Research Center (Swetox); the National Natural Science Foundation of China (Grant No. 41401571); the Fundamental Research Funds for the Central Universities (2013KJ022) and through the Chinese 111 program.

Appendix A Supplementary data

Additional experimental details (chemicals, extraction and cleanup procedure, and instrument analysis); identification of chlorinated paraffins (CPs); and additional figures and tables. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2016.02.176.

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