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Trophic Transfer of Dechloranes in the Marine Food Web of Liaodong Bay, North China

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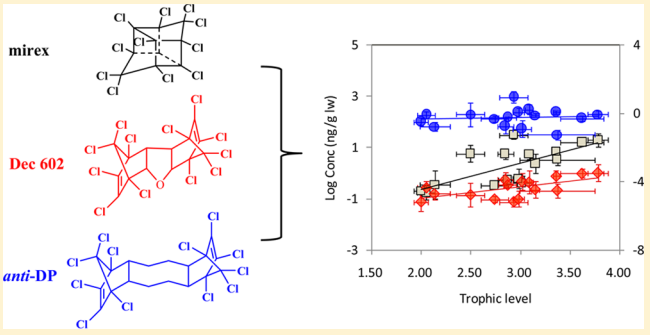
Supporting Information

ABSTRACT: Dechloranes are of particular concern because of their ubiquity in environmental matrices, but little is known about their trophic transfer in aquatic food web. This study investigated the trophic transfer of seven dechloranes in a marine food web from Liaodong Bay, China. Dechloranes were determined in sediments and 15 marine species including benthic invertebrates, fish and gulls collected from Liaodong Bay. Biomagnification factors (BMF_{TL}) of dechloranes in black-headed gulls were calculated to be 6.4, 1.7, 0.45, 0.36, 0.14, and 0.11 for mirex, Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603), antiundecachloropentacyclooctadecadiene (anti-Cl_{11}DP), syn-dechlorane plus (syn-DP), and anti-DP. Significantly positive relationships were found between lipid equivalent concentrations of mirex, Dec 602, and anti-Cl_{11}DP and trophic levels, and the trophic magnification factors (TMFs) were 13, 3.7, and 5.6, respectively, indicating that these compounds undergo trophic magnification in the aquatic food web. Lipid equivalent concentrations of Dec 603 and DP isomers did not exhibit a statistically significant correlation with trophic levels. The relatively low trophic magnification potentials of Dec 603 and DP isomers were possibly due to their extreme hydrophobicity ($\log K_{OW}$: 11.2−11.3) and subsequent low bioavailabilities compared with mirex (7.0), Dec 602 (8.1) and anti-Cl_{11}DP. The results provided important information for understanding the ecological risk of dechloranes.



INTRODUCTION

Dechloranes including mirex, dechlorane plus (DP), Dechlorane 602 (Dec 602), and Dechlorane 603 (Dec 603) are used in coatings, plastic materials and other polymeric systems as highly chlorinated flame retardants (HFRs).[1] Dechloranes were found to be persistent and ubiquitous in the environment.[2−4] Among dechloranes, DP has been classified as a high-production-volume chemical (500−5000 tons/year) by the United States Environmental Protection Agency (EPA),[5] and has been widely detected in different environmental matrices including sediment,[2,6,7] atmosphere,[8−10] surface water,[9,11] and wildlife.[4,12] Exposure to DP has been linked to the effects of carbohydrate, lipid, nucleotide, and energy metabolism in rat.[13] Dec 602 and Dec 603 were manufactured by the same manufacturer (Oxychem) as DP since the late 1960s and 1970s,[14] and in 2010 Shen et al. first detected Dec 602 and Dec 603 in sediments and fish from the Great Lakes.[14,15] Several subsequent studies have identified their occurrences in sediment and wildlife.[15−17]

While these studies reported the wide occurrence and environmental persistence of dechloranes, trophic transfer in food web is another vital criterion for assessing their potential ecological risk. In the aquatic food web, concentrations of nonmetabolizing chemicals with log octanol−water partition coefficient ($\log K_{OW}$) of 5.0−8.0 showed high biomagnification potentials.[18] Isomers of DP, as the main dechloranes, exhibited high K_{OW} value with logarithm of 11.3.[19] Because of such extreme hydrophobicity, DP was not considered to be of high biomagnification potential. However, the reported trophic magnification of DP in aquatic food web is inconclusive: trophic dilution of DP was observed in food web from Lake Ontario, but trophic biomagnification of anti-DP was observed in food web from Lake Winnipeg.[4] Besides DP, other new dechloranes including dechlorinated metabolites of DP (undecachloropentacyclooctadecadiene, Cl_{11}DP), Dec 602, and Dec 603 have also been detected in upper trophic level organisms including fish,[20] birds[16] and human.[21] The K_{OW} values of Cl_{11}DP was expected to be lower than DP due to the less chlorine atom, and field investigation has reported their 10-folds higher bioaccumulation potentials in freshwater fish compared to parent DP.[20] As for Dec 602 and Dec 603, their $\log K_{OW}$ values were 8.1 and 11.2, respectively,[19] and experimental exposure data on Atlantic salmon indicated relatively high bioaccumulation potential of Dec 602 compared with Dec 603 and DP.[22] Similar high bioaccumulation potential of Dec 602 than Dec 603 and DP were also found in lake trout from Great Lakes,[14,17] and marine invertebrates in coastal

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environment of Northern China.[23] While these reports have been published concerning the bioaccumulation of dechloranes in the field and in laboratory aquatic organisms, there is no information about the trophic transfer of Dec 602, Dec 603 and dechlorinated DP in food webs.

In addition, Cl_{11}DP have been detected in fish,[20] birds[16] and human,[21] highlighting their potential ecological and health risk. Although Cl_{11}DP has been suggested to be metabolized from DP in organisms,[20] our study on Chinese sturgeon did not observe Cl_{11}DP after exposing high DP concentrations to liver microsomes while high proportion of Cl_{11}DP has been observed in Chinese sturgeon.[24] Result of a recent study has detected Cl_{11}DP in the sediments from Niagara River,[7] indicating that sediment could be an alternative source for Cl_{11}DP in organisms. Thus there is a need to explore metabolism and accumulation of the pollutants simultaneously to clarify the contribution of dechlorinated DP in organisms from sediment or metabolism.

Liaodong Bay is an enclosed inner sea in North China, and its food web model has been established and applied to clarify the characterization of trophic transfer for PBDEs.[25,26] In this study, we analyzed seven dechloranes (mirex, Dec 602, Dec 603, syn-Cl_{11}DP, anti-Cl_{11}DP, syn-DP, and anti-DP) in the same food web including five invertebrate species, eight fish species, and two gull species. Trophic magnifications of dechloranes were further explored by analyzing the relationships between contaminant concentrations and trophic levels in different species.

MATERIALS AND METHODS

Chemicals and Reagents. The standards of dechloranes (syn-DP, anti-DP, anti-Cl_{11}DP, Dec 602, Dec 603, and mirex) and $^{13}C_{12}$-PCB180 were obtained from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Commercial product of DP was obtained from Jiangsu Anpon Electrochemical Company in 2011. Dichloromethane (DCM), *n*-hexane, methyl *tert*-butyl ether (MTBE), and methanol were pesticide residue grade obtained from OmniSolv (EM Science, Lawrence, KS). 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).

Sample Collection. Liaodong Bay is in the north region of the Bohai Sea, north China (40°52′41.17″N, 121°51′55.98″E), with an area of about 10 000 km^2 and a maximum depth of about 32 m. All biota and sediment samples were collected on the coast of Liaodong Bay in November 2006 as described previously,[25,26] and the sampling map was shown in Figure S1, Supporting Information (SI). Sediments (n = 15) were freeze-dried, grounded, and sieved through a 0.2 mm mesh before storage at −20 °C. Twenty three gulls including seventeen black-tailed gulls (*Larus crassirostris*) and six black-headed gulls (*Larus ridibundus*) were collected (Table S1, SI). Eight fish species including redeye mullet (*Liza hematocheila*) (n = 5), goby (*Synechogobius hasta*) (n = 5), small yellow croaker (*Pseudosciaena polyactis*) (n = 6), Japanese spanish mackerel (*Scomberomrus niphonius*) (n = 3), half-smooth tongue-sole (*Cynoglossus semilaevis*) (n = 6), flathead fish (*Platycephalus indicus*) (n = 3), China anchovy (*Thrissa kammalensis*) (n = 10), and black spotfedbass (*Lateolabrax japonicas*) (n = 3), and five invertebrates including short-necked clam (*Ruditapes philippinarum*) (n = 3), mactra quadrangularis (*Mactra veneriformis, Reeue*) (n = 3), rock shell (*Rapana venosa*) (n = 3), Chinese mitten-handed crab (*Eriocheir sinensis H. Milne-Eswards*) (n = 3), mole cricket (*Upogebia major(de Haan)*) (n = 4) were collected with a bottom trawl. Among the fishes collected, China anchovy (*Thrissa kammalensis*) was reported as the major diet of gulls.[27,28] Body length (from the nose to the caudal fin basis) and body weight of fish were recorded. As for gulls, body length (from the nose to the tail) and body weight was recorded, and juvenile gulls were distinguished based on the characteristics of feather, legs, and beak. Trophic levels (TL) of all these organisms used in this study were determined by stable nitrogen isotopes as described in our previous paper.[26] Ratios of stable isotopes were measured in soft tissues of invertebrates (n = 3 for each species) and muscle tissues from fishes (n = 3 for each species) and seabirds (n = 16 for black-tailed gull, and n = 7 for black-headed gull). Muscle was chosen for both isotope and chemical analysis, because different turnover rates of isotope ratios exist among tissues, and the turnover rates in muscle were relatively slow.[29] All the biota samples were stored at −20 °C prior to analysis.

***In Vitro* Microsomal Incubation.** Microsomes were isolated from black-tailed gulls, according to the method improved by Benedict et al,[30] and dithiothreitol (DTT) was included in the homogenization, wash, and resuspension buffers to preserve the catalytic activity of reductases. In brief, liver of gulls were removed and separated and were stored in liquid nitrogen until microsomal preparation. Then, liver were homogenized on ice using 3 times weight by volume of homogenization buffer containing 0.1 M NaH_2PO_4, 0.15 M KCl, 1 mM Na_2EDTA, 10 mM dithiothreitol (DTT), and 20% v/v glycerol, PH 7.4. After centrifugation at 10 000*g* for 30 min, the supernatant was transferred to a new tube. Then, the liver microsome pellet was collected after centrifugation at 100 000*g* for 60 min. 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 an exposure chemical. The concentration for syn-DP or anti-DP in the incubation mixture was 50 ng/mL. The protein concentration in the reaction vial was 7.5 mg/mL and the CYP1A1-catalyzed EROD activity was 12 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.

Sample Preparation. The analysis of dechloranes followed the procedures reported previously.[24] Tissues (or sediments) were freeze-dried, and then approximately 1−5 g dry weight (dw) subsamples were spiked with ^{13}C-labeled PCB ($^{13}C_{12}$-PCB180), and extracted by accelerated solvent extraction (Dionex ASE-200, Sunnyvale, CA). The extraction employed two cycles of 10 min: the first cycle was performed with *n*-hexane/dichloromethane (DCM) (1:1) at 100 °C and 1500 psi, followed by a second cycle with *n*-hexane/methyl tert-butyl ether (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 transferred to 15 mL glass tubes by 8 mL hexane, and then 4 mL 0.5 M KOH in 50% ethanol was added. 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 eluates were further purified

Table 1. Mean Biological Parameters and Concentrations of Dechloranes in Sediments (pg/g Dry Weight) and Organisms (pg/g wet weight) Collected from Liaodong Bay, North China.

species[a]	TL	*n*	length (cm)	weight (g)	lipid content (%)	mirex	Dec 602	Dec 603	anti-Cl_{11}DP	syn-DP	anti-DP
SED[b]		15				8.0 ± 8.0	3.1 ± 5.1	ND-27	33 ± 66	6.7 ± 16	33 ± 73
Invertebrates											
RP	2.00 ± 0.07	3			0.28 ± 0.08	1.0 ± 1.0	0.2 ± 0.2	1.2 ± 0.6	ND	0.4 ± 0.2	1.6 ± 1.2
MVR	2.05 ± 0.09	3			1.9 ± 0.09	22 ± 40	6.1 ± 3.0	0.19 ± 0.01	0.34 ± 0.18	24 ± 12	17 ± 6.0
RV	2.87 ± 0.09	3			0.30 ± 0.16	2.0 ± 2.1	1.2 ± 0.8	0.4 ± 0.2	ND	0.4 ± 0.2	1.8 ± 1.2
ESME	2.74 ± 0.14	3			0.64 ± 0.06	1.0 ± 0.9	0.6 ± 0.2	0.6 ± 0.6	ND	0.4 ± 0.2	2.6 ± 1.8
UM	2.93 ± 0.12	4			1.5 ± 0.95	465 ± 191	2.3 ± 3.5	0.2 ± 0.1	2.8 ± 2.1	2.8 ± 2.1	112 ± 115
Fish											
LH	2.14 ± 0.15	5	38 ± 1.7	671 ± 31	2.9 ± 1.0	35 ± 40	9.3 ± 12	3.1 ± 3.4	0.21 ± 0.31	3.7 ± 2.3	7.6 ± 6.3
SH	2.50 ± 0.14	5	24 ± 1.2	76 ± 8.7	0.78 ± 0.18	478 ± 431	13 ± 16	3.9 ± 3.5	5.7 ± 6.0	51 ± 28	34 ± 41
PP	2.85 ± 0.08	6	27 ± 2.3	168 ± 31	1.9 ± 0.38	141 ± 138	17 ± 16	1.6 ± 1.0	0.45 ± 0.39	7.2 ± 6.7	8.0 ± 10.0
TK	2.98 ± 0.06	10	14 ± 0.58	16 ± 12	9.8 ± 0.11	75 ± 15	17 ± 14	3.9 ± 6.5	21 ± 15	21 ± 11	145 ± 91
SN	3.01 ± 0.09	3	47 ± 1.2	525 ± 12	4.5 ± 0.27	25 ± 23	34 ± 37	5.2 ± 6.8	0.34 ± 0.18	24 ± 5.2	12 ± 15
CS	3.09 ± 0.04	6	30 ± 1.7	170 ± 12	1.4 ± 0.18	120 ± 127	33 ± 32	8.7 ± 7.4	1.7 ± 3.2	69 ± 96	60 ± 79
PI	3.15 ± 0.04	3	33 ± 23	175 ± 58	1.23 ± 0.06	104 ± 135	4.7 ± 4.4	2.3 ± 3.2	0.5 ± 0.8	ND	10 ± 0.5
LJ	3.36 ± 0.03	3	78 ± 12	3540 ± 170	0.62 ± 0.06	47 ± 18	5.2 ± 2.3	1.2 ± 1.4	0.4 ± 0.8	ND	7.8 ± 3.0
Gulls											
J-LC	3.37 ± 0.38	5	51 ± 4.3	963 ± 300	6.70 ± 0.2	310 ± 255	26 ± 31	3.3 ± 6.6	3.9 ± 4.2	1.8 ± 1.1	10 ± 14
LC	3.62 ± 0.22	12	43 ± 7.0	541 ± 244	6.40 ± 0.1	1571 ± 96	96 ± 122	4.8 ± 6.8	29 ± 32	10 ± 10	58 ± 60
LR	3.78 ± 0.10	6	33 ± 0.76	344 ± 32	7.20 ± 0.53	2330 ± 2310	150 ± 193	1.8 ± 2.7	56 ± 54	17 ± 13	118 ± 128

[a]SED = sediment; RP = short-necked clam (*Ruditapes philippinarum*); MVR = mactra quadrangularis (*Mactra veneriformis,Reeue*); RV = rock shell (*Rapana venosa*); ESME = Chinese mitten-handed crab (*Eriocheir sinensis H. Milne-Eswards*); UM = mole cricket (*Upogebia major(de Haan)*); LH = redeye mullet (*Liza hematocheila*); SH = goby (*Synechogobius hasta*); PP = small yellow croaker (*Pseudosciaena polyactis*); TK =China anchovy (*Thrissa kammalensis*); SN = Japanese spanish mackerel (*Scomberomrus niphonius*); CS = half-smooth tongue-sole (*Cynoglossus semilaevis*); PI = flathead fish (*Platycephalus indicus*); LJ = black spotfedbass (*Lateolabrax japonicas*); LR = black-headed gull (*Larus ridibundus*); LC = black-tailed gull (*Larus crassirostris*); J-LC = juvenile black-tailed gull (*Larus crassirostris*). [b]TOC content of sediment was 0.48 ± 0.04%. TL, trophic level; ND, not detected. All values were indicated by mean ± SD. Muscle was used to determine dechloranes for fish and gulls, whole body was used for invertebrates.

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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 hexane was discarded. The second fraction, which contained 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 before analysis by GC-ECNI-MS analysis. As for some species with low concentrations of dechloranes, including redeye mullet (*Liza hematocheila*), goby (*Synechogobius hasta*), small yellow croaker (*Pseudosciaena polyactis*), Japanese spanish mackerel (*Scomberomrus niphonius*), half-smooth tongue-sole (*Cynoglossus semilaevis*), rock shell (*Rapana venosa*), and mole cricket (*Upogebia major(de Haan)*), about 20 g wet weight of tissues were used for accelerated solvent extraction, followed by treatment of acidified silica gel column and neutral alumina column before the GC-ECNI-MS analysis..

To determine the impurities of dechlorinated DP in commercial product, the commercial product was dissolved and then diluted by hexane to about 5 μg/L for GC-ECNI-MS analysis.

Instrumental Analysis. Identification and quantification of dechloranes were performed using a gas chromatography-electron capture negative ionization mass spectrometer (GC-ECNI-MS) (Shimadzu QP 2010 plus, Japan). Chromatographic separation was achieved on a VF-5MS capillary column (15 m × 0.25 mm × 0.1 μm film thickness; J&W Scientific, Folsom, CA). 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 interface temperature was maintained at 285 °C and the source temperature was kept at 220 °C. The carrier gas was helium at a constant flow rate of 5 mL/min. Data acquisition was conducted in selected ion monitoring mode.

Quality Assurance/Quality Control. The isotopically labeled PCBs have been used as a surrogate for analysis of dechloranes by previous study.[14] In the present study, the concentrations of all dechloranes in sample extracts were determined relative to $^{13}C_{12}$-PCB180. The recoveries of dechloranes were 81−97% for sediments, and 72−89% for biota samples as shown in Table S2, SI. Recoveries of $^{13}C_{12}$-PCB180 were 85 ± 19% and 83 ± 24% in sediment and biota samples respectively. All equipment rinses were carried out with acetone and 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 DP, which was detected in blank samples with minor concentrations, were set to be the three times of the mean concentration in the blank samples, and concentrations of the compounds were blank corrected. The MDLs for other compounds, which were not detected in blank samples, were set to the instrumental minimum detectable amounts with a signal-to-noise ratio of 3. The MDLs were 0.8−2.0 pg/g dw for dechloranes in sediments, and 0.08−2.0 pg/g ww for biota samples (Table S2, SI).

Data Analysis. An increasing number of studies have reported trophic transfer of contaminants by correlating the concentration of pollutants in food web organisms and TL to describe the trophic magnification of pollutants.[29] In this study, short-necked clams (*Ruditapes philippinarum*) were used to estimate the $\delta^{15}N$ baseline and were assumed to represent the trophic position 2.0 as used in our previous studies.[25,26] For organisms other than seabirds, the trophic positions can be calculated by the equation (1):

$$TL_{consumer} = 2 + (\delta^{15}N_{consumer} - \delta^{15}N_{Ruditapes\ philippinarum})/3.8, \quad (1)$$

where $\delta^{15}N_{Ruditapes\ philippinarum}$ was determined as 8.98, and 3.8 is the trophic enrichment factor of $\delta^{15}N$.[26] For seabirds, the relationship was modified by the equation (2):

$$TL_{seabird} = 3 + (\delta^{15}N_{seabird} - \delta^{15}N_{Ruditapes\ philippinarum} - 2.4)/3.8. \quad (2)$$

Trophic magnification factor (TMF) can be estimated using the following relationship as described in our previous studies.[25,26] Concentrations of dechloranes on a lipid basis in all organisms were used to reduce the variance introduced by lipid content in the statistical analysis.

$$\log \text{dechloranes concentration} = a + b\,TL \quad (3)$$

where TL was the trophic level. The b in eq 3 was used to calculate TMF by eq 4:

$$TMF = 10^{b} \quad (4)$$

Trophic level (TL) adjusted biomagnification factors (BMF_{TL}) of dechloranes in gulls were calculated by the following equation as described in the paper by Conder et al.[31] China anchovy (*Thrissa kammalensis*) is suggested to be the major diet of gulls,[27,28] which is also supported by their similar stable carbon isotope ratios, thus the BMF_{TL} values were calculated based on concentrations in China anchovy by eq 5.

$$BMF_{TL} = 10^{[\log 10(([gull]/[prey])/(TLgull - TLprey))]} \quad (5)$$

where [gull] and [prey] are the lipid corrected concentrations of dechloranes in gulls and China anchovy, respectively.

Biota-sediment accumulation factor (BSAF) of dechloranes was calculated by dividing the lipid-normalized concentrations in organisms by the concentration in sediment normalized to the concentration of total organic carbon:[25]

$$BSAF = ([biota]/f_{lipid})/([sediment]/f_{OC}) \quad (6)$$

where [biota] is the concentration of dechloranes in biota samples, [sediment] is the concentrations in sediments, f_{OC} is the fraction of organic carbon in sediments, and f_{lipid} is the fraction of lipid in biota samples.

When the *p* value was below 0.05, the linear regression between the log-transformed dechloranes concentrations and trophic level was regarded as significant. Concentrations less than their respective MDLs were assigned a proxy value of MDL/2. In this study, when more than 30% of samples were below the MDLs (syn-Cl_{11}DP), the chemical was not included in the calculations of TMFs. In all the tests, SPSS 15.0 software was used (SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Concentrations of Dechloranes in Aquatic Organisms and Sediments. All seven dechloranes were detected in sediments and organisms (Table 1). All dechloranes showed the highest concentrations in seabirds (ranged from 0.8 ± 2.2 pg/g ww (mean ± SD) for syn-Cl_{11}DP to 2330 ± 2310 ww for mirex) except for Dec 603 (8.7 ± 7.4 pg/g ww in half-smooth tongue-sole), syn-DP (69 ± 96 pg/g ww in half-smooth

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tongue-sole) and anti-DP (145 ± 91 pg/g ww in China anchovy). As for the most often reported DP isomers, their concentrations in gulls from Liaodong Bay were lower than those in herring gulls from Great Lakes (310−1400 pg/g ww for syn-DP and 130−4400 pg/g ww for anti-DP).[32] When the concentrations were expressed on a lipid weight basis, the highest concentrations of dechloranes were still detected in black-headed gulls (ranged from 221 ± 153 pg/g lw for Dec 603 to 31700 ± 28000 pg/g lw for mirex) except for DP isomers. Previous studies on dechloranes concentrations in air-breathing organisms are limited especially for new dechloranes including Dec 602, Dec 603 and dechlorinated DP, and only one study has reported the presence of these dechloranes in eggs of Peregrine Falcon from Spain and Canada.[16] To compare the dechlorane levels with other studies, concentrations of individual congener calculated to lipid-based results were used. The average concentrations of total DP isomers (∑DP) were 817 ± 1030 pg/g lw in black-tailed gulls and 1780 ± 1650 pg/g lw in black-headed gulls, which were comparable to those (1.78 ng/g lw) in the eggs of Peregrine Falcon from Spain.[16] And the lipid-based concentrations for Dec 602 were 1110 ± 1320 pg/g lw in black-tailed gulls and 2020 ± 2290 pg/g lw in black-headed gulls, which were lower than those of Peregrine Falcon from Spain (9.78 ng/g lw).[16] Such different concentrations between DP and Dec 602 compared to Peregrine Falcon may be due to the different trophic position or diet since DP and Dec 602 exhibited different bioaccumulation potential as reported in previous studies.[14] The concentrations of total dechloranes in fish species (59−586 ng/g lw) were comparable with those in fish from Great Lakes (0.48−540 ng/g lw).[14] Relatively low concentrations of dechloranes in sediment (33 ± 73 pg/g dw for anti-DP and 3.1 ± 5.1 pg/g dw for Dec 602) were also observed in this study compared to those in sediment from Lake Ontario (0.3−720 ng/g dw for DP and 0.03−0.62 ng/g dw for Dec 603).[14] Overall, the dechloranes concentrations in Liaodong Bay were relatively low compared with a previous study on their occurrence in the sediment from Great Lakes,[14] partly due to the relatively strong dilution in marine environment.

Profiles of Dechloranes in Aquatic Organisms and Sediments. As shown in Figure 1 (a), profile of dechloranes in different organisms showed great variation. Anti-DP was the predominant dechlorane in sediment and invertebrates, accounting for 39% and 24−50% of total dechloranes, respectively. The contribution of anti-DP was decreased to 4.6−21% in fish species at high trophic levels, and was further decreased to 2.8−4.4% in seabirds. In these organisms at high trophic levels, mirex was the predominant dechlorane which contributed to 87−89% of total dechloranes in seabirds and 25−86% in fish species, which were much higher than those in sediments (9.5%) and invertebrates (19−33%) (except for mole cricket which was 79%). While mirex was predominant over dechloranes, its concentration was 10-fold lower than the concentrations of PBDEs in the same individuals,[26] of which phenomenon was also reported in previous study where contribution of mirex to total POPs was relatively low.[33] After excluding mirex, Dec 602 was the predominant dechlorane in organisms at high trophic levels and contributed to 44−58% of total dechloranes in seabirds and 8.2−49% in fish species, which were higher than those in sediments (4.1%) and invertebrates (5.9−32%) (Figure 1 (b)). The different profiles of Dec 602, mirex and DP in organisms with different trophic levels were possibly attributed to the different biomagnification potentials of dechloranes.

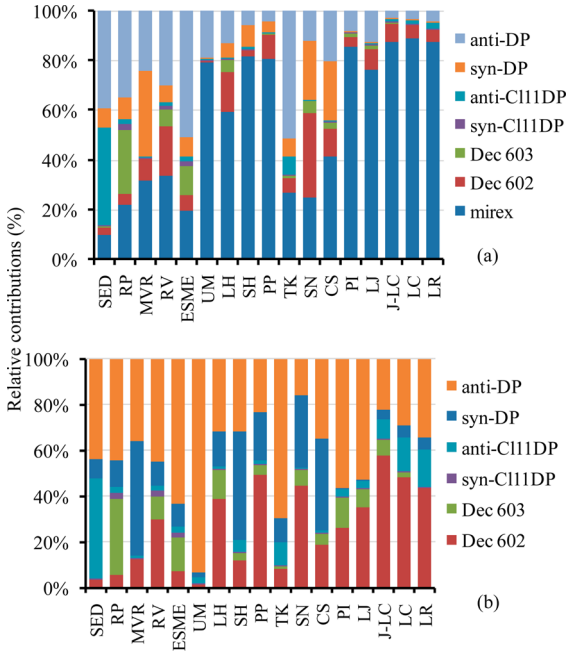

Figure 1. Profiles of dechloranes in sediment and organisms. (a) all dechloranes; (b) all dechloranes except for mirex.

As possible degradation products from DP, syn-Cl_{11}DP was only detected in three black-tailed gull samples, and anti-Cl_{11}DP was detected in 21 of the 23 gull samples. This is accordant with previous study in which anti-Cl_{11}DP was detected in all bird species from different locations, while syn-Cl_{11}DP was only detected in two bird species from urban.[34] It should be noted that relatively high proportions of anti-Cl_{11}DP were detected in the present study as indicated by the concentration ratios of anti-Cl_{11}DP to total concentrations of anti-Cl_{11}DP and anti-DP ($f_{\text{anti-Cl11DP}}$). The ratio ($f_{\text{anti-Cl11DP}}$) with values higher than 0.5 meant that concentration of anti-Cl_{11}DP was higher than its parent compound (anti-DP). $f_{\text{anti-Cl11DP}}$ was calculated to be 0.38 ± 0.13 in black-tailed gulls and 0.36 ± 0.13 in black-headed gulls in the present study (Figure 2), which were 4 folds higher than that (0.09) in the

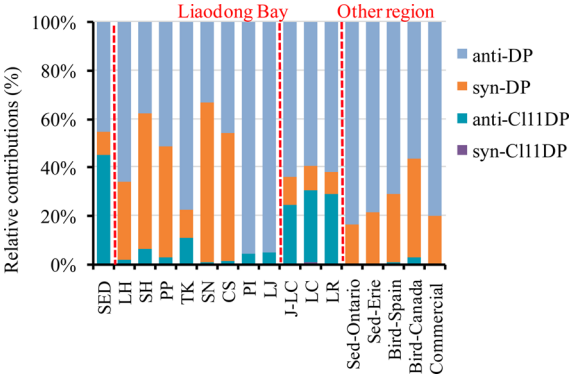

Figure 2. Comparison of profiles of dechlorane plus (DP) and dechlorinated DP in sediments and gulls from Liaodong Bay with those in sediments from Ontario and Erie,[7] eggs of Peregrine Falcon from Spain and Canada,[16] and commercial product of DP from Jiangsu Anpon Electrochemical Co.

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eggs of Peregrine Falcon from Canada.[16] Significantly positive correlations between concentrations of anti-Cl_{11}DP and anti-DP in gulls were observed as shown in Figure 3 (r = 0.93, p < 0.001). This may be due to natural accumulation of anti-Cl_{11}DP from sediments through the food web to gulls, or metabolism of anti-DP to anti-Cl_{11}DP in gulls after accumulating DP. The latter hypothesis was explored by *in vitro* metabolism study of DP using microsomal fractions of black-tailed gull liver since the metabolism of DP has been suggested to be responsible for dechlorinated DP in human or wildlife.[20,21] After a 24-h exposure, dechlorinated DP was not observed, and the result was consistent with our previous study using liver microsomes of Chinese sturgeon exposed to high DP concentrations in which no dechlorinated product of DP was detected.[24] Thus, metabolism of DP would not be the source of dechlorinated DP in gulls from Liaodong Bay. Indeed, relatively high proportions of dechlorinated DP were also observed in sediments ($f_{anti\text{-}Cl11DP}$ = 0.33 ± 0.19) and fish species (0.03–0.14) from Liaodong Bay (Figure 2). The proportions in sediment were higher than those in sediment from Great Lakes, where high DP levels (2.23–586 ng/g dw in Lake Ontario) were found while the concentration of Cl_{11}DP was under the detection limits.[7] Significantly positive correlations between anti-Cl_{11}DP concentrations and anti-DP concentrations were also observed in sediments (r = 0.90, p < 0.001) and China anchovy (r = 0.80, p = 0.005) (Figure 3). The results suggested that anti-DP and anti-Cl_{11}DP would be from the same emission sources or anti-Cl_{11}DP would be potentially transformed from anti-DP in environment. To explore the source of dechlorinated DP in sediments from Liaodong Bay, we analyzed the impurities in the commercial product of DP from Jiangsu Anpon Electrochemical Co., the main manufacturer of DP in China, and dechlorinated DP could not be detected ($f_{anti\text{-}Cl11DP}$ < 0.05). Therefore, dechlorinated DP in sediments and biota samples would be from the degradation of DP in environment as exemplified by the preferential photodegradation of anti-DP compared to syn-DP under UV treatment, and possibly leading to the significant correlations between anti-DP and anti-Cl_{11}DP in all the investigated matrices.[7]

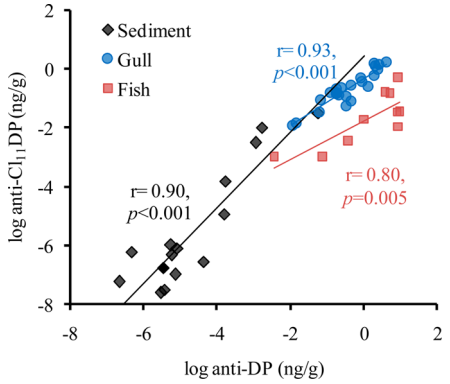

Figure 3. Correlations between log-transformed concentrations of anti- undecachloropentacyclooctadecadiene (anti-Cl_{11}DP) and anti-dechlorane plus (anti-DP) in sediments, fish (China anchovy), and gulls from Liaodong Bay.

BSAFs and BMFs of Dechloranes in Gulls. Dechloranes exhibited relatively high concentrations in gulls compared with other organisms as mentioned above, thus the accumulation of dechloranes from sediments to gulls was of special concern and was assessed. After adjusted by TOC and lipid content, the BSAFs of dechloranes were estimated to be ranged from 0.05 ± 0.07 g TOC/g lipid (syn-DP) to 8.9 ± 10 g TOC/g lipid (mirex) in black-tailed gulls and ranged from 0.12 ± 0.11 g TOC/g lipid (anti-Cl_{11}DP) to 15 ± 13 (mirex) g TOC/g lipid in black-headed gulls (Table 2), which were much lower than those of PBDEs in the same gull individuals (>25 g TOC/g lipid for total PBDEs).[26] It should be noted that the BSAFs of Dec 602 and mirex in the gulls were one or 2 orders of magnitudes higher than those of DP, indicating that bioaccumulation potentials of DP in gulls were less than those of Dec 602 and mirex, which was consistent with the results of previous studies.[12,14,23] Since metabolism of DP was not observed in gulls liver microsomes, relatively high K_{OW} values and subsequent low bioavailability of DP should be responsible for its low bioaccumulation potentials.

BMF values of dechloranes between gulls and China anchovy were investigated to further clarify the accumulation of the compounds from diet to gulls. Trophic level (TL) adjusted biomagnification factors (BMF_{TL}) were calculated according to the formula by Conder et al.[31] BMF_{TL} values were ranged from 0.11 (anti-DP) to 6.4 (mirex) for mirex, Dec 602, Dec 603, anti-Cl_{11}DP, syn-DP and anti-DP in black-tailed gulls, and from 0.32 (anti-DP) to 8.4 (mirex) in black-headed gulls, respectively (Table 2). BMF_{TL} value of mirex was similar to the model predicted value (14) in seabirds by Kelly et al.[18] Both the BSAF and BMF_{TL} values indicated that mirex and Dec 602 were the two most bioaccumulative chemicals in both investigated gull species. Of the dechloranes, the BMF_{TL} values were only reported for DP in aquatic organisms, and BMF_{TL} values in most feeding relationships were less than 1.0,[4] which was similar to the results in our study. The results indicated the

Table 2. Parameters of Regression Analysis between Logarithm of Concentration and Trophic Levels, Biota/Sediment Bioaccumulation Factors (BSAFs), Predator/Prey Biomagnification Factors (BMFs), and Trophic Magnification Factors (TMFs).

	mirex	Dec 602	Dec 603	syn-Cl_{11}DP	anti-Cl_{11}DP	syn-DP	anti-DP
BSAF in black-tailed gulls[a]	8.9	1.8	0.08	NA	0.05	0.05	0.08
BSAF in black-headed gulls[a]	15	3.2	0.41	NA	0.12	0.15	0.25
BMF_{TL} in black-tailed gulls	6.4	1.7	0.45	NA	0.36	0.14	0.11
BMF_{TL} in black-headed gulls	8.4	3.0	1.0	NA	0.70	0.34	0.33
r (TL)	0.52	0.47	0.00	NA	0.52	0.05	0.03
TMF	13	3.7	1.0	NA	5.6	2.2	1.6
p (TL)	**0.003**	**0.007**	0.99	NA	**0.004**	0.43	0.54

[a]BSAF values in black-tailed gulls (*Larus crassirostris*). [a]BSAF values in black-headed gulls (*Larus ridibundus*). [c]p values underlined in bold print represent statistically significant TMF values (p < 0.05). NA indicates not analyzed.

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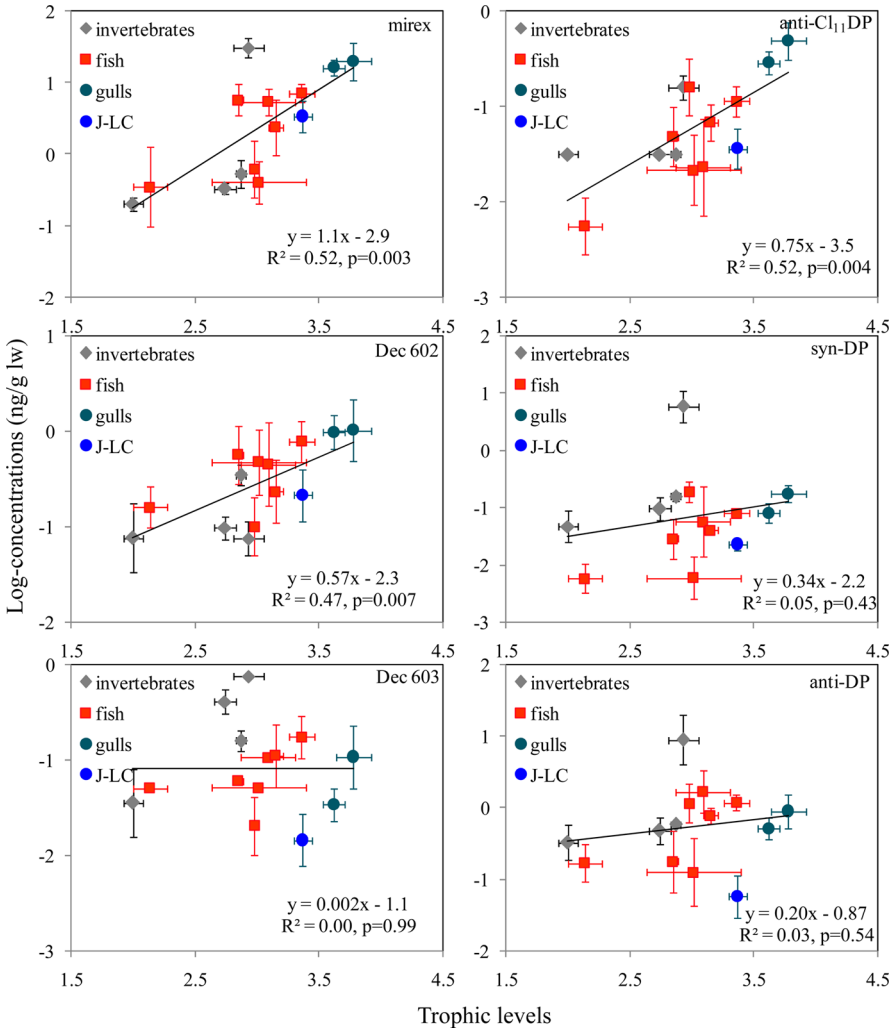

Figure 4. Relationships between log-transformed concentrations of dechloranes (ng/g lw) and trophic levels in all organisms from Liaodong Bay. Error bar indicated ± standard error. Regression based on the mean concentrations of dechloranes in each species. J-LC = juvenile black-tailed gull (*Larus crassirostris*).

low biomagnification potential of DP in both air-breathing and water-breathing organisms. In addition, it is interesting to note that anti-Cl_{11}DP showed higher biomagnification in both gull species than parent anti-DP possibly due to its one less chlorine atom and relatively lower logK_{OW}.

Trophic Transfer of Dechloranes in the Food Web. Figure S2 (SI) shows the stable carbon and nitrogen isotope values for organisms collected from Liaodong Bay. The stable nitrogen isotope ratios were 8.98 ± 0.44 to 12.5 ± 0.81 for invertebrates, 9.50 ± 1.0 to 14.1 ± 0.23 for fishes, and 12.8 ± 1.4 to 14.2 ± 1.2 for gulls. The trophic enrichment factor for stable nitrogen isotope was estimated to be 2.4−4.8‰ by examining isotopic differences between consumers and their diets such as RP and UM. The enrichment factor corresponded to that reported for marine ecosystem in Bohai Bay (3.8‰)[35] and Arctic (3.8‰),[36] for lake food web (3.8‰).[37] By using 3.8‰ as the enrichment factor, the trophic levels of small yellow croaker and black spot-fed bass calculated by nitrogen stable isotope ratios were 2.85 ± 0.13 and 3.36 ± 0.06, respectively, which is comparable to those obtained from traditional stomach content analysis (2.99 and 3.37, respectively).[38] The stable carbon isotope ratios were from −15.7 ± 0.09 to −17.9 ± 0.25 for invertebrates except for mactra quadrangularis (−12.6 ± 0.30), from −15.3 ± 1.1 to −17.2 ± 0.86 for fishes except for goby (−12.7 ± 2.1), and from −18.6 ± 1.3 to −20.9 ± 2.7 for gulls. The stable carbon isotope ratios of mactra quadrangularis and goby appeared unrelated with other species in the food web (Figure S2, SI). The differences in carbon isotope ratios of mactra quadrangularis and goby may be due to their diets on bacteria or benthic organisms,[38] and the relatively high $\delta^{13}C$ value of benthic organisms were also observed previously.[39] Thus, the two species were not included in the TMF calculation. And juvenile and adult gulls were separated in the TMF calculation due to their clear difference on physiological parameters and stable isotope values, thus 14 species were included in the TMF calculation (Table 1). Not surprisingly, strong positive relationships were found between lipid-normalized mirex concentrations and trophic levels in biota, showing the high trophic magnification potential of the chemical in the marine foodweb from the Liaodong Bay (Figure 4). The increase of concentrations of mirex with trophic level was statistically significant (p = 0.003), and the TMF of mirex determined from the slope of concentration-trophic level relationship in the present study was 13 (Table 2). Previous papers have documented the significant trophic magnification of mirex in both Canadian Arctic terrestrial and

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marine foodwebs although the TMF values were not provided,[18,32] therefore the magnification of mirex observed in this paper proved that the foodweb from Liaodong Bay is appropriate for testing the trophic magnification of dechloranes.

The statistical results for other dechloranes are listed in Table 2, and no significant trend was found for DP isomers (TMF values were 2.2 for syn-DP and 1.6 for anti-DP). To date, two studies have reported the trophic behaviors of DP in freshwater foodweb. The trophic transfer study of syn-DP and anti-DP in the Great Lakes found that syn-DP undergo trophic dilution in the aquatic food web (TMFs were 0.44 in Lake Winnipeg and 0.45 in Lake Ontario), but trophic magnification of anti-DP was observed in Lake Winnipeg with TMF of 2.5.[4] Another study on freshwater aquatic foodweb also observed magnification of syn-DP (TMF was 11.3) and anti-DP (TMF was 6.5).[12] Those studies included fish as the top predators in the aquatic foodweb, while bird is important for comprehensive assessment of trophic magnifications of chemicals in aquatic foodweb. Compared to previous studies, the present study is the first to investigate trophic magnification of dechlorane compounds in a marine foodweb including invertebrates, fishes, and gulls, confirming that DP did not biomagnify in this marine foodweb. Different from DP, significantly increasing trends of Dec 602 and anti-Cl_{11}DP with trophic levels were observed and their TMFs were estimated to be 3.7 (p = 0.007) and 5.6 (p = 0.004), respectively (Figure 4). The increasing trend of Dec 603 was also observed, but the correlations were not statistically significant (p = 0.44). As the first study about trophic magnification of Dec 602, Dec 603 and dechlorinated DP in food web, the observation of biomagnification of Dec 602 and anti-Cl_{11}DP proposed new concern on their potential ecological risk. The preferential biomagnification of Dec 602 and mirex in food web may be due to their relatively low logK_{OW} values (7.0 for mirex and 8.1 for Dec 602) and subsequent high bioavailabilities compared with DP (11.3),[19] and experimental exposure on Atlantic salmon also observed relatively high bioaccumulation potential of Dec 602 compared with Dec 603 and DP.[22] The TMF values of dechloranes were also calculated after excluding gulls species, and significance was also found for mirex (TMF=11, p = 0.05) and anti-Cl_{11}DP (TMF=4.1, p = 0.05), while increasing trend was found for Dec 602 without statistical significance (TMF=3.2, p = 0.07). Previous investigations about the trophic magnification of PBDEs, OH-PBDEs and MeO-PBDEs in the same foodweb provide an opportunity to compare the TMFs of dechloranes with those of other chemicals. The TMF values of dechloranes were lower than those of PBDEs (6.84, 13.4, 7.43 for BDE-47, BDE-99, and BDE-118),[26] but much higher than those of OH-PBDEs (0.21 for 6-OH-BDE47 and 0.15 for 2′-OH-BDE68).[25] The relatively low TMF values of dechloranes compared to PBDEs was not surprising since logK_{OW} values of dechloranes were much higher than those of PBDEs (6.0 for BDE-47 and 6.8 for PBDE-99), and therefore leading to low bioavailability in organisms.[18]

Overall, the study clarified the magnification of dechloranes especially for new dechloranes including Dec 602 and anti-Cl_{11}DP in the marine food web, which suggested a new class of bioaccumulative substances that require regulatory assessment for potential ecological risks.

■ ASSOCIATED CONTENT

Supporting Information

Figures and Tables addressing (1) Trophic levels, biological parameters and dechloranes concentrations of 23 gull individuals; (2) Recoveries (n = 3) and method detection limits (MDLs) of dechloranes in sediments and biota samples; (3) Sampling map of sediments, gulls and fish; (4) Stable nitrogen and carbon isotope values in different organisms. 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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