



# Distribution and sources of DDT and its metabolites in porewater and sediment from a typical tropical bay in the South China Sea<sup>☆</sup>

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## ABSTRACT

Dichlorodiphenyltrichloroethane (DDT) is well known for its harmful effects and has been banned around the world. However, DDT is still frequently detected in natural environments, particularly in aquaculture and harbor sediments. In this study, 15 surface sediment samples were collected from a typical tropical bay (Zhanjiang Bay) in the South China Sea, and the levels of DDT and its metabolites in sediment and porewater samples were investigated. The results showed that concentrations of DDXs (i.e., DDT and its metabolites) in bulk sediments were 1.58–51.0 ng g<sup>-1</sup> (mean, 11.5 ng g<sup>-1</sup>). DDTs (DDT and its primary metabolites, dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE)) were the most prominent, accounting for 73.2%–98.3% (86.1% ± 12.8%) of the DDXs. Additionally, high-order metabolites (i.e., 1-chloro-2,2-bis(4'-chlorophenyl)ethylene (*p,p'*-DDMU), 2,2-bis(p-chlorophenyl)ethylene (*p,p'*-DDNU), 2,2-bis(p-chlorophenyl)ethanol (*p,p'*-DDOH), 2,2-bis(p-chlorophenyl) methane (*p,p'*-DDM), and 4,4'-dichlorobenzophenone (*p,p'*-DBP)) were also detected in most of the sediment and porewater samples, with DDMU and DBP being predominant. The DDTs concentration differed among the sampling sites, with relatively high DDTs concentrations in the samples from the aquaculture zone and an area near the shipping channel and the Haibin shipyard. The DDD/DDE ratios indicated a reductive dichlorination of DDT to DDD under anaerobic conditions at most of the sampling sites of Zhanjiang Bay. The possible DDT degradation pathway in the surface sediments of Zhanjiang Bay was *p,p'*-DDT/*p,p'*-DDD(*p,p'*-DDE)/*p,p'*-DDMU/*p,p'*-DDNU/.../*p,p'*-DBP. The DDXs in the sediments of Zhanjiang Bay were mainly introduced via mixed sources of industrial DDT and dicofol, including fresh input and historical residue. The concentrations of DDXs in porewater samples varied from 66.3 to 250 ng L<sup>-1</sup>, exhibiting a distribution similar to that in the accompanying sediments. However, the content of high-order metabolites was relatively lower in porewater than in sediment, indicating that high-order degradation mainly occurs in particles. Overall, this study helps in understanding the distribution, source, and degradation of DDT in a typical tropical bay.

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## 1. Introduction

Dichlorodiphenyltrichloroethane (DDT) is a typical persistent organic pollutant (POP) that has a high toxicity and low degradability and undergoes bioaccumulation (Woodwell et al., 1971; Burns and Villeneuve, 1987). It was widely used in China as a

pesticide for pest control and mosquito abatement beginning in the 1950s (Zhang et al., 2002). However, because of its serious threats to the ecosystem and human health, such as neural tube defects in fetuses (Ren et al., 2011; Wang et al., 2014a), the production and usage of DDT-related pesticides were gradually restricted and banned in many countries in the 1970s–1990s (Guo et al., 2013; Hitch and Day, 1992; Iwata et al., 1993; Tanabe et al., 1994; Wolff et al., 1993). Nevertheless, large amounts of DDT have been introduced into the environment, and their residues can persist for a long time. Additionally, some fresh DDT is still released into the

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environment as a result of dicofol production, and there are some specialty applications of DDT in antifouling paints in some developing countries, including China (Lin et al., 2009; Yu et al., 2011b). DDT and its metabolites (DDXs) are still one of the most important POPs in China, and high concentrations of DDXs are detectable in various environmental media (Xu et al., 2013; Lin et al., 2017), especially in aquaculture and harbor areas (Feng et al., 2016; Guo et al., 2013; Lin et al., 2009; Tolosa et al., 2010; Wu et al., 2016; Yu et al., 2011b, 2011c). Despite being the “hot spot” areas of DDXs contamination, knowledge on the concentration, distribution, and degradation behavior of DDT in these areas for both risk assessment and remediation actions is still limited.

Among the various environmental media, sediments are the primary sink for DDXs because of their high octanol-water partition coefficient ( $K_{OW}$ ) and their ability to readily bind to suspended particulates and ultimately bury them (Kan et al., 1994; Wu et al., 1999). When DDT is buried in the sediment, it can be further degraded to various metabolites via aerobic or anaerobic processes in the environment (Smith, 1948, 1962; Kallman and Andrews, 1963). Additionally, some high-order metabolites (the metabolites except DDD and DDE) (Denk and Milutinović, 2018; Denk et al., 2019; Hitch and Day, 1992; Huang et al., 2001; Kallman and Andrews, 1963; Planche et al., 1979; Wedemeyer, 1967; Yu et al., 2011a; Zhu et al., 2019), such as 4,4'-dichlorobenzophenone ( $p,p'$ -DBP), are more toxic than DDT (Megharaj et al., 1999). Thus, sediments can also become a continuing source of contamination, releasing adsorbed chemicals into the overlying water through the sediment–water interface and further damaging the aquatic environment (Booij et al., 2003; Thibodeaux, 2005). Some investigations have demonstrated that porewater is an important junction that dictates the biogeochemical cycling of many environmentally relevant chemicals via molecular diffusion, resuspension, and bioturbation (Josefsson et al., 2010, 2012; Lick, 2006; Sabin et al., 2010), and a considerable portion of DDTs in porewater may be associated with this cycling in bodies of water and sediments. Thus, to better understand its availability in the environment, it is necessary to investigate the degradation pathways and distribution of DDTs between the sediment and porewater.

Zhanjiang Bay is a typical tropical bay ( $110^{\circ}25'24.39''$ ,  $21^{\circ}10'19.82''$ ) located in western Guangdong Province, China, bordering the South China Sea, with an average annual temperature of approximately  $20^{\circ}\text{C}$  (Li et al., 2014; Zhang et al., 2018). It is a semi-enclosed bay with a water depth ranging from 5 to 55 m (Fig. S1), thereby providing excellent conditions for harbors and agricultural activities. Additionally, Zhanjiang Bay is also a heavily polluted region because of the discharge of municipal wastewaters from various human activities, such as aquaculture, shipping transportation, and sewage discharge (Fig. 1 and S1). In this study, DDXs are investigated in sediment and porewater collected from Zhanjiang Bay. The objectives of this study are to (1) determine the concentration and distribution of DDXs in sediment and porewater and (2) explore the degradation process and possible sources of DDXs in Zhanjiang Bay. The results obtained will provide up-to-date information on DDXs pollution, as well as a useful reference for environmental protection in this region.

## 2. Material and methods

### 2.1. Materials

Target analytes, including  $o,p'$ - and  $p,p'$ -isomers of DDT and its metabolites, namely, dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), 1-chloro-2,2-bis(4'-chlorophenyl)ethylene ( $p,p'$ -DDMU), 2,2-bis(p-chlorophenyl)ethylene ( $p,p'$ -DDNU), 2,2-bis(p-chlorophenyl)ethanol ( $p,p'$ -

DDOH), 2,2-bis(p-chlorophenyl)methane ( $p,p'$ -DDM), and 4,4'-dichlorobenzophenone ( $p,p'$ -DBP), were mainly purchased from AccuStandard (New Haven, CT, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Herein, DDTs refers to the sum of the concentrations of  $o,p'$ -DDT,  $p,p'$ -DDT, and their primary metabolites  $o,p'$ -DDE,  $p,p'$ -DDE,  $o,p'$ -DDD, and  $p,p'$ -DDD, whereas DDXs indicates the sum of DDTs and their high-order metabolites ( $p,p'$ -DDMU,  $p,p'$ -DDNU,  $p,p'$ -DDOH,  $p,p'$ -DDM, and  $p,p'$ -DBP). The internal standard (PCB-82) and surrogate standards (PCB-67 and PCB-191) were purchased from AccuStandard (New Haven, CT, USA).

The organic solvents, dichloromethane (DCM), hexane, acetone, and methanol (MeOH) were purchased from HPLC, Oceanpak (Switzerland). Neutral silica gel (80–100 mesh, Macklin, Shanghai, China) was extracted for 72 h with a mixture of DCM and MeOH at a volume ratio of 93:7 via Soxhlet extractors, then baked at  $180^{\circ}\text{C}$  for 12 h, and deactivated by adding 3% deionized water. Florisil (60–100 mesh; CNW, Germany) was baked at  $250^{\circ}\text{C}$  for 12 h. Anhydrous sodium sulfate (GR, Macklin, Shanghai, China) was baked at  $450^{\circ}\text{C}$  for 4 h and stored in a glass desiccator. The copper sheet was treated with diluted hydrochloric acid, washed to neutralize, and cleaned thrice with DCM. All the glassware used in the experiment was baked at  $450^{\circ}\text{C}$  for 4 h in a muffle oven.

### 2.2. Sample collection

The sediment samples were collected from Zhanjiang Bay, a typical semi-enclosed bay located in the west of Guangdong Province in South China (Fig. 1). The Suixi River is the only input of fresh water, and water from the South China Sea is exchanged through the mouth of the bay. Sediment samples were collected with a stainless-steel grab on March 01–02, 2018, from the estuary to the mouth of Zhanjiang Bay, covering different functional regions, including estuary, agriculture, harbor, and ship channels (Fig. 1) (Zhanjiang city government, 2012). All the samples were transported to the laboratory in ice and stored at  $-20^{\circ}\text{C}$  until the analysis.

The sediment samples were wet-sieved to remove large fragments, i.e., shells and sundries, and the residues were further

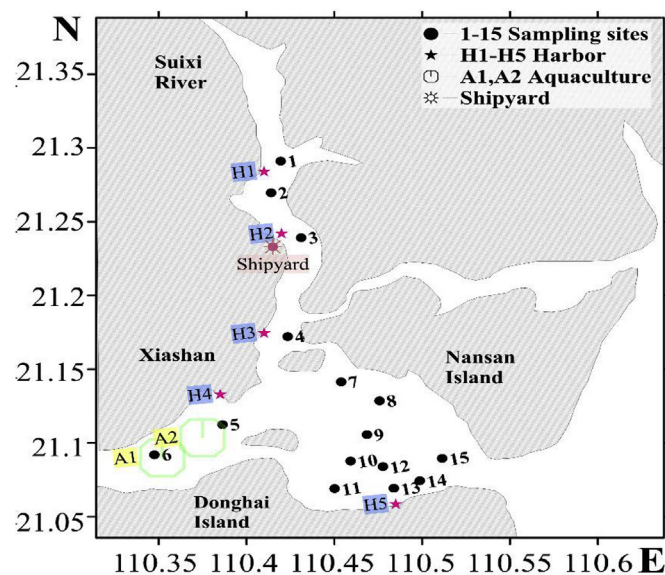


Fig. 1. Map showing stations of sampling sites (1–15), harbors (H1–H5), Tiaoshun port, Xiahai harbor, Yuren harbor, Baoman harbor, and Donghai port, aquaculture areas (A1, A2), and Haibin Shipyards in Zhanjiang bay.

fractionated into coarse (particle size  $\geq 200 \mu\text{m}$ ) and fine (particle size  $< 200 \mu\text{m}$ ) particles using a stainless-steel mesh screen. All samples were dried in a freezer dryer. Finally, 45 sediment samples, including 15 bulk sediment samples, 15 coarse fractions, and 15 fine fractions were obtained. Porewater samples were obtained by centrifuging the sediments at  $3500\times g$  for 15 min and filtering with a  $0.45\text{-}\mu\text{m}$  Poly tetra fluoroethylene filter (PTFE, Thermos, USA) (Elderfield et al., 1981; Zhou et al., 2000). Finally, 12 porewater samples were obtained, excluding samples from sites 7, 9, and 15, which were too sandy to acquire water (Table 1).

### 2.3. Measurements of the total organic carbon and dissolved organic carbon

The total organic carbon (TOC) content was determined according to a previously described method with modifications (Hawthorne et al., 2007). Briefly, approximately 1 g of sediment sample was weighed into a glass tube and the inorganic carbonates were removed with 1 M HCl. Then, the organic carbon contents in the treated solid samples were analyzed using a high-temperature combustion method with an elemental analyzer (Elementar Vario EL cube, Hanau, Germany). Each sample was analyzed in duplicate, and the average relative difference was less than  $\pm 0.3\%$ . The dissolved organic carbon (DOC) content in the porewater samples was determined using a TOC-VCPH analyzer (Shimadzu, Kyoto, Japan). The samples and standards were examined in triplicate, and the average relative difference was less than  $\pm 0.5\%$ .

### 2.4. Extraction

#### 2.4.1. Sediments

Approximately 10 g of the sediment samples were weighed in Teflon tubers (50 mL, CNW, Germany) and spiked with surrogate standards (20  $\mu\text{L}$  of  $5 \text{ mg L}^{-1}$  PCB-67 and PCB-191, respectively). Copper sheets were added to remove the sulfate. The sediment samples were sonicated thrice in 20 mL of organic solvents (2:2:1 = DCM: hexane: acetone) for 15 min (Wu et al., 2016; Yu et al., 2011c). The extracts were then concentrated and solvent-exchanged to 0.5 mL in hexane by using a rotary evaporator (R-210, BUCHI, Switzerland) and further purified on a chromatographic column packed with 4 mL of florisil/neutral silica gel (3:1, V:V). The target compounds were eluted with 5 mL of *n*-hexane and 10 mL of a DCM/*n*-hexane mixture (1:9, V:V). Each eluate was concentrated to 0.2 mL under a gentle stream of nitrogen and

spiked with the internal standard (PCB-82).

#### 2.4.2. Porewater

The porewater was extracted using liquid–liquid separation (Maharjan and Takahashi, 2013). First, the prepared porewater was taken in a 250-mL Teflon separator funnel (CNW, Germany) and surrogate standards (20  $\mu\text{L}$  of  $5 \text{ mg L}^{-1}$  PCB-67 and PCB-191, respectively) were added. Second, an equal volume of dichloromethane was added and shaken for 15 min. The extraction process was repeated thrice, and the combined organic extracts were treated with anhydrous sodium sulfate to remove the residual moisture. Finally, the extracts were concentrated and purified similarly to the sediment extracts.

### 2.5. Instrumental analysis

All target analytes were analyzed with an Agilent gas chromatograph coupled to a mass spectrometer (Agilent 7890/5975C GC/MS) with a DB-5MS capillary column (60 m  $\times$  0.25 mm i.d. with a 0.25  $\mu\text{m}$  film thickness, Agilent, USA). A one microliter aliquot of the sample solution (1  $\mu\text{L}$ ) was automatically injected into the spitless inlet at a temperature of  $290 \text{ }^\circ\text{C}$ . According to a previous study (Guan et al., 2009), the column temperature was initially kept at  $60 \text{ }^\circ\text{C}$  for 1 min, then increased to  $220 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C min}^{-1}$  (held for 2 min), then increased to  $250 \text{ }^\circ\text{C}$  at  $2 \text{ }^\circ\text{C min}^{-1}$  (held for 2 min), and finally increased to  $300 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C min}^{-1}$  with a 15 min hold. The mass spectra were acquired under a single ion monitoring (SIM) mode with an electron impact energy of 70 eV and a scan range of  $m/z$  50–500. The ion source temperature was set at  $250 \text{ }^\circ\text{C}$  and the high-purity carrier gas helium was set at 1.0 mL/min.

### 2.6. Quality assurance and quality control

In this study, a standard solution of *p,p'*-DDT, a procedural blank sample (solvent), a spiked blank (standards spiked into the solvent), a spiked matrix (standards spiked into the pre-extracted sediment), and a sample duplicate were analyzed for each batch of 15 samples. The extent of the *p,p'*-DDT breakdown was checked daily and controlled to be lower than 15%. PCB-67 and PCB-191 were further used as surrogate standards with procedural recoveries of  $85\% \pm 21\%$  and  $92\% \pm 15\%$  in sediment and  $75\% \pm 9\%$  and  $80\% \pm 5\%$  in porewater, respectively. The method detection limits (MDLs) of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDMU were 0.02, 0.10, and 0.07  $\text{ng L}^{-1}$  in porewater and 0.02, 0.07, and 0.05  $\text{ng g}^{-1}$  in

**Table 1**

Concentrations of DDTs, DDXs (average  $\text{ng}\cdot\text{g}^{-1}$  dry weight) in the bulk sediments and porewater collected from Zhanjiang Bay.

Sites	Depth (m)	TOC ( $\text{mg}\cdot\text{g}^{-1}$ )	DOC ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Bulk sediment				Porewater	
				DDD $\text{ng}\cdot\text{g}^{-1}$	DDE $\text{ng}\cdot\text{g}^{-1}$	DDTs $\text{ng}\cdot\text{g}^{-1}$	DDXs $\text{ng}\cdot\text{g}^{-1}$	DDTs $\text{ng}\cdot\text{L}^{-1}$	DDXs $\text{ng}\cdot\text{L}^{-1}$
S1	16.0	1.33	22.7	1.81	2.52	8.10	9.67	166	169
S2	15.5	1.76	31.4	1.28	1.17	5.56	7.02	103	101
S3	16.0	1.17	32.6	0.89	0.42	3.36	4.59	128	133
S4	6.50	1.30	35.9	5.53	1.35	14.1	15.9	151	154
S5	6.00	1.10	54.5	21.2	11.3	49.8	51.0	246	250
S6	4.00	1.11	35.5	3.31	2.25	16.8	19.0	156	160
S7	5.00	0.94	–	2.24	1.47	6.56	6.67	–	–
S8	5.00	1.36	30.6	2.32	1.40	6.31	7.26	129	136
S9	5.00	0.89	–	1.04	0.74	4.43	4.68	–	–
S10	8.00	1.26	12.1	0.32	0.24	1.53	1.88	76.6	79.6
S11	11.5	1.00	26.2	0.28	0.57	1.25	1.58	63.2	66.3
S12	11.0	0.92	15.8	4.28	3.13	12.2	12.5	96.1	98.9
S13	15.0	1.02	31.7	0.61	1.40	3.38	4.36	169	174
S14	7.00	1.04	16.3	0.15	0.91	1.20	1.62	66.7	69.6
S15	20.0	1.02	–	0.91	0.83	4.21	4.67	–	–

"–" means no data.

sediment, respectively. The concentrations of the target compounds were corrected according to the similarity of their physicochemical properties. The details were as following: *p,p'*-DBP, *o,p'*-DDE, *p,p'*-DDNU, *p,p'*-DDMU, *p,p'*-DDOH, and *p,p'*-DDM were mainly corrected by PCB-67; the other target compounds, including *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDD, and *p,p'*-DDD, were corrected by PCB-191.

### 3. Results and discussion

#### 3.1. Occurrences of DDXs in sediments

The concentrations of the DDTs and DDXs in the surface sediments are presented in Tables S1–S3 in the Supplementary Materials (SM). As shown in Table 1, DDTs and DDXs were detected in all the sediment samples, and their total concentrations were 1.08–49.8 ng g<sup>-1</sup> (mean, 9.25 ng g<sup>-1</sup>) and 1.58–51.0 ng g<sup>-1</sup> (mean, 11.5 ng g<sup>-1</sup> dry weight (d.w.)), respectively. DDTs were the dominant constituent in all the samples, accounting for 73.2%–97.5% of the total DDXs compounds. *p,p'*-DDT presented the highest mean content (2.74 ng g<sup>-1</sup>), followed by *p,p'*-DDD (2.24 ng g<sup>-1</sup>), *p,p'*-DDE (1.55 ng g<sup>-1</sup>), *o,p'*-DDT (1.45 ng g<sup>-1</sup>), *o,p'*-DDD (0.84 ng g<sup>-1</sup>), *o,p'*-DDE (0.42 ng g<sup>-1</sup>), *p,p'*-DDMU (0.48 ng g<sup>-1</sup>), *p,p'*-DBP (0.23 ng g<sup>-1</sup>), *p,p'*-DDNU (0.11 ng g<sup>-1</sup>), *p,p'*-DDM (0.06 ng g<sup>-1</sup>), and finally *o,p'*-DDOH (0.03 ng g<sup>-1</sup>).

Table S4 summarizes the concentrations and sources of DDTs in the surface sediment of bay and harbor areas in other regions of China and other countries since the late 2000s. It can be observed that the concentrations of DDTs in Zhanjiang Bay are comparable with the DDTs concentrations in the sediments of bays, harbors, and coasts throughout the world. As shown in Table S4, the concentrations of DDTs in the sediments of Zhanjiang Bay are much higher than those in the Seto Inland Sea of Japan (0.01–2.51 ng g<sup>-1</sup>) (Asaoka et al., 2019), the English Bay in Canada (0.69 ng g<sup>-1</sup>) (Carmen et al., 2017), the Edremit Bay in Aegean Sea of Turkey (nd–1.16 ng g<sup>-1</sup>) (Darilmaz et al., 2019), the Northern South China Sea (0–0.82 ng g<sup>-1</sup>) (Kaiser et al., 2018), and the Hangzhou Bay (0.21 ng g<sup>-1</sup>) in China (Zhao et al., 2016); comparable with the concentrations of DDTs in most of the sediments collected from Beibu Gulf (2010) (0.03–92.3 ng g<sup>-1</sup>, 0.59–126 ng g<sup>-1</sup>) (Kaiser et al., 2015) (Xu et al., 2013) and Quanzhou Bay (2011) (1.53–53.3 ng g<sup>-1</sup>) (Yang et al., 2013), the coastal sediments of Hong Kong (9.95–44.4 ng g<sup>-1</sup>) (Wang et al., 2014b), the Yellow Sea (nd–5.10 ng g<sup>-1</sup>) (Zhao et al., 2018), and the East China Sea (2011) (nd–4.15 ng g<sup>-1</sup>) (Wang et al., 2020), the estuary sediments of the Nansha Mangrove (5.61–7.50 ng g<sup>-1</sup> d) (Wu et al., 2015), the Minjiang River (28.8–52.1 ng g<sup>-1</sup>) (Zhang et al., 2003), and the Daliao River (2.10–21.3 ng g<sup>-1</sup>) (Tan et al., 2009); and lower than the concentrations of DDTs in sediments collected from some bays and harbors, such as Macao (967–5810 ng g<sup>-1</sup>), Zhuhai (55.0–3040 ng g<sup>-1</sup>), Shenzhen (17.0–1460 ng g<sup>-1</sup>), Hong Kong (76.0–7350 ng g<sup>-1</sup>), Sanya (108–561 ng g<sup>-1</sup>), Maoming (361–1250 ng g<sup>-1</sup>), Zhoushan (9.0–563 ng g<sup>-1</sup>) (Lin et al., 2009), and Hailing Bay in China (450–5600 ng g<sup>-1</sup>) (Wu et al., 2016). These concentrations are also lower than the concentrations of DDTs in sediments collected from Palo Gulf in the USA (1000–2000 ng g<sup>-1</sup>) (Eganhouse et al., 2018; Liao et al., 2017), and Kosi Bay in South Africa (26.3–283 ng g<sup>-1</sup>) (Archibold and Humphries, 2017). However, the concentrations of DDTs in the sediments of the bay and harbor areas did not significantly decrease with the implementation of a DDT usage ban. For example, high concentrations of DDTs (4100 ng g<sup>-1</sup>) were detected in the sediments of Hailing Bay Harbor in 2014 (Wu et al., 2016). Nevertheless, when compared with Hailing Bay, the sediments of Zhanjiang Bay were, relatively, less contaminated with DDT, despite being heavily industrialized,

which may be due to the relatively low agricultural activities and fish boat maintenance facilities in Zhanjiang Bay.

As shown in Fig. 2a, the concentrations of DDTs were significantly different among the sampling sites, which might be due to the variations in the source composition and degradation process in the sampling sites. The highest concentration of DDTs was found in a sample collected from site 5 (49.8 ng g<sup>-1</sup>); additionally, the concentrations of DDTs in samples collected from sites 4, 6, and 12 were also relatively high (12.2–16.8 ng g<sup>-1</sup>). Among these highly polluted sites, sites 5 and 6 are located in an aquaculture zone (Fig. 1), which is usually associated with high levels of DDTs (Lin et al., 2009). The input of fish feed and antifouling paint flakes has been demonstrated to be an important contributor to high DDTs concentrations in these areas (Yu et al., 2011b; Zhong et al., 2011). In site 4, located in the shipping channel and near the Zhanjiang Haibin Shipyard (Fig. 1), antifouling paint flakes (containing DDT) may be an important source of DDT (Wu et al., 2016; Yu et al., 2011b), whereas the higher concentrations of DDTs in site 12 might be attributed to the vessel input in the shipping channel. In contrast, the sediment samples from other sites contained relatively low concentrations of DDTs (4.43 ± 2.83 ng g<sup>-1</sup>).

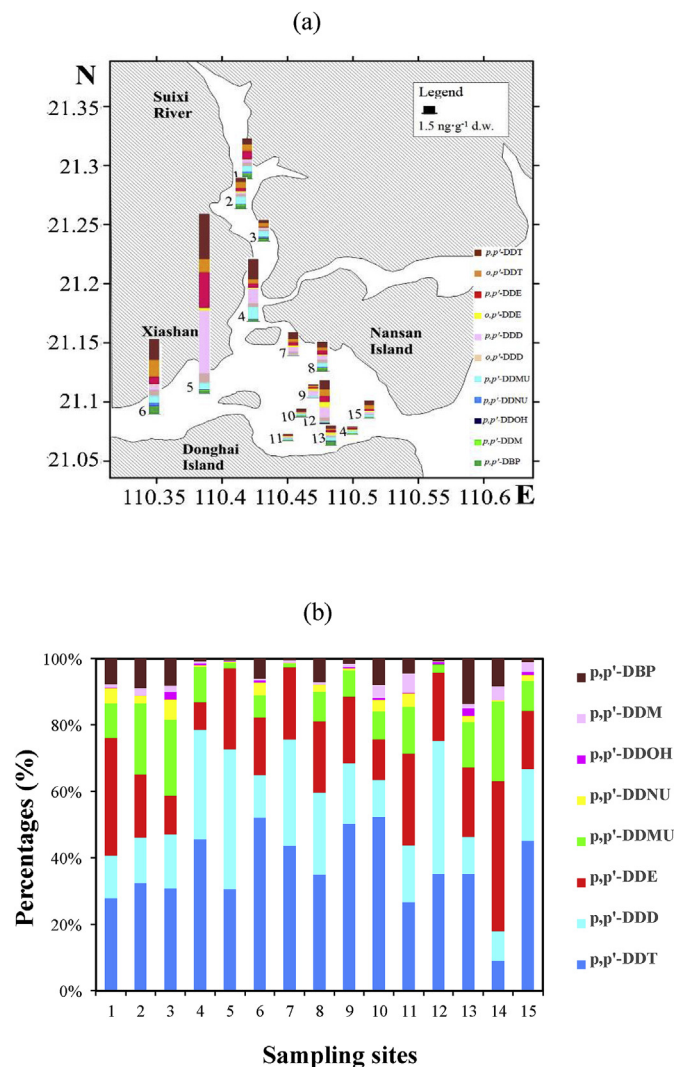


Fig. 2. Spatial distribution of DDXs (average ng·g<sup>-1</sup> dry weight) and its component in bulk sediments collected from Zhanjiang Bay in Guangdong Province, South China sea (a); the percentage contents of the metabolites of *p,p'*-DDT in total DDXs (b).

In general, sedimentary organic matter has a strong absorbing ability to hydrophobic organic pollutants, and therefore a positive correlation between the contents of organic pollutants and TOC in sediment have been frequently observed in some previous studies (Cornelissen et al., 2005; Hung et al., 2007; Koh et al., 2006). However, in the present study no significant correlations ( $p > 0.05$ ) were found between the concentrations of DDTs and DDXs and the TOC contents in the sediments. Therefore, TOC was not the key factor responsible for the accumulation of DDTs in the sediments of Zhanjiang Bay. Furthermore, studies on the particle size fractionation of sediments can be used to indicate the influence of different adsorbents on pollutant distribution. Coarse components ( $\geq 200 \mu\text{m}$ ) in offshore sediments have been found to contain high concentrations of contaminants, and mainly consist of biomass and anthropogenic debris that could absorb or contain DDT (Amymarie and Gschwend, 2002; Wu et al., 2004). Human debris sources, such as paint flakes, have been shown to be an important contributor to DDT contamination (Wu et al., 2016; Yu et al., 2011b). Fine particles have a larger specific surface area and can easily absorb organic compounds (Amymarie and Gschwend, 2002; Wu et al., 2004). As shown in Tables S2 and S3, the concentrations of DDXs compounds in coarse ( $\geq 200 \mu\text{m}$ ) and fine ( $< 200 \mu\text{m}$ ) fractions were 2.62–79.4 and 0.62–11.6  $\text{ng g}^{-1}$ , respectively, indicating that most of the sediment samples (Fig. S2, excluding site 1 in Zhanjiang Bay) have higher concentrations of DDXs in coarse particles, which are consistent with the results of DDXs in the sediments of Hailing Bay (Wu et al., 2016). Therefore, it can be concluded that DDXs compounds in the sediments of Zhanjiang Bay might have been largely generated by the deposition of DDT-containing paint flakes in the sediment (Wu et al., 2016).

### 3.2. Ecological risk assessment

The ecological risks of DDT in the Zhanjiang Bay sediments were evaluated using the sediment quality guidelines (Long et al., 1995, 1998b) that have been widely used by environmental protection agencies in the USA, Canada, and other countries (Long et al., 2006). These guidelines consist of the effect range-low level (ERL), the effect range-medium level (ERM) (Long et al., 1995), the threshold effect level (TEL), and the probable effect level (PEL) values (CCME). The DDTs concentrations in the Zhanjiang Bay sediments were compared with the sediment quality guidelines to assess the potential ecological risk. As shown in Table 2,  $p,p'$ -DDD had the highest ecotoxicological risk among all the DDT congeners, with 73% and 60% of the sediment samples exceeding the ERL value ( $1 \text{ ng g}^{-1}$ ) and TEL value ( $1.19 \text{ ng g}^{-1}$ ) for  $p,p'$ -DDD, respectively. However, only 6% and 20% of the sediment samples exceeded the ERM value ( $7 \text{ ng g}^{-1}$ ) and PEL value ( $4.77 \text{ ng g}^{-1}$ ) for  $p,p'$ -DDD, respectively. Furthermore, 20% and 40% of the sediment samples exceeded the ERL value ( $2 \text{ ng g}^{-1}$ ) and TEL value ( $1.22 \text{ ng g}^{-1}$ ) for  $p,p'$ -DDD concentrations, respectively, among which 7% exceeded the PEL value ( $7.81 \text{ ng g}^{-1}$ ). Moreover, 13% and 20% of the sediment samples exceeded the ERL value ( $2.2 \text{ ng g}^{-1}$ ) and the TEL value ( $2.07 \text{ ng g}^{-1}$ )

of  $p,p'$ -DDE concentrations, respectively, among which 7% exceeded the PEL value ( $3.74 \text{ ng g}^{-1}$ ). Regarding the total DDTs concentrations, 80% and 67% of the samples exceeded the ERL value and TEL value, respectively, with only one of the sediment samples exceeding the ERM value and none of the samples exceeding the PEL values. These findings indicated that DDT-contaminated sites can occasionally produce adverse biological effects on the biota associated with the studied bay area.

### 3.3. Compositions of DDTs and possible degradation pathways

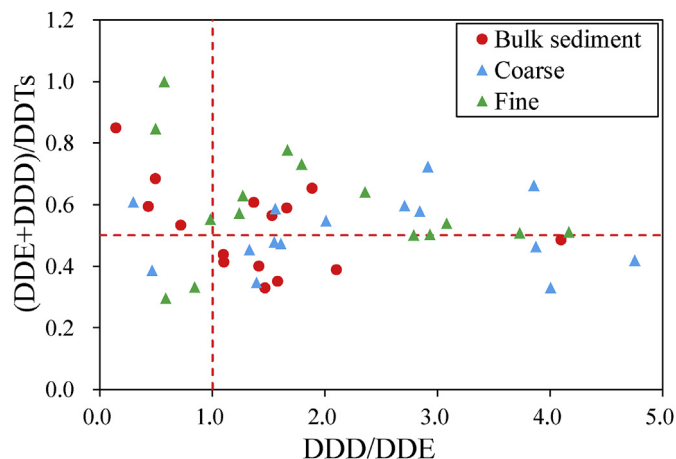
After entering the sediment, the parent DDT can be continuously degraded into metabolites, and the distribution of metabolites is a useful indicator of the input source and degradation pathway. Table S1 shows the concentrations of DDTs and their metabolites in sediments, which mainly included the parent DDT, primary metabolites (DDD and DDE), and high-order metabolites (DDMU, DDNU, DDOH, DDM, DBP). DDT and its primary metabolites, DDD and DDE, were the most prominent components, accounting for 73.2%–98.3% ( $86.1\% \pm 12.8\%$ ) of DDXs. The concentrations of high-order metabolites were 0.12–2.14  $\text{ng g}^{-1}$ , which accounted for 1.75%–26.8% ( $14.0\% \pm 12.8\%$ ) of DDXs. DDMU and DBP were the most prominent high-order metabolites (Table S1). Although the proportions of these metabolites were not too high, previous risk assessment studies have reported that some metabolites, such as DBP, are more toxic than DDT (Megharaj et al., 1999) and should be taken into consideration. Furthermore, some differences can be observed from the relative proportions of DDT and its metabolites in different samples (Fig. 2b). For instance,  $p,p'$ -DBP accounts for 0.4–14% of the total  $p,p'$ -DDXs, with relatively higher contents in sites 1, 2, 3, 6, 8, 10, 13, and 14, whereas relatively higher contents of  $p,p'$ -DDD were detected in sites 4, 5, 7, and 12. It is well known that the transformation process of DDT in aquatic environments are very complex, which may be comprised of various types of reactions and could generate various types of metabolites (Andrews, 1963; Denk and Milutinović, 2018; Denk et al., 2019; Huang et al., 2001; Kallman and Planche et al., 1979; Wedemeyer, 1967). Therefore, these spatial differences in the concentration and components of DDXs may be related to the degradation mode and degradation pathway of DDT as well as the input sources.

It has been widely reported that DDT is likely to be dechlorinated to DDD under an anaerobic condition, whereas it is degraded into DDE in an aerobic setting. Therefore, the ratio of DDD/DDE is a good indicator of whether DDT is degraded under aerobic or anaerobic conditions (Hong et al., 1999; Long et al., 2006). In the present study, the values of DDD/DDE ranged from 0.14 to 4.10 (mean, 1.41) in bulk sediment samples (Fig. 3), and more than 73% of the sediment samples showed values higher than 1. This result is consistent, to some extent, with those reported in other studies on DDT in sediments, such as the surface sediment values for the Palos Verdes Shelf Superfund Site (DDD/DDE,  $1.92 \pm 1.1$ ) and sediments from the fishing harbors (1.1–11.8 (mean 4.5)) (Lin et al., 2009; Taylor et al., 2019). This dominance of DDD over DDE in these

**Table 2**  
Ecological risk of DDTs in bulk sediments from Zhanjiang Bay.

Compounds	Contents / $\text{ng} \cdot \text{g}^{-1}$	ERL / $\text{ng} \cdot \text{g}^{-1}$	ERM / $\text{ng} \cdot \text{g}^{-1}$	Proportion (% , $n = 15$ )			TEL / $\text{ng} \cdot \text{g}^{-1}$	PEL / $\text{ng} \cdot \text{g}^{-1}$	Proportion (% , $n = 15$ )		
				<ERL	ERL ~ ERM	>ERM			<TEL	TEL ~ PEL	>PEL
$p,p'$ -DDD	0.09–18.3	2	20	80	20	0	1.22	7.81	60	33	7
$p,p'$ -DDE	0.20–10.5	2.2	27	87	13	0	2.07	3.74	80	13	7
$p,p'$ -DDT	0.09–13.2	1	7	27	67	6	1.19	4.77	40	40	20
$\Sigma$ DDTs	1.08–49.8	1.58	46.1	20	74	6	3.89	51.7	33	67	0

$\Sigma$ DDTs sum of  $o,p'$ ,  $p,p'$ -DDD, DDE, DDT.



**Fig. 3.** Ratios of DDD/DDE and (DDD + DDE)/DDTs in Zhanjiang Bay sediment. DDD is sum of  $p,p'$ -DDD and  $o,p'$ -DDD; DDE is sum of  $p,p'$ -DDE and  $o,p'$ -DDE; DDTs sum of  $o,p'$ - $p,p'$ -DDT, DDD, DDE.

sediments indicated a reductive dichlorination of DDT to DDD under anaerobic conditions at most of the sampling sites of Zhanjiang Bay. The spatial distribution revealed that the DDD/DDE ratios for sediments collected from sites 1, 11, 13, and 14, were lower than 1. These sites are located in the estuary (site 1) and Donghai island port area (sites 11, 13, and 14), both of which present aerobic conditions. The disturbance of vessels in the Donghai island port area may be one of the reasons for oxygen abundance in this area, while the reason for estuary area being a favorable environment requires further investigation.

In the present study, the most abundant high-order derivatives were  $p,p'$ -DDMU and  $p,p'$ -DBP, which were detected in all the sediment samples from Zhanjiang Bay. It is noted that  $p,p'$ -DDMU can be formed from the reductive dechlorination of  $p,p'$ -DDE or dehydrochlorination of  $p,p'$ -DDD, while  $p,p'$ -DDNU could have transformed from  $p,p'$ -DDE and  $p,p'$ -DDMU (Eggen and Majcherczyk, 2006; Huang et al., 2018; Yu et al., 2011a; Wetterauer et al., 2012). Additionally,  $p,p'$ -DDMU is also an endocrine disruptive chemical and is harmful to the environment and human health (Quensen et al., 1998; Wetterauer et al., 2012). It has been reported that  $p,p'$ -DDOH and  $p,p'$ -DDM could be transformed to  $p,p'$ -DBP or other metabolites (Yu et al., 2011a), and hence could not be detected in some sediment columnar samples (Kucher and Schwarzbauer, 2017; Yu et al., 2011a). The  $p,p'$ -DDM detection rate in Zhanjiang Bay was 79%, while that of  $p,p'$ -DDOH was significantly lower, reaching only 40%.

Based on the findings of previous works and the present study on the surface sediment of the bay (Eggen and Majcherczyk, 2006; Denk and Milutinović, 2018; Huang et al., 2018; Wedemeyer, 1967; Yu et al., 2011a; Wetterauer et al., 2012), the degradation pathways of  $p,p'$ -DDT and its metabolites were proposed as follows: 1)  $p,p'$ -DDT degraded to  $p,p'$ -DDD under anaerobic condition, which was presumably predominant but then transformed to  $p,p'$ -DDE under aerobic conditions; 2)  $p,p'$ -DDD and  $p,p'$ -DDE were further converted to  $p,p'$ -DDMU or  $p,p'$ -DDNU; and 3)  $p,p'$ -DDMU was also further transformed to  $p,p'$ -DDNU, which in turn degraded to  $p,p'$ -DDOH,  $p,p'$ -DDM, and  $p,p'$ -DBP. 4)  $p,p'$ -DDT could directly transform to  $p,p'$ -DBP. To further verify these degradation pathways, a Pearson correlation analysis was used to investigate the relationships between different compounds and provide field evidence for the degradation pathways. As shown in Table S6, a strong correlation was found between  $p,p'$ -DDNU and  $p,p'$ -DDE ( $r = 0.87$ ,  $p < 0.01$ ) and  $p,p'$ -DDD ( $r = 0.86$ ,  $p < 0.01$ ), which suggests that  $p,p'$ -DDNU could

be the metabolite of  $p,p'$ -DDE and  $p,p'$ -DDD. Moreover,  $p,p'$ -DBP was not only significantly correlated with the original  $p,p'$ -DDT ( $r = 0.64$ ,  $p < 0.05$ ),  $p,p'$ -DDD ( $r = 0.73$ ,  $p < 0.01$ ), and  $p,p'$ -DDE ( $r = 0.76$ ,  $p < 0.01$ ), but also presented a significant relationship with high-order metabolites  $p,p'$ -DDNU ( $r = 0.80$ ,  $p < 0.01$ ) and  $p,p'$ -DDMU ( $0.52$ ,  $p < 0.05$ ). These findings may suggest that  $p,p'$ -DBP could be transformed from the original  $p,p'$ -DDT, the primary metabolites ( $p,p'$ -DDD and  $p,p'$ -DDE) and the high-order metabolites ( $p,p'$ -DDNU and  $p,p'$ -DDMU). Therefore,  $p,p'$ -DDT/ $p,p'$ -DDD( $p,p'$ -DDE)/ $p,p'$ -DDMU/ $p,p'$ -DDNU/.../ $p,p'$ -DBP may be the major degradation pathway of DDT in the bay sediment, which is similar to the pathways identified in the Hailing Bay sediment and the reductive condition in surface paddy soil (Yu et al., 2011a; Huang et al., 2018). However, it is noted that the transformation process of DDT in sedimentary environments are very complex, which may be comprised of various types of reactions, and meaning this is only the apparent degradation pathway. Therefore, further research is warranted to determine the transformation process of DDT in specific environments.

#### 3.4. Source diagnostic indices

The primary emission sources of DDXs in the environment include the production and use of technical DDT, pesticides containing DDT, such as dicofol, and boat antifouling paints (He et al., 2015). The source of DDXs can be investigated by their composition (He et al., 2012). It has been reported that the  $o,p'$ -DDT/ $p,p'$ -DDT ratio in technical DDT ranges from 0.2 to 0.3, while that in dicofol is approximately 7, because technical DDT contains 65%–80%  $p,p'$ -DDT and 15%–21%  $o,p'$ -DDT, whereas 1 kg of Chinese dicofol contains 17 g of  $p,p'$ -DDT and 114 g of  $o,p'$ -DDT (Qiu et al., 2004). The  $o,p'$ -DDT/ $p,p'$ -DDT ratio has been used to estimate the relative contributions of the dicofol formulation and technical DDT to DDT contamination (Qiu et al., 2005). In the present study, the  $o,p'$ -DDT/ $p,p'$ -DDT ratio in the bulk sediment of Zhanjiang Bay ranged from 0.14 to 1.31 (Fig. S3), with a geometric mean of 0.66. Furthermore, the  $o,p'$ -DDT/ $p,p'$ -DDT ratio was higher than 0.3 for 80% of the samples, indicating that the recent DDT contaminations are mainly caused by mixed sources of industrial DDT and dicofol. The highest values were mainly determined near the estuary (sites 1, 2, and 3), suggesting higher dicofol contamination in these sites.

The fresh input problem of DDT can be evaluated by the ratio of (DDD + DDE)/DDTs (Hong et al., 1999), with ratios higher than 0.5 indicating historical inputs of parent DDT, whereas ratios less than 0.5 suggest recent inputs of the parent DDT. As shown in Fig. 3, the (DDD + DDE)/DDTs ratio for the samples ranged from 0.33 to 0.85 (mean, 0.53). Approximately 47% of the samples showed a (DDD + DDE)/DDTs ratio lower than 0.5, which indicated that almost half of the sampling sites still had recent DDT inputs. In addition, some recent studies have demonstrated the widespread occurrence of high-order metabolites of DDT in soil and sediments with (DDXs – DDT)/DDXs ratios higher than 0.5, revealing a fresh input of DDT derived from weathered residues (Yu et al., 2011a). In the present study, the (DDXs – DDT)/DDXs ratios were in the range of 0.41–0.89 (mean, 0.59), and only 27% of the samples exhibited (DDXs – DDT)/DDXs ratios lower than 0.5, implying that the DDXs compounds were mainly derived from historical inputs (Fig. S4a). The differences between these two source diagnostic indices suggested that the traditional (DDD + DDE)/DDTs ratio may overestimate the new input of DDT. Notably, the ratios of (DDXs – DDT)/DDXs were lower than 0.5 for 33% of the coarse-sized samples but were higher than 0.5 for 7% of the fine-sized samples (Fig. S4b, c). Thus, it can be concluded that the coarse-sized fractions ( $\geq 200 \mu\text{m}$ ) contained more DDT compounds derived from fresh inputs, whereas the fine-sized fractions ( $< 200 \mu\text{m}$ ) consisted of moderate

amounts of DDT compounds from historical residues. However, this finding does not necessarily implicate historical residues as the main source of DDT, because paint flakes have been observed to present (DDD + DDE)/DDTs or (DDXs - DDT)/DDXs ratios lower than 0.5 (Wu et al., 2016). It must be noted that paint flakes tend to exhibit this ratio for a long period of time and are more likely to be found in coarse particles in some places, especially in sediments near ports or shipyards. Therefore, the prudent application of source diagnostic indices is necessary for nearshore sediment, which may have an antifouling paint input.

### 3.5. DDXs in the porewater of Zhanjiang Bay

Table 1 shows a summary of the concentrations of DDTs and DDXs in the sediment porewater, and Table S5 provides the concentrations of each compound. The concentrations of the DDXs in porewater samples varied from 66.3 to 250 ng L<sup>-1</sup> with a median of 133 ng L<sup>-1</sup>. As shown in Table S5, the concentrations of DDXs in the study area are comparable with those in sediments collected from Hailing Bay, but lower than those in the sediments of the Minjiang River Estuary (467–1794 ng g<sup>-1</sup>) and the Daliao River Estuary (157–830 ng g<sup>-1</sup>) (Tan et al., 2009; Zhang et al., 2003). The major DDXs in porewater samples were DDTs (sum of *o,p'*-, *p,p'*-DDD, DDE, DDT), which accounted for more than 95% in all the porewater samples. Furthermore, *o,p'*-DDD was detected in all the porewater samples, while *p,p'*-DDT was found in 83% of the porewater samples. As shown in Fig. 4, high-order metabolites, such as DDMU, DDNU, DDOH, DDM, and DBP, were also detected in the porewater samples, and the main components were DDMU and DBP. It must be noted that the proportion of high-order metabolites was only approximately 2%–5% in porewater, which was significantly lower than that in bulk sediment (9%–30%). These differences may mainly be because hydrophobic organic compounds are more easily adsorbed on solid materials than water and high-order degradation predominantly occurs on particles. For example, some studies have found that DDXs can bind to solid substances through trapping, van der Waals forces, and covalent bonding (Gevao et al., 2000; Zhu et al., 2019).

The concentrations of DDXs in the porewater samples exhibited a distribution similar to those in the accompanying sediments, indicating a good correlation ( $R^2 = 0.64$ ). As shown in Fig. 4, the

highest concentrations of DDXs were found in the agriculture zone (site 5), as well as in the solid phase of the agriculture zone (Fig. 2a). The lowest relative concentrations of DDXs were detected in porewater samples located in sites 10, 11, and 14, which correlates well with the spatial distribution of sediments in the outlet zone.

It is known that the concentration of DDXs in porewater is controlled by the separation between the solid phase (sediment) and the liquid phase (porewater). In the current study, organic carbon normalized sediment-water distribution coefficients ( $K_{OC}$ ) were calculated and used to indicate the DDXs distribution between the sediment and porewater (the equations are given in the SM). As shown in Table S7, the  $\log K_{OC}$  values of the DDXs compounds were in the range of 6.12–7.4 ( $6.66 \pm 0.38$ ) L·kg<sup>-1</sup> for *p,p'*-DDT, 6.17–7.58 ( $6.80 \pm 0.37$ ) L·kg<sup>-1</sup> for *p,p'*-DDE, 5.68–7.74 ( $6.48 \pm 0.57$ ) L·kg<sup>-1</sup> for *p,p'*-DDD, and 6.53–7.85 ( $7.27 \pm 0.29$ ) L·kg<sup>-1</sup> for *p,p'*-DDMU. Although the  $\log K_{OC}$  values of the four target analytes presented some differences, they were all similar to those calculated for the other areas (Table S7), indicating that the  $K_{OW}$  of each organic compound is the main factor affecting its distribution between the sediment and porewater. The  $\log K_{OC}$  values were obviously different among the 12 sites, with deviation values of 0.38, 0.37, 0.57, and 0.29 for *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDMU, respectively. These variations may be related to the differences in the organic matter composition of sediments obtained at different sites, and further studies are needed to explain the underlying reason.

The movement of higher-order metabolites from sediment to porewater may be affected by other processes, such as adsorption to DOC, and has been often observed as an important transport junction for organic compounds between sediment and the overlying water (Gao et al., 1997; Kan et al., 1994). The concentration of DDXs in porewater is controlled by a variety of factors related to its  $K_{OW}$  and DOC concentration. DOC has frequently been observed as a favorable transport medium and has a good correlation with the concentrations of POPs in porewater (De Bruijn et al., 1989; Kan et al., 1994). As shown in Fig. S5, the concentrations of DDXs in porewater have a positive correlation with the concentration of DOC in porewater, with a correlation coefficient of 0.68 for DDXs. The high value of the DOC concentration often corresponds to a high value of the concentrations of DDXs (Fig. S5). The DDXs content increases as a function of the organic matter content, similar to

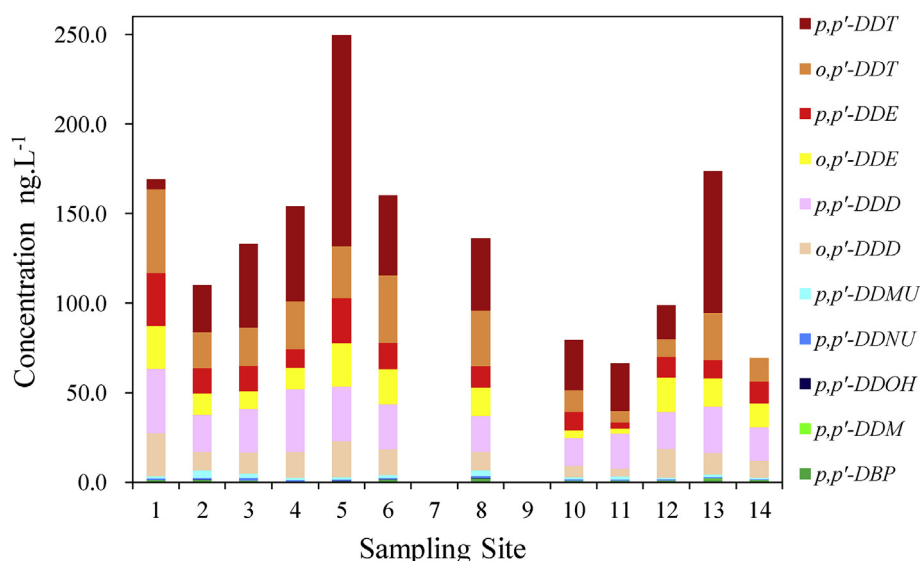


Fig. 4. Spatial distribution of DDXs (ng·L<sup>-1</sup>) and its component in porewater of Zhanjiang Bay.

those observed in other studies, and is defined as a “solubilization effect” (Gao et al., 1997, 1998). Due to the “solubilization effect,” DDXs adsorbed on DOC and/or colloids can easily be dispersed in the aquatic environment. Furthermore, the restricted DDXs may be released into the overlying water again, causing new pollution and increasing their availability to organisms.

#### 4. Conclusions

In this study, the concentrations, distributions, sources, and possible degradation pathways of DDT and its related metabolites in the surface sediment of Zhanjiang Bay in Guangdong, China were investigated. The concentrations of DDXs in sediment and pore-water samples ranged from 1.58 to 51.0 ng g<sup>-1</sup> and from 66.3 to 250 ng L<sup>-1</sup>, respectively. In the sediment, DDT and its primary metabolites, DDD and DDE, were the most prominent components, accounting for 73.2%–98.3% of the DDXs. Additionally, high-order metabolites (DDMU, DDNU, DDOH, DDM, and DBP) were also detected, among which DDMU and DBP were predominant. The concentrations of DDTs were different among the sampling sites, with relatively high DDTs concentrations in the samples collected from the aquaculture zone and areas near the shipping channel and the Haibin shipyard. The health risk assessment suggested that DDT-contaminated sites can occasionally produce adverse biological effects on the biota associated with the studied bay area.

A Pearson correlation analysis and other evidence revealed that the possible degradation pathway of DDT in the Zhanjiang Bay sediment was: *p,p'*-DDT/*p,p'*-DDD(*p,p'*-DDE)/*p,p'*-DDMU/*p,p'*-DDNU/ ... /*p,p'*-DBP. The DDXs in the sediments of Zhanjiang Bay were mainly introduced via mixed sources of industrial DDT and dicofol, including fresh input and historical residue. The concentrations of DDXs in porewater samples varied from 66.3 to 250 ng L<sup>-1</sup> with a median of 133 ng L<sup>-1</sup>, exhibiting a distribution similar to that in the accompanying sediments. The log $K_{OC}$  values were similar to log $K_{OW}$ , indicating that the  $K_{OW}$  of each organic compound is the main factor affecting its distribution between the sediment and porewater. Moreover, other processes, such as adsorption to DOC, were favorable for DDXs dispersion in the aquatic environment.

#### Author statement

Jianzhong Song and Ping'an Peng designed the research, Jianzhong Song and Shiyun Peng, Methodology, Writing - original draft. Deming Kong, Liting Li, and Meiju Li, Sample collection. Shiyun Peng and Chunlin Zou, the extraction and isolation of DDXs. Tao Cao and Chiling Yu, GC-MS analysis. Fajin Chen, Wanglu Jia, and Ping'an Peng, Writing, -Reviewing and Editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.115492>.

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