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Levels and distribution of Dechlorane Plus in coastal sediments of the Yellow Sea, North China

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ABSTRACT

Dechlorane Plus (DP) has been determined in surface sediments from three Chinese coastal bays, e.g. Jiaozhou, Sishili and Taozi Bay in North China. DP concentrations ranged from <1.2 to 187 pg g^{-1} dry weight (dw) (mean: 24.7 pg g^{-1} dw) in Jiaozhou Bay, <1.2 to 135 pg g^{-1} dw (mean 69.9 pg g^{-1} dw) in Sishili Bay and <1.2 to 66.7 pg g^{-1} dw (mean: 40.4 pg g^{-1} dw) in Taozi Bay, respectively. Additionally, two dechlorinated species were quantified, which accounted for 0.6–5.1% of the ∑DP concentration.

The f_{syn} values (*syn*-isomer/(*syn*- + *anti*-isomer)) in sediments from Jiaozhou Bay (mean 0.29) were close to the technical DP mixture (0.2–0.4), probably indicating local inputs of DP. In contrast, sediments in Sishili and Taozi Bay showed much lower f_{syn} values (mean 0.16). During transportation the DP isomers are subject to stereo selective degradation which partly resulted in the relative enrichment of *anti*-DP in coastal sediments.

1. Introduction

Dechlorane Plus (DP, $C_{18}H_{12}Cl_{12}$), the common name of bis(hexachlorocyclopentadieno) cyclooctane, which is used as a substitute for the toxic Dechlorane (Mirex) has been produced for about four decades (Gauthier et al., 2007; Qiu et al., 2007). As a highly chlorinated flame retardant, DP has been used in plastic roofing material, hardware connectors for computers and for coating electrical wires and cables (Tomy et al., 2008). The annual production of DP was reported to be 5000 tons, and it is sold in North America, Europe and Asia (Kang et al., 2010; Wang et al., 2010a). As a result of its wide application, DP has been detected in various environmental compartments, such as air, water, sediment, fish and human serum (Hoh et al., 2006; Tomy et al., 2007; Ren et al., 2009; Möller et al., 2010; Qi et al., 2010; Wang et al., 2010b). Bioaccumulation and biomagnifications were reported for organisms of high tropic levels, resulting in a potential threat for humans (Tomy et al., 2008; Ren et al., 2009).

In China DP has been produced by Anpon Corporation for 7 years, with an estimated total volume between 2100 and 7000 tons. This manufacturing plant has been recognized as the main DP source for the surrounding area (Wang et al., 2010b). The DP concentration in soil near the plant was 1490 ± 3580 ng g^{-1} dry weight (dw), which is one magnitude higher than the maximum concentration in Lake Ontario (586 ng g^{-1} dw) (Sverko et al., 2008; Wang et al., 2010b). Ren et al. (2008) collected air samples from 97 Chinese urban and rural sites, and stated that the highest concentration was found in Kunming more than 1800 km away from the DP production facility. In Harbin, an industrial city of Northeast China without DP manufacturers, the mean concentration of DP was 0.11 ± 0.05 ng g^{-1} dw in urban sediments (Qi et al., 2010). Besides domestic usage, the import of DP or DP containing products (including e-waste) from overseas could also elevate the levels in the Chinese environment. Yu et al. (2010) found that in an e-waste recycling site in Qingyuan, the concentration of DP reached up to 3327 ng g^{-1} dw in surface soil.

Sediments have been regarded as one of the major sinks for persistent organic pollutants (POPs), e.g. polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and brominated flame retardants (BFRs) (Hung et al., 2006; Minh et al., 2007; Guzzella et al., 2008). These pollutants enter the marine sediments through atmospheric deposition, riverine runoff and direct release from human activities on the ocean (Moon et al., 2007b). Both, the *syn*- and *anti*-isomers have a high octanol–water partition coefficient (log-K_{ow}) value of 9.3, which is similar to some polybrominated diphenyl ethers (PBDEs) that strongly adsorbed to sediments (Palm et al., 2002; Moon et al., 2007a; Sverko et al., 2008). The OxyChem report

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employing EPIWIN version 3.12 presented that 66.6% of the DP was distributed in sediments (US, 2008). High concentrations of DP have been detected in sediments from Lake Ontario with an inventory of DP calculated to about 20 tons (Qiu et al., 2007; Sverko et al., 2008). Presently, only few data are available on the distribution of DP in coastal sediments. Our study focuses on the concentrations, distribution and possible sources of DP in surface sediments of three Chinese bays.

2. Materials and methods

2.1. Sample collection

Surface sediments (0–5 cm) were collected in coastal zones of Yellow Sea in April, 2010. The locations of all the 48 samples are shown in Fig. 1. Twenty-five samples were collected in the Jiaozhou Bay which is surrounded by Qingdao City (35°35′–37°09′N, 119°30′–121°00′E), and four river sediment samples were collected in Dagu River and Qingdao River, discharging into the Jiaozhou Bay. Six samples were collected in Taozi Bay and 13 in Sishili Bay near Yantai City (36°16′–38°23′N, 119°34′–121°57′E). The sediments were collected by stainless spades and then sealed in polyethylene (PE) bags. They were frozen at −20 °C immediately after sampling until extraction. Prior to extraction, sediments were freeze-dried for 3 d at −55 °C and then ground, homogenized by agate mortar and pestle and wrapped up in pre-cleaned filter papers.

2.2. Extraction and clean-up

All solvents were analytical grade and were re-distilled before using. Filter papers were Soxhlet extracted for 72 h using dichloromethane (DCM). Samples were spiked with 20 ng of PCB 209 as surrogate standard prior to extraction. Twenty gram of sediments were extracted in a Soxhlet apparatus for 72 h using DCM. Activated copper slices were added to the collection flask to remove elemental sulfur. Extracts were evaporated to 10 mL and the solvent was changed to hexane before further evaporation to <2 mL. A 8 mm i.d. modified column packed with 1 cm anhydrous sodium sulfate, 3 cm 50% sulfuric acid silica, 3 cm neutral silica gel and 3 cm neutral alumina from the top to the bottom was employed for clean-up. The silica was pre-cleaned with acetone and DCM,

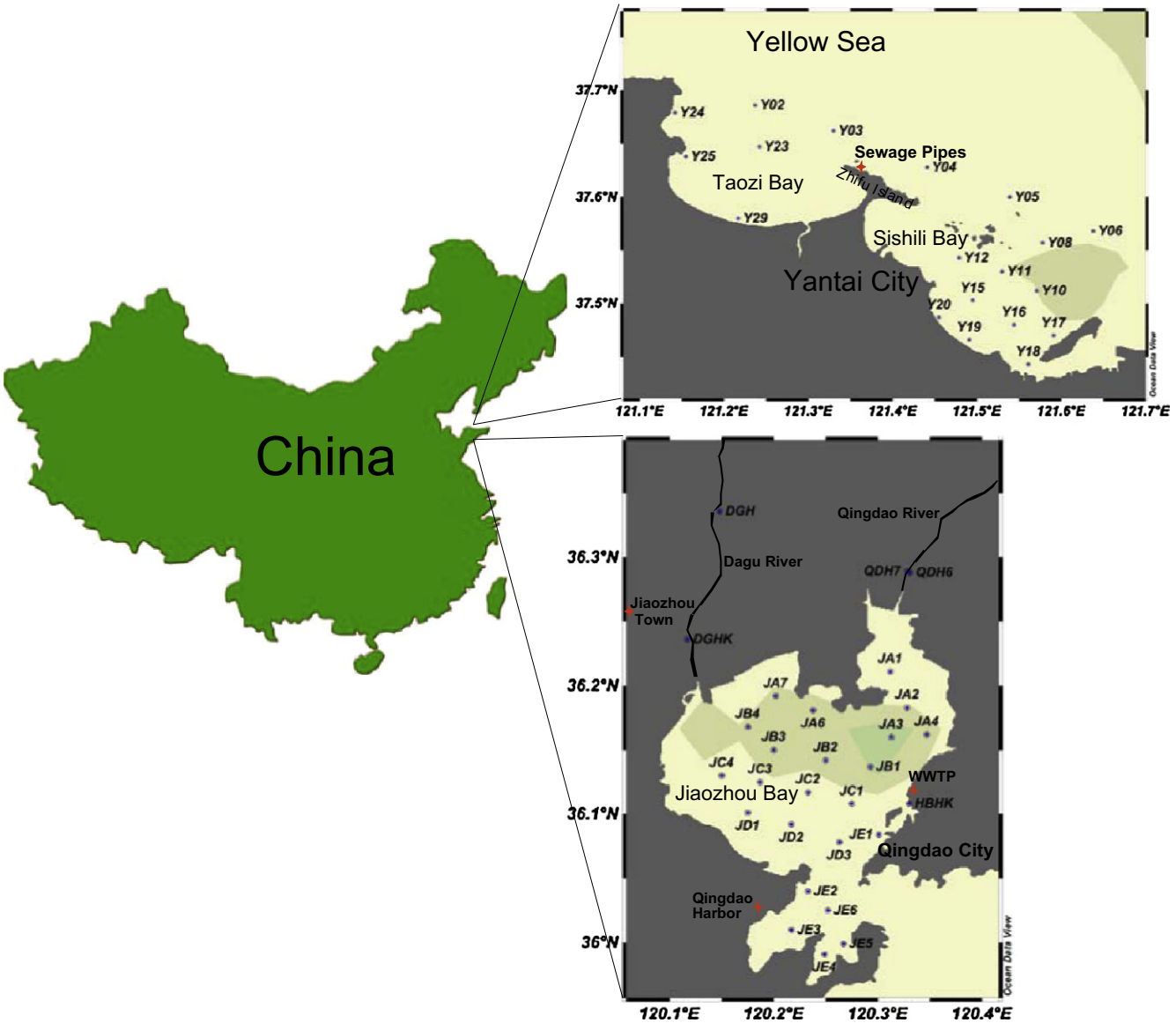

Fig. 1. The sampling sites in Taozi, Sishili and Jiaozhou Bay.

activated at 180 °C for 12 h and further 3% deactivated using Millipore water. The neutral alumina was treated in a similar way, activated at 250 °C. Sulfuric acid silica was prepared by adding 50% (w/w) HPLC grade sulfuric acid (98%) to the deactivated silica. The anhydrous sodium sulfate was baked at 450 °C for 4 h. The fraction was concentrated to 50 μL under a gentle high-purity nitrogen (>99.99%) stream. Twenty nanogram of BDE77 was spiked as an internal standards before injection.

2.3. Instrument analysis

The standards of *syn*-DP, *anti*-DP, and two dechlorinated species, $aCl_{11}DP$ and $aCl_{10}DP$, were obtained from Wellington Laboratories. An Agilent 7890A GC equipped with a 30 m × 0.25 mm i.d. (0.25 μm film thickness, J&W Scientific) DB-5 fused silica capillary column was connected to a 5975C MSD under a negative chemical ionization (NCI) mode using methane as the reagent gas. The injector temperature was 280 °C employed in splitless mode with 1 μL injection volume. The oven program was as follows: initial 60 °C for 2 min, 30 °C min^{-1} to 180 °C, 2 °C min^{-1} to 280 °C, 30 °C min^{-1} to 300 °C and held for 6 min, and then ramped at 30 °C min^{-1} to 310 °C and held for a final 7 min. MS was operated in single ion monitoring (SIM) mode with ion source, quadrupole and transfer line temperatures held at 150, 150 and 280 °C, respectively. The following ions were monitored: *m*/*z* 653.8, 617.9 and 583.9 for *syn*- and *anti*-DP; *m*/*z* 617.8, 583.7 and 547.8 for $aCl_{11}DP$; *m*/*z* 583.8, 549.9 and 513.8 for $aCl_{10}DP$; *m*/*z* 79.0 and 81.0 for BDE77; and *m*/*z* 497.7 and 499.7 for PCB209.

2.4. QA/QC

The criteria for the identification and quantification of target compounds are given as follow: (1) The retention times matched those of the standard compounds within ±0.05 min. (2) The signal-to-noise (S/N) ratio of all peaks was greater than 5:1. (3) The theoretical isotopic ratios of the qualifier ions were within ±15% of the standard values. The linear dynamic range of the instrument was between 2 and 25 pg on the column ($R^2 > 0.996$) for DP isomers and their dechlorinated species. PCB 209 was spiked in every sample as DP recovery indicator. The mean recovery rate was 96 ± 12%. Concentrations of sediments were not recovery corrected. In three procedure blanks, both DP isomers and their dechlorinated moieties were not detected. Method detection limits (MDLs) were calculated based on the instrumental S/N ratios of 10. They were 0.4 pg g^{-1} for *syn*-DP, 0.8 pg g^{-1} for *anti*-DP, 0.5 pg g^{-1} for $aCl_{10}DP$ and 0.9 pg g^{-1} for $aCl_{11}DP$, respectively.

3. Results and discussion

3.1. Concentrations and spatial distribution of Dechlorane Plus

The concentrations of total DP (*syn*- + *anti*-DP) in river and marine sediments are shown in Table 1. DP was detected in all surface sediment samples from Jiaozhou, Taozi and Sishili Bay. Large spatial variations of total DP were observed, with <1.2–187 pg g^{-1} in Jiaozhou Bay, <1.2–66.7 pg g^{-1} in Taozi Bay and <1.2–135 pg g^{-1} in Sishili Bay, respectively. Qi et al. (2010) reported DP in sediments from Songhua River, Northeast China. The concentrations (>4.5–160 pg g^{-1} dw) were similar to those found in this study. Comparing with data from the sediments near manufactory locations, the concentrations in the three bays were one to three orders of magnitude lower (Table 2). Wang et al. (2010a, b) reported concentrations ranging from 1.86 to 8.0 ng g^{-1} dw in the canal sediments near Anpon Corporation in Huai'an, China, and Sverko et al. (2008) reported high concentrations in sediment of Great Lakes ranging from 0.061 to 586 ng g^{-1} near the OxyChem company. According to Wang et al. (2010a, b), DP was only manufactured by Anpon Corporation in Huai'an, China, which is 300–

Table 1
Concentrations (pg g^{-1} dry weight) of syn-DP, anti-DP, $aCl_{10}DP$, and $aCl_{11}DP$ and the f_{syn} value in surface sediments of Jiaozhou Bay, Taozi Bay and Sishili Bay, North China.

Location	syn-DP	anti-DP	$aCl_{10}DP$	$aCl_{11}DP$	*syn*- + *anti*-DP	f_{syn}
Dagu River						
DGH	13.9	42.3	<0.5	<0.9	56.3	0.25
DGHK	0.8	2.2	<0.5	<0.9	3.0	0.27
Qingdao River						
QDH6	9.0	14.8	<0.5	<0.9	23.8	0.38
QDH7	7.0	10.8	<0.5	<0.9	17.8	0.39
Jiaozhou Bay						
HBHK	61.1	126	<0.5	2.4	187	0.33
JA1	1.0	7.5	<0.5	<0.9	8.4	0.11
JA2	13.1	26.1	<0.5	<0.9	39.2	0.33
JA3	4.9	14.5	<0.5	<0.9	19.4	0.25
JA4	12.1	25.5	<0.5	<0.9	37.6	0.32
JA5	2.4	7.3	<0.5	<0.9	9.7	0.25
JA6	6.6	12.2	<0.5	<0.9	18.9	0.35
JA7	4.1	11.7	<0.5	<0.9	15.7	0.26
JB1	3.3	12.4	<0.5	<0.9	15.8	0.21
JB2	1.1	3.2	<0.5	<0.9	4.3	0.26
JB3	3.0	8.0	<0.5	<0.9	10.9	0.27
JB4	5.4	11.2	<0.5	<0.9	16.5	0.33
JC1	0.8	2.2	<0.5	<0.9	3.0	0.26
JC2	11.3	17.7	<0.5	<0.9	29.0	0.39
JC3	0.8	2.2	<0.5	<0.9	3.0	0.28
JC4	2.7	8.1	<0.5	<0.9	10.8	0.25
JD1	4.7	16.0	<0.5	<0.9	20.7	0.23
JD2	2.1	6.4	<0.5	<0.9	8.5	0.25
JD3	7.7	15.4	<0.5	<0.9	23.1	0.33
JE1	22.2	46.6	<0.5	1.0	68.8	0.32
JE2	1.5	2.6	<0.5	<0.9	4.0	0.36
JE3	10.4	21.4	<0.5	<0.9	31.8	0.33
JE4	<0.4	<0.8	<0.5	<0.9	<1.2	–
JE5	1.2	3.0	<0.5	<0.9	4.2	0.28
JE6	0.7	1.3	<0.5	<0.9	2.0	0.35
Maximum	61.1	126	–	2.4	187	0.39
Minimum	<0.4	<0.8	–	<0.9	<1.2	0.11
Mean	7.7	17.0	–	1.7	24.7	0.29
SD	12.5	25.3	–	1.0	37.8	0.06
Taozi Bay						
Y02	1.1	4.0	<0.5	<0.9	5.1	0.21
Y03	11.4	55.3	<0.5	<0.9	66.7	0.17
Y23	3.7	21.7	<0.5	<0.9	25.4	0.15
Y24	8.4	57.9	<0.5	<0.9	66.3	0.13
Y25	5.7	33.1	<0.5	<0.9	38.8	0.15
Y29	<0.4	<0.8	<0.5	<0.9	<1.2	-
Maximum	11.4	57.9	–	–	66.7	0.21
Minimum	<0.4	<0.8	–	–	<1.2	0.13
Mean	6.1	34.4	–	–	40.4	0.16
SD	4.0	22.8	–	–	26.6	0.03
Sishili Bay						
Y04	15.0	88.9	<0.5	1.0	104	0.14
Y05	8.0	44.3	<0.5	<0.9	52.3	0.15
Y06	10.2	67.8	<0.5	<0.9	77.9	0.13
Y08	11.4	63.6	<0.5	1.6	75.0	0.15
Y10	15.2	120	<0.5	3.5	135	0.11
Y11	15.8	116	<0.5	2.7	131	0.12
Y12	5.8	34.2	<0.5	<0.9	40.0	0.15
Y15	21.7	87.4	<0.5	1.4	109	0.20
Y16	3.0	22.0	<0.5	1.3	24.9	0.12
Y17	10.0	59.9	<0.5	1.0	69.9	0.14
Y18	0.6	2.4	<0.5	<0.9	3.0	0.20
Y19	2.7	13.3	<0.5	<0.9	16.0	0.17
Y20	<0.4	<0.8	<0.5	<0.9	<1.2	–
Maximum	21.7	120	–	3.5	135	0.20
Minimum	<0.4	<0.8	–	<0.9	<1.2	0.11
Mean	9.9	59.9	–	1.8	69.9	0.15
SD	6.3	38.4	–	0.9	44.1	0.03

–: No data.

Table 2
Comparisons of DP level in China and other area in the world.

Location	Matrix	DP concentrations	f_{syn}	Sampling year	References
China					
Huai'an	Air	7737–26 734 pg m^{-3}	0.22–0.37	2009	Wang et al. (2010a, b)
Huai'an	Soil	3.84–13 400 ng g^{-1}	0.03–0.35	2009	Wang et al. (2010a, b)
Huai'an	Canal sediment	1.86–8.0 ng g^{-1}	0.24–0.30	2009	Wang et al. (2010a, b)
Huai'an	Soil	0.83–1200 ng g^{-1} dw[a]	0.15–0.33	2009	Wang et al. (2010a, b)
Harbin	Urban water	<0.0045–2.4 ng L^{-1}	0.34 ± 0.095	2006	Qi et al. (2010)
Harbin	Urban sediment	<0.0045–0.15 ng g^{-1} dw	0.26 ± 0.081	2006	Qi et al. (2010)
Songhua River	River water (urban)	<0.0045–1.2 ng L^{-1}	0.31 ± 0.15	2006	Qi et al. (2010)
Songhua River	River sediment (urban)	<0.0045–0.14 ng g^{-1} dw	0.29 ± 0.032	2006	Qi et al. (2010)
Songhua River	River water (rural)	<0.0045–0.23 ng L^{-1}	0.36 ± 0.054	2006	Qi et al. (2010)
Songhua River	River sediment (rural)	<0.0045–0.16 ng g^{-1} dw	0.21 ± 0.042	2006	Qi et al. (2010)
Gui yun	Serum	7.8–465 ng g^{-1} lw[b]	0.23–0.6	2005	Ren et al. (2009)
Haojiang	Serum	0.93–50.5 ng g^{-1} lw	0.22–0.43	2005	Ren et al. (2009)
Yantai	Air	15.43 pg m^{-3}	0.25	2005	Ren et al. (2008)
Jiaozhou Bay	Surface sediment	<1.2–187 pg g^{-1} dw	0.11–0.39	2010	This study
Sishili Bay	Surface sediment	<1.2–135 pg g^{-1} dw	0.11–0.32	2010	This study
Taozi Bay	Surface sediment	<1.2–66.7 pg g^{-1} dw	0.13–0.26	2010	This study
Canada					
Lake Erie	Sediment	0.061–8.62 ng g^{-1} dw	0.216 ± 0.066	1997–1998	Sverko et al. (2008)
Lake Ontario	Sediment	2.23–586 ng g^{-1} dw	0.167 ± 0.061	1998	Sverko et al. (2008)
	Sediment	206 ± 26.3 pg g^{-1} dw	0.14	1998	Tomy et al. (2007)
	Sediment	150 ng g^{-1} dw	0.24	2004	Qiu et al. (2007)
Lake Winnipeg	Sediment	30.0 ± 3.2 pg g^{-1} dw	0.39	2000–2003	Tomy et al. (2007)
USA					
	Sewage sludge	112–175 ng g^{-1} TOC[c]	0.61–0.46	2002–2008	Guardia et al. (2010)
	Tree bark	0.008–4.08 ng g^{-1}	–	2008	Salamova and Hites (2010)
	Tree bark	0.025–115 ng g^{-1}	0.71–0.83	2006	Qiu and Hites (2008)
Laurentian Great Lakes (Canada and USA)	Eggs of herring gulls	1.5–4.5 ng g^{-1} ww[d]	–	2004	Gauthier et al. (2007)
Great Lakes (Canada and USA)	Sediment	0.0138–4.39 ng g^{-1} dw	0.08–0.52	2001, 2002, 2006, 2007	Shen et al. (2010)
Great Lakes (Canada and USA)	Fish	0.063–2.6 ng g^{-1} lw	0.18–0.68	2001, 2002 2006, 2008	Shen et al. (2010)

–: No data.
[a] dw: dry weight.
[b] lw: lipid weight.
[c] TOC: total organic carbon.
[d] ww: wet weight.

500 km north of the study area. No DP production facilities are documented near Jiaozhou, Taozi and Sishili Bay.

Significant differences of the DP distributions have been found between Jiaozhou Bay and Taozi and Sishili Bay (student *t*-test, $p < 0.05$). In Jiaozhou Bay, the highest concentration (187 pg g^{-1} dw) was found at the estuary of Haibo River, where one of Qingdao waste water treatment plants (WWTP) is located nearby (Fig. 2). The concentration at this site was one to three orders of magnitudes higher than those at other sites. Guardia et al. (2010) detected DP in sewage sludge from a WWTP in USA ranging from 112 to175 ng g^{-1} TOC with the content of the TOC ranging from 7% to 28% (Guardia et al., 2010). Assuming all of the sewage sludge contained 7% TOC, the calculated lowest DP concentration should be 7.8–12.3 ng g^{-1} dw. It was higher than most of reported concentrations in sediments except Lake Ontario (Canada), which indicates that the WWTP might be a major DP source for the adjacent area. The three highest concentrations of DP in the coastal sediments of Jiaozhou Bay were found near the Haibo estuary, which may be influenced by the WWTP, too. In riverine sediments from the Dague River, the DP concentration in the upstream sediment (3.0 pg g^{-1} dw) was one order of magnitude lower than that in the downstream sediment (56.9 pg g^{-1} dw). Discharge from the Jiaozhou town (36.17°N, 120.00°E) located near Dagu River might be the local source of DP.

Concentration of DP in the sediment collected near the Qingdao Harbor, which is the third busiest harbor in China, was 31.8 pg g^{-1} dw, however, in more distant locations, the levels were one order of magnitude lower (4.0 and 2.0 pg g^{-1} dw).

In Taozi and Sishili Bay, the mean concentrations of DP (33.8 and 64.5 pg g^{-1} dw, respectively) were higher than that of Jiaozhou Bay (23.7 pg g^{-1} dw). The spatial distribution was showed in Fig. 3. In Sishili Bay, high concentrations were found in the inner bay but not along the coastal zone. Ren et al. (2008) reported significant correlation between the airborne DP concentration and the population over 1 million in one city. Yantai City has a population of 1800 000 which is smaller than that of Qingdao City (a population of 2296 000). The DP concentration in Yantai should be lower than that of Qingdao, which indicated the high levels in the sediments may not mainly come from the local atmospheric deposition. Harbors were also suspected as possible source because of intensive human activities. Yantai Harbor is settled at the west coast of Sishili Bay, but it is smaller than the Qingdao Harbor (southwest of Jiaozhou Bay), which means Yantai Harbor may not contribute much to the DP contamination in Sishili Bay. There was no intensive industrial source reported in this area, either. The suspected input source is the WWTP located at Zhifu Island. This WWTP has only limited ability to treat domestic and industrial wastewater, and discharges waste water directly into the sea.

3.2. Fractional abundances of Dechlorane Plus isomers

The f_{syn} value was calculated as *syn*-DP/(*syn*-DP + *anti*-DP) (Qi et al., 2010). The mean f_{syn} values for Jiaozhou, Taizi and Sishili Bay were 0.29 ± 0.06, 0.18 ± 0.05, and 0.15 ± 0.07, respectively. Wang et al. (2010a, b) reported the f_{syn} for commercial DP mixture to be 0.40 in China which is higher than the DP (f_{syn} = 0.2–0.35)

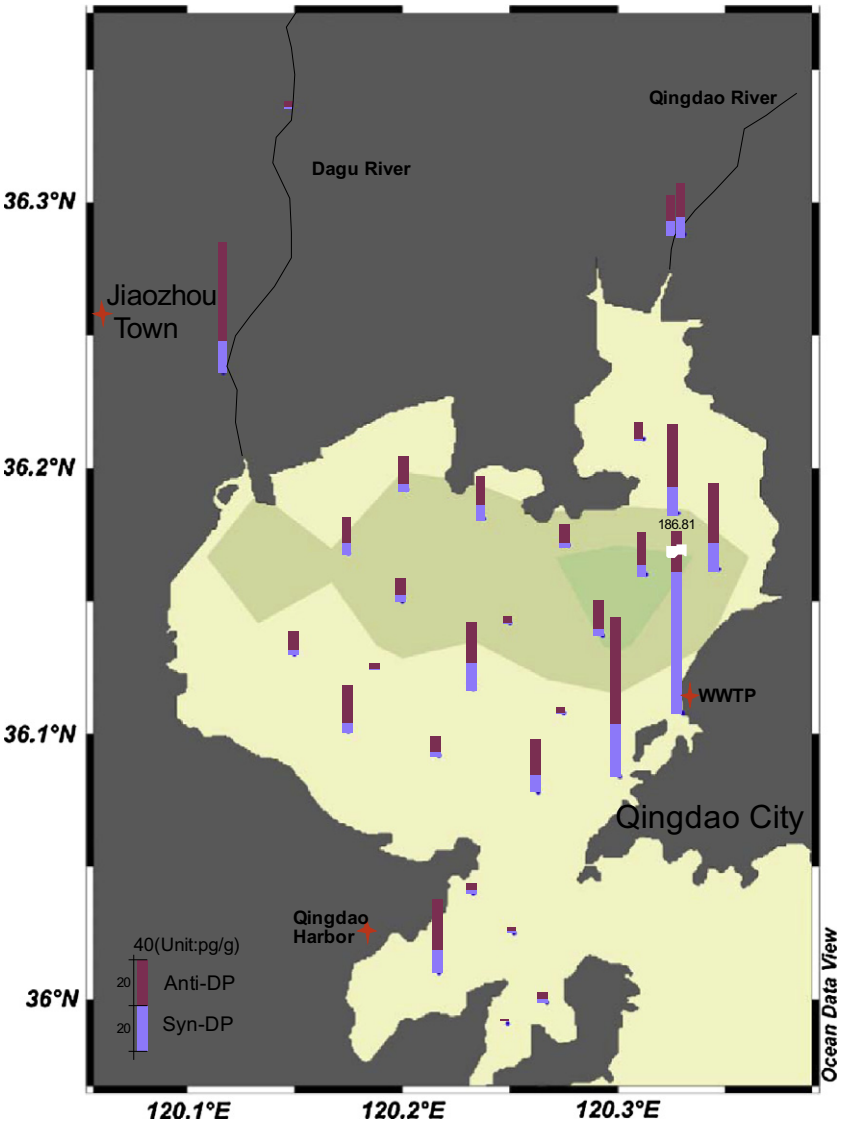

Fig. 2. Distributions of DP in surface sediments from Jiaozhou Bay.

produced and widely used in North America (Hoh et al., 2006; Tomy et al., 2007). In Chinese coastal sediments, the values of f_{syn} were all below 0.40, and only 8 out of 48 samples showed $\geqslant$0.35 f_{syn} values. This indicates definite stereo selective degradation of DP and the *anti*-DP seems to be more stable than *syn*-DP in the coastal sediments.

In the semi-closed Jiaozhou Bay, as shown in Table 1, most of f_{syn} values (0.21–0.39, except one site with a value of 0.11) were close to the technical DP mixture. They were comparable with that of Huai'an canal sediments (0.24–0.30) which were close to the manufacture area (Wang et al., 2010b). The DP in this bay should come from the input of the technical mixture from the adjacent region.

Both Sverko et al. (2008) and Tomy et al. (2008) found that the f_{syn} in the Lake Ontario was below 0.20, but the concentrations of total DP were much higher than that of the sediments from other places, e.g. Lake Winnepig (30.0 ± 3.2 pg g^{-1} dw) and Lake Erie (0.061–8.62 ng g^{-1} dw)(Tomy et al., 2007; Sverko et al., 2008). The same trend was obvious in this study. In Sishili and Taozi Bay, the concentrations were significantly correlated with the f_{syn} values (r = 0.58, n = 19, p < 0.05), and the higher concentration was accompanied by the lower f_{syn} values. In contrast to Jiaozhou Bay, Sishili and Taozi Bay are more open. Coastal sediments from these bays may not only receive input from land, but also the inner Bohai Sea (Cheng and Gao, 2000). As shown in Fig. 4, the two bays were at the south-east of the Bohai strait. Marine current runs through the narrow strait with a high speed carrying the sediments from the Bohai Sea. When it comes to the Yellow Sea, the current velocity slows down. As a result, some suspended sediments settle down, and some bottom sediments stop moving. The arrows in Fig. 4 show the main direction of the sediment movement which supported that Taozi and Sishili Bay receive sediment from Bohai Sea. Sverko et al. (2008) reported f_{syn} below 0.1 in Niagara and Lake Ontario non-depositional sediments. This suggests that the imported sediments would enrich *anti*-DP and decrease the f_{syn} value. The Bohai Sea is a hot spot when considering contamination with POPs. High concentrations of PAHs, PBDEs and PCBs have been found in the sediments (Zhao et al., 2005; Liu et al., 2009; Pan et al., 2010). Though there are no DP data in Bohai Sea reported, high concentration of DP can be supposed as it receives large input of contaminations from surrounding cities. More research should be conducted to investigate the sources and distribution pathways of DP in the Bohai Sea.

3.3. Dechlorinated species of Dechlorane Plus

Sverko et al. (2008) reported DP decomposition in the environmental compartments. To assure the ion fragment clusters truly

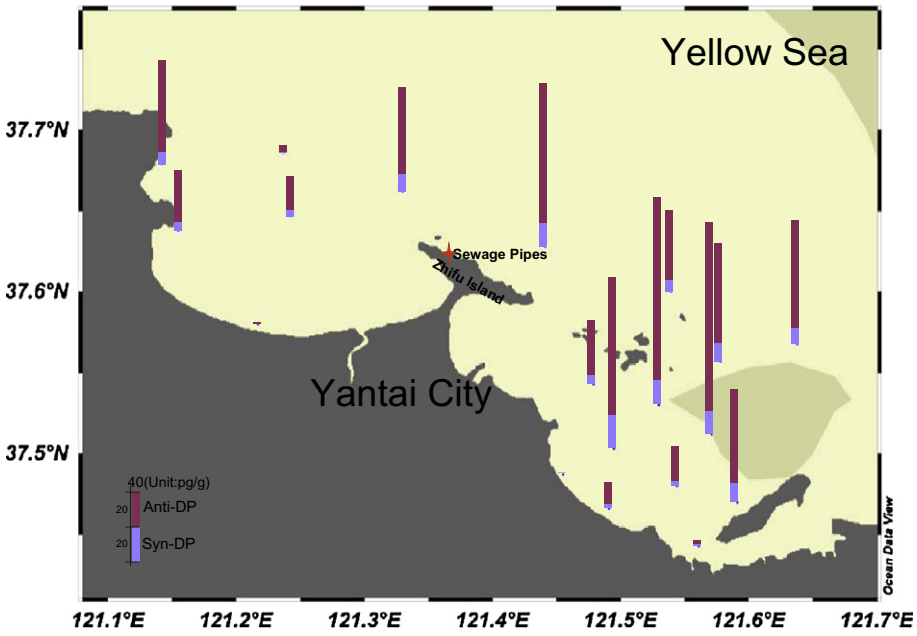

Fig. 3. Distributions of DP in surface sediments from Toazi and Sishili Bay.

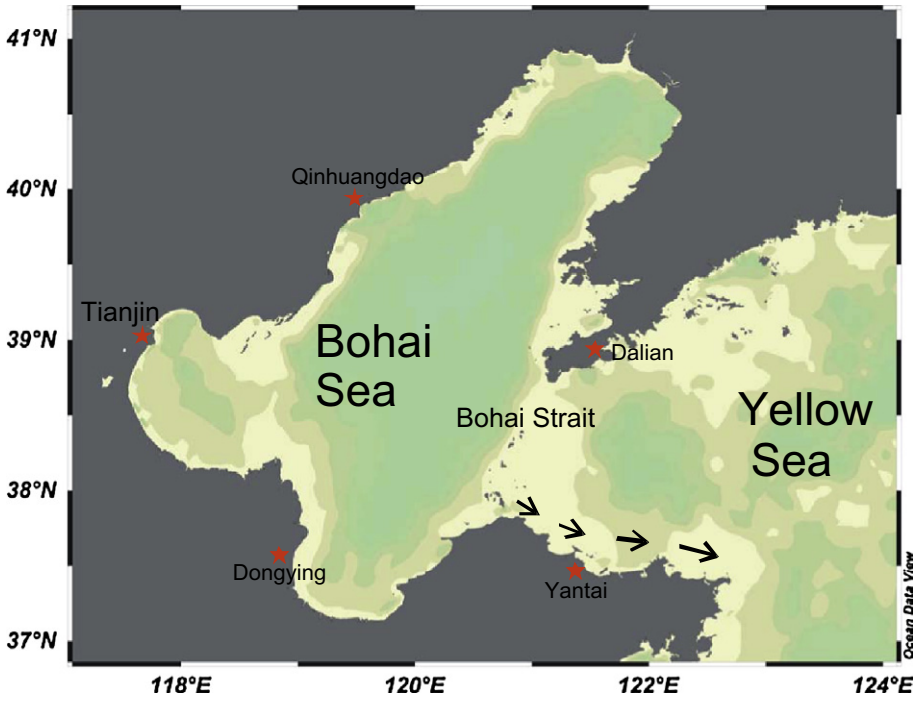

Fig. 4. Sketch map of sediment transportation. Five-pointed stars represent some cities with population over one million.

come from the environmental samples but not from artifact formation during the analytical procedure, a new GC liner was applied before injection. Moreover, one 10 pg μL^{-1} quality control standard (including *syn*-DP, *anti*-DP, aCl10DP and aCl11DP) was analyzed after every eight samples to supervise the possible degradation in GC-MS system. The relative deviation of all target compounds in QC standards were within 15% of the original standards in all cases, which means no obvious decomposition of *syn*- and *anti*-DP had happened in the GC-MS system. In all of the 48 samples, 9 samples showed aCl11DP concentration above the MDL, whereas, all the samples showed aCl10DP concentration below the MDL. 7 out of 13 samples were detected aCl11DP in Sishili Bay, and the degradation rate ((aCl10DP + aCl11DP)/(*syn*-DP + *anti*-DP + aCl10DP + aCl11DP)%) ranged from 0.9% to 5.1%. Both photodegradation and aerobic microbial degradation may happen in surface sediments which result in the appearance of dechlorinated species (Sverko et al., 2008).

3.4. Inventory of DP in the marine sediment

The inventory of DP in sediment in the bays was calculated by the equation as follow:

Table 3
Inventory parameters of Jiaozhou. Taozi and Sishili Bay, China.

Sampling zone	C (pg g^{-1})	ρ (g cm^{-3})	A (km^2)	D (cm a^{-1})	Inventory (kg)
Jiaozhou Bay	23.7	1.01[a]	388	0.704[a]	0.33
Taozi Bay	33.8	0.95[b]	184	1.24[b]	0.37
Sishili Bay	64.5	0.95[b]	130	1.24[b]	0.49

[a] Li et al. (2003).
[b] Qi et al. (2004).

$$\text{Inventory} = C \times \rho \times A \times D \times a$$

where C (pg g^{-1}) is the mean concentration of DP in the bay, ρ (g cm^{-3}) is the dry density of the sediment. A (cm^2) represents the area of the bay, D (cm a^{-1}) is the sedimentation rate and a (a) is the number of years considered for the inventory.

The parameters for the three bays were presented in Table 3. The sedimentation rate of the three bays were close to 1 cm a^{-1}, so it is estimated for 5-year inventories. They were 0.33 kg in Jiaozhou Bay, 0.37 kg in Taozi Bay and 0.49 kg in Sishili Bay. The smallest Sishili Bay (130 km^2) stores most of DP (0.49 kg). Qiu et al. (2007) reported the inventory of DP per area (9 cm and 16 cm depth) was 120 ng cm^{-2} in Lake Ontario, and Wang et al. (2010a, b) calculated the 20.3 ± 7.5 cm soil inventory to be 15 000–110 000 ng cm^{-2} in Huai'an. The 5 cm depth burdens of DP were 8.5 ng cm^{-2} in Jiaozhou Bay, 20.1 ng cm^{-2} in Taozi Bay and 37.7 ng cm^{-2} in Sishili Bay, respectively. Sediment would store DP for a long time as one of the possible major sinks (Wang et al., 2010a, b). With a half-live of 14 years, DP is bioavailable for many aquatic organisms, and it might be harmful especially to the benthic biota (Ismail et al., 2009).

4. Conclusions

DP was detected in all surface sediments from three Chinese bays, but different distribution patterns and sources were found. In semi-closed Jiaozhou Bay, higher concentrations were detected near the WWTP which was considered as the major DP source. Usage of commercial DP products resulted in the contamination in Jiaozhou Bay. In contrast, high DP concentrations were found in the inner places of Sishili Bay with low f_{syn}. DP in Taozi and Sishili Bay may come from the transportation from Bohai Sea. A WWTP at Zhifu Island could elevate DP level in Sishili Bay. The 5-year inventories in the three bays indicated Sishili Bay stores more DP than the other two bays.

References

Cheng, P., Gao, S., 2000. Net sediment transport patterns over the northwestern Yellow Sea, based upon grain size trend analysis. Ocean Limnol. Sinica. 31 (in Chinese).

Gauthier, L.T., Hebert, C.E., Weseloh, D.V.C., Letcher, R.J., 2007. Current-use flame retardants in the eggs of herring gulls (Larus argentatus) from the Laurentian Great lakes. Environ. Sci. Technol. 41, 4561–4567.

Guardia, M.J.L., Hale, R.C., Harvey, E., Chen, D., 2010. Flame-retardants and other organohalogens detected in sewage sludge by electron capture negative ion mass spectrometry. Environ. Sci. Technol. 44, 4658–4664.

Guzzella, L., Roscioli, C., Binelli, A., 2008. Contamination by polybrominated diphenyl ethers of sediments from the Lake Maggiore basin (Italy and Switzerland). Chemosphere 73, 1684–1691.

Hoh, E., Zhu, L., Hites, R.A., 2006. Dechlorane plus, a chlorinated flame retardant, in the Great Lakes. Environ. Sci. Technol. 40, 1184–1189.

Hung, C.-C., Gong, G.-C., Jiann, K.-T., Yeager, K.M., Santschi, P.H., Wade, T.L., Sericano, J.L., Hsieh, H.-L., 2006. Relationship between carbonaceous materials and polychlorinated biphenyls (PCBs) in the sediments of the Danshui River and adjacent coastal areas, Taiwan. Chemosphere 65, 1452–1461.

Ismail, N., Gewurtz, S.B., Pleskach, K., Whittle, D.M., Helm, P.A., Marvin, C.H., Tomy, G.T., 2009. Brominated and chlorinated flame retardants in Lake Ontario, Canada, lake trout (Salvelinus namaycush) between 1979 and 2004 and possible influences of food-web changes. Environ. Toxicol. Chem. 28, 910–920.

Kang, J.-H., Kim, J.-C., Jin, G.-Z., Park, H., Baek, S.-Y., Chang, Y.-S., 2010. Detection of dechlorane plus in fish from urban-industrial rivers. Chemosphere 79, 850–854.

Li, F., Song, J., Li, X., Wang, Y., Qi, J., 2003. Modern sedimentation rate and flux in the Jiaozhou Bay. Mar. Geol. Quaternary Geol. 23, 29–33 (in Chinese).

Liu, A., Lang, Y., Xue, L., Liu, J., 2009. Ecological risk analysis of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from Laizhou Bay. Environ. Monitor. Assess. 159, 429–436.

Minh, N.H., Minh, T.B., Kajiwara, N., Kunisue, T., Iwata, H., Viet, P.H., Cam Tu, N.P., Tuyen, B.C., Tanabe, S., 2007. Pollution sources and occurrences of selected persistent organic pollutants (POPs) in sediments of the Mekong River delta, South Vietnam. Chemosphere 67, 1794–1801.

Möller, A., Xie, Z., Sturm, R., Ebinghaus, R., 2010. Large-scale distribution of dechlorane plus in air and seawater from the Arctic to Antarctic. Environ. Sci. Technol. 44, 8977–8982.

Moon, H.-B., Kannan, K., Choi, M., Choi, H.-G., 2007a. Polybrominated diphenyl ethers (PBDEs) in marine sediments from industrialized bays of Korea. Mar. Pollut. Bull. 54, 1402–1412.

Moon, H.-B., Kannan, K., Lee, S.-J., Choi, M., 2007b. Polybrominated diphenyl ethers (PBDEs) in sediment and bivalves from Korean coastal waters. Chemosphere 66, 243–251.

Palm, A., Cousins, I.T., Mackay, D., Tysklind, M., Metcalfe, C., Alaee, M., 2002. Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers. Environ. Pollut. 117, 195–213.

Pan, X., Tang, J., Li, J., Guo, Z., Zhang, G., 2010. Levels and distributions of PBDEs and PCBs in sediments of the Bohai Sea, North China. J. Environ. Monitor. 12, 1234–1241.

Qi, J., Li, F., Song, J., Gao, S., Wang, G., Cheng, P., 2004. Sedimentation rate and flux of the North Yellow Sea. Mar. Geol. Quaternary Geol. 24, 9–14 (in Chinese).

Qi, H., Liu, L., Jia, H., Li, Y.-F., Ren, N.-Q., You, H., Shi, X., Fan, L., Ding, Y., 2010. Dechlorane plus in surficial water and Sediment in a northeastern Chinese river. Environ. Sci. Technol. 44, 2305–2308.

Qiu, X.H., Hites, R.A., 2008. Dechlorane plus and other flame retardants in tree bark from the Northeastern United States. Environ. Sci. Technol. 42, 31–36.

Qiu, X., Marvin, C.H., Hites, R.A., 2007. Dechlorane plus and other flame retardants in a sediment core from Lake Ontario. Environ. Sci. Technol. 41, 6014–6019.

Ren, N., Sverko, E., Li, Y.-F., Zhang, Z., Harner, T., Wang, D., Wan, X., McCarry, B.E., 2008. Levels and isomer profiles of dechlorane plus in Chinese air. Environ. Sci. Technol. 42, 6476–6480.

Ren, G., Yu, Z., Ma, S., Li, H., Peng, P., Sheng, G., Fu, J., 2009. Determination of Dechlorane plus in serum from electronics dismantling workers in south China. Environ. Sci. Technol. 43, 9453–9457.

Salamova, A., Hites, R.A., 2010. Evaluation of tree bark as a passive atmospheric sampler for flame retardants, PCBs, and organochlorine pesticides. Environ. Sci. Technol. 44, 6196–6201.

Shen, L., Reiner, E.J., Macpherson, K.A., Kolic, T.M., Sverko, E., Helm, P.A., Bhavsar, S.P., Brindle, I.D., Marvin, C.H., 2010. Identification and screening analysis of halogenated norhornene flame retardants in the Laurentian Great Lakes: Dechloranes 602, 603, and 604. Environ. Sci. Technol. 44, 760–766.

Sverko, E., Tomy, G.T., Marvin, C.H., Zaruk, D., Reiner, E., Helm, P.A., Hill, B., McCarry, B.E., 2008. Dechlorane plus Levels in sediment of the lower Great Lakes. Environ. Sci. Technol. 42, 361–366.

Tomy, G.T., Pleskach, K., Ismail, N., Whittle, D.M., Helm, P.A., Sverko, E., Zaruk, D., Marvin, C.H., 2007. Isomers of dechlorane plus in Lake Winnipeg and Lake Ontario food webs. Environ. Sci. Technol. 41, 2249–2254.

Tomy, G.T., Thomas, C.R., Zidane, T.M., Murison, K.E., Pleskach, K., Hare, J., Arsenault, G., Marvin, C.H., Sverko, E., 2008. Examination of isomer specific bioaccumulation parameters and potential in vivo hepatic metabolites of syn- and anti-dechlorane plus isomers in juvenile rainbow trout (Oncorhynchus mykiss). Environ. Sci. Technol. 42, 5562–5567.

US, E., 2008. US Environmental Protection Agency. HPV Voluntary Robust Summary.

Wang, B., Iino, F., Huang, J., Lu, Y., Yu, G., Morita, M., 2010a. Dechlorane plus pollution and inventory in soil of Huai'an City, China. Chemosphere 80, 1285–1290.

Wang, D.-G., Yang, M., Qi, H., Sverko, E., Ma, W.-L., Li, Y.-F., Alaee, M., Reiner, E.J., Shen, L., 2010b. An Asia-specific source of dechlorane plus: concentration, isomer profiles, and other related compounds. Environ. Sci. Technol. 44, 6608–6613.

Yu, Z.Q., Lu, S.Y., Gao, S.T., Wang, J.Z., Li, H.R., Zeng, X.Y., Sheng, G.Y., Fu, J.M., 2010. Levels and isomer profiles of Dechlorane Plus in the surface soils from e-waste recycling areas and industrial areas in South China. Environ. Pollut. 158, 2920–2925.

Zhao, X., Zheng, M., Liang, L., Zhang, Q., Wang, Y., Jiang, G., 2005. Assessment of PCBs and PCDD/Fs along the Chinese Bohai Sea coastline using mollusks as bioindicators. Arch. Environ. Contam. Toxicol. 49, 178–185.