Persistent organic pollutants (POPs), such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and dichlorodiphenyltrichloroethane (DDT), have been of worldwide concern for several decades due to their persistence, bioaccumulation and toxicity. PBDEs, as an additive brominated flame retardant, have been used in a wide array of commercial and household products, including electronics, plastics, textiles, airplanes, motor vehicles, wire insulation, polyurethane foams, and building materials (Alaee et al., 2003). There are three major PBDE commercial formulations: Penta-, Octa- and Deca-BDE. Penta- and Octa-BDE technical mixtures have been added to the list of new POPs by the Stockholm Convention in May 2009, while Deca-BDE, banned in Europe and America, is still used in Asia (Yue and Li, 2013). PCBs were historically used in a variety of applications as dielectric and coolant fluids, for example in transformers, capacitors, and electric motors (Xing et al., 2005). DDT was extensively used as an insecticide during 1940–1970s, and is still used today to control malaria in some countries (van den Berg, 2009). PCBs and DDT were recognized among the 12 initial POPs under the Stockholm Convention in 2001. The semi-volatility and persistence of these chemicals result in long-range transport by atmospheric exchange, ocean currents and animal migration to some remote areas, such as the Arctic and the Antarctic (Lohmann et al., 2007).

The monitoring for environmental fate, transport and sink of POPs in marine environment is of great importance since oceans play an important role in controlling the global biogeochemistry of POPs. In recent years, several studies on the distribution of POPs in marine ecosystems from temperate and arctic regions have been reported (Braune et al., 2005; Sobek et al., 2010; Wöhrnschimmel et al., 2013). However, few studies have been conducted to investigate the environmental behavior of POPs in tropical marine ecosystems, which are expected to be totally different from those in temperate and frigid marine environments due to the prevailing climate of high temperature and heavy rainfall. Therefore, it is necessary to monitor the environmental behavior of POPs in the tropical sea to get better understanding of their global dynamics.

The South China Sea (SCS), with an area of 3.5 million km² and an average depth of 1200 m, is the third largest marginal sea in the world (Morton and Blackmore, 2001). It is surrounded by several developing countries, including China, Vietnam, Philippines and...
Malaysia, which are considered as a potentially important source of POPs (Li et al., 2012a; Zhang et al., 2007). These countries historically had higher applications of DDT. For instance, the usage volume for DDT in China during 1950–2003, Vietnam during 1957–1990, and Malaysia during 1991–1998 were 45,900, 24,042 and 253,989 tons, respectively (Hu et al., 2007; Ibrahim, 2007; Minh et al., 2008). Meanwhile, this region has become the largest dismantling center of electronic waste (e-waste) in the world, where it has been estimated that approximately 20–50 million metric tons e-wastes are disposed each year, accounting for about 70% of the global production (Zhang et al., 2012). The prevailing e-waste recycling activities may become the major sources of PBDEs and PCBs in the region. The SCS, located at the tropic of cancer, belongs to a low-latitude and tropical deep sea (Morton and Blackmore, 2001). The tropical marine monsoon climate and surface current system with warm water of SCS make it possible to transport POPs to the colder and higher latitude regions, owing to the global distillation effect. Thus, investigation on the behavior, fate and distribution of POPs in SCS is essential to comprehensively understand their global distribution.

In the present study, five marine fish species from the Natuna Island, SCS were collected and analyzed for PBDEs, PCBs, DDT and its metabolites. The primary objectives of this study were to investigate levels and composition profiles of these three classes of POPs, explore the potential sources of POPs, and examine the interspecies differences of POPs in marine fish.

The Natuna Island (4°00′N, 108°15′E), with an area of 1992.8 km², is located in the southwest part of SCS (Fig. 1). It is surrounded by deep seas that border the waters of Vietnam, Malaysia and Indonesia, providing good habitats for a large variety of coral reefs and fish. There are about 100,000 people living on the island and most of local residents depend on fisheries for their livelihood. The Natuna Island now serves as an offshore exploitation base, and is subject to a tropical marine monsoon climate influenced by the southwest monsoon in summer and the northeast monsoon in winter. The annual average temperature is around 26.5 °C, with quite a small temperature difference of 3–4 °C. The rainy season lasts 5–6 months every year, usually from June to November, with an average annual rainfall of 2500 mm.

A total of 27 fish samples, including Brushtooth lizardfish (BL, Saurida undosquamis, n = 6), Russell’s mackerel-scad (RM, Decapetorus russelli, n = 5), Striped fin goatfish (SG, Upeneus bensasi, n = 7), Snakefish (SF, Trachinocephalus myops, n = 5) and Truncatetaille big-eye (TB, Priacanthus macracanthus, n = 4), were collected from the Natuna Island, SCS in April 2013. The specimens were caught using trawling. The samples were kept in the refrigerator and immediately carried back to the laboratory. Fish were cleaned with deionized water and their body length and weight were measured (Table 1). Dorsal muscles were excised from each fish and stored at −20 °C until further analysis.

A homogenized sample of approximately 12 g wet weight muscle tissue was freeze-dried, ground into fine powder, mixed with anhydrous sodium sulfate, spiked with surrogate standards (BDE 77, 181 and 205, 13C12-BDE 209, PCB 30, 65 and 204) and then Soxhlet extracted with 200 mL acetone/hexane (v/v = 1:1) for 48 h. The extract solution was subsequently concentrated to 10 mL by a rotary evaporator and divided into two parts. One aliquot of 1 mL was used for gravimetric determination of lipid content. Another extract used for chemical analysis was purified by a gel permeation chromatographic column packed with 40 g SX-3 Bio-Beads (Bio-Rad Laboratories, Hercules, CA) and eluted with dichloromethane/hexane (v/v = 1:1) for lipid removal. Eluate from 90 to 280 mL containing target compounds was collected and concentrated to 1 mL, further cleaned up on a multilayer column filled with 8 cm neutral silica, 8 cm acidified silica, and 1 cm anhydrous sodium sulfate from bottom to top. The extract was eluted with 30 mL hexane/dichloromethane (v/v = 1:1). The eluate was concentrated to near dryness under a gentle nitrogen flow and reconstituted in 50 μL of isooctane. Known amounts of internal standards (BDE 118 and 128, 4-F-BDE 67, 3-F-BDE 153, PCB 24, 82 and 198) were spiked before instrumental analysis.

BDE 47, 66, 100, 99, 85, 154, and 153 were analyzed by an Agilent 6890 gas chromatograph (GC) connected with an Agilent 5975 mass spectrometer (MS) using electron capture negative ionization (ECNI) in the selective ion-monitoring (SIM) mode. A DB-5XL column (30 m × 0.25 mm × 0.25 μm, J&W Scientific) was used for separation. BDE 209 was quantified by a Shimadzu model 2010 GC coupled with a model QP 2010 MS (Shimadzu, Japan) using ECNI in the SIM mode and separated by a DB-5HT column (15 m × 0.25 mm × 0.10 μm, J&W Scientific). Quantification of PCBs and DDTs was performed with an Agilent 7890 GC equipped with an Agilent 5975 MS using electron impact in the SIM mode. Separation of PCBs and DDTs was performed on a DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm, J&W Scientific). Details on the GC conditions and monitored ions can be found elsewhere (Sun et al., 2012).

Quality assurance and quality control procedures included regular rejection of solvent blanks and standard solutions, and analysis of procedural blanks, spiked blanks and matrices (10 PBDE congeners and 20 PCB congeners). A procedural blank was processed consistently in each batch of the sample analysis. Trace amounts of BDE 100, 154 and 209 were detected in the procedural blanks (n = 3) and were subtracted from the samples. The average recoveries of PBDEs and PCBs in the spiked blanks (n = 3) ranged from 86% to 109% and 89% to 106%, respectively. The mean recoveries of PBDEs and PCBs in the spiked matrices (n = 3) ranged from 75% to 88% and 87% to 114%, respectively. The relative standard deviations (SD) of all targets were less than 16%. The average recoveries of surrogate standards in all samples were as follows: 85.5 ± 5.1% for BDE 77 (mean ± SD), 67.3 ± 3.7% for BDE 181, 61.2 ± 3.7% for BDE 205, 89.0 ± 12.5% for 13C12-BDE 209, 64.1 ± 2.5% for PCB 30, 78.2 ± 10.5% for PCB 65 and 74.6 ± 3.7% for PCB 204. Method detection limit (MDL) was defined as mean value plus three times the standard deviation in the procedural blanks. For the undetected compounds in the procedural blanks, MDL was set as a signal of 5 times the noise level. Based on the mean lipid weight (lw) of the samples, MDLs of PBDEs, PCBs, and DDTs...
Concentrations of PBDEs, PCBs and DDTs in marine fish (ng/g lw) from the Natuna Island, South China Sea.

<table>
<thead>
<tr>
<th>Species</th>
<th>N</th>
<th>Lipid (%)</th>
<th>Body length (cm)</th>
<th>Body weight (g)</th>
<th>PBDEs&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PCBs&lt;sup&gt;c&lt;/sup&gt;</th>
<th>DDTs&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brushtooth lizardfish</td>
<td>6</td>
<td>0.90 ± 0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>18.4 ± 0.63</td>
<td>39.0 ± 2.97</td>
<td>5.55 ± 0.67</td>
<td>26.4 ± 4.12</td>
<td>16.7 ± 2.96</td>
</tr>
<tr>
<td>Russell’s mackerel-scad</td>
<td>5</td>
<td>0.72 ± 0.02</td>
<td>22.5 ± 0.33</td>
<td>107.2 ± 3.40</td>
<td>7.64 ± 2.27</td>
<td>31.9 ± 3.14</td>
<td>24.4 ± 6.21</td>
</tr>
<tr>
<td>Striped fin goatfish</td>
<td>7</td>
<td>1.65 ± 0.28</td>
<td>14.4 ± 0.29</td>
<td>30.5 ± 2.01</td>
<td>2.85 ± 1.16</td>
<td>14.3 ± 3.36</td>
<td>10.8 ± 2.81</td>
</tr>
<tr>
<td>Snakefish</td>
<td>5</td>
<td>0.46 ± 0.11</td>
<td>17.4 ± 1.30</td>
<td>44.4 ± 5.54</td>
<td>7.82 ± 2.02</td>
<td>48.1 ± 6.83</td>
<td>40.3 ± 4.48</td>
</tr>
<tr>
<td>Truncatetail bigeye</td>
<td>4</td>
<td>0.66 ± 0.06</td>
<td>24.8 ± 1.39</td>
<td>172.4 ± 31.9</td>
<td>3.13 ± 0.20</td>
<td>24.9 ± 4.53</td>
<td>7.99 ± 2.06</td>
</tr>
</tbody>
</table>

<sup>a</sup> mean ± SE.
<sup>b</sup> Sum of BDE 47, 66, 85, 99, 100, 153, 154, 209.
<sup>c</sup> Sum of PCB 95, 101, 110, 117, 118, 128, 130, 138, 139, 146, 153, 161, 175, 178, 180, 187, 190, 193.
<sup>d</sup> Sum of p,p′-DDD, o,p′-DDD, p,p′-DDE, o,p′-DDE, p,p′-DDE.

The level of significance was acceptable at \( p < 0.05 \). One-way analysis of variance (ANOVA) accompanied by LSD’s test was used to determine interspecific differences in POPs concentrations of marine fish.

Concentrations of PBDEs, PCBs and DDTs were observed in SF and TB, and relatively low levels of these POPs were found in SFG and BL (Table 1). The differences in POPs concentrations among marine fish can probably be attributed to their different feeding and living habits. SF is carnivorous species mainly feeding on crustaceans, cephalopods and fish, while SFG and TB are omnivorous fish, indicating that SF might occupy a higher trophic level than those of SFG and TB (Zhang and Chen, 2005). Furthermore, SF is a bottom-dwelling species and often inhabits in muddy and/or sandy areas, which may increase its exposure to POPs in the bottom sediment. Relatively higher concentrations of POPs were also found in bottom-feeding marine fish from China and the United States (Morgan and Lohmann, 2010; Xia et al., 2012; Sun et al., 2014).

PCBs constituted the predominant group of POPs in all marine fish, with average contributions of 54%, 53%, 50%, 50% and 70% for BL, RM, SFG, SF and TB, respectively (Fig. 2). DDTs also contributed relatively larger proportions of POPs (average, 21.2–42.2%). The contribution of PBDEs to total POPs was less than 13.3% in all marine fish species. The fractions of PCBs to POPs were significantly greater than those of DDTs for each marine fish (\( p < 0.03 \)). This pattern was similar to those in marine fish from the Gulf of Naples, Southern Italy (Naso et al., 2005), the Mediterranean Sea...
(Storelli et al., 2009), the Aleutian Islands of Alaska, USA (Hardell et al., 2010), and the Norwegian Coast (Bustnes et al., 2012), in which PCB concentrations were significantly higher than those of DDTs, but different from those reported in our previous study for marine fish from Yongxing Island, SCS, in which DDTs were the predominant contaminants (Sun et al., 2014). The predominance of PCBs in marine fish from Europe and North America may probably be attributed to the extensive historical use of PCBs (Jaward et al., 2005).

Generally, marine fish from the Natuna Island had similar PBDE congener distribution patterns (Fig. 3). BDE 47 was the dominant congener and contributed more than 40% to total PBDEs. The ratios of BDE 47 to BDE 99 in marine fish (mean, 2.53) were higher than those in Penta-BDE technical products (1.0 in Bromkal 70-5DE and 0.8 in DE-71). Similarly, the ratios of BDE 100 to BDE 99 in marine fish (mean, 0.77) were also higher compared to those in Penta-BDE commercial products (0.17 in Bromkal 70-5DE and 0.27 in DE-71). These patterns were similar to a previous study on wild marine fish from China (Meng et al., 2008). These discrepancies can be partly explained that BDE 99 was easily debrominated in fish due to the presence of meta-substituted bromine (Roberts et al., 2011). BDE 209 was detected in 70% of the samples and also contributed relatively larger proportions to total PBDEs (mean, 5.7–14.9%), indicating that BDE 209 can be bioaccumulated in marine fish. Deca-BDE technical mixture is currently the highest used brominated flame retardants in countries surrounding the SCS. Therefore, further research on bioaccumulation, biomagnification and biodegradation of BDE 209 in marine biota should be concerned.

PCB 153 was the predominant congener in all marine fish from the Natuna Island, followed by PCB 190, 138, 128, 118 and 117, with minor contributions from PCB 99, 110, 146 and 193 (Fig. 4). PCB 153 contributed 40.2%, 30.7%, 40.9%, 37.6% and 37.9% for BL, RM, SFG, SF and TB, respectively. A substantial accumulation of PCB 153 may indicate extensive use of Aroclor1254. Furthermore, this pattern is probably related to a slow metabolism and elimination of PCB153 in biota due to the presence of unsubstituted adjacent meta-para positions on the phenyl rings (Drouillard et al., 2001).

Different compositional patterns of DDTs were found in five marine fish species from the Natuna Island, SCS (Fig. 5). \( p,p' \)-DDE dominated over other component of DDTs in BL, SFG and SF, and its fractions were 67.3%, 64.7% and 56.9%, respectively. RM and TB contained significantly higher abundances of \( p,p' \)-DDT than those of \( p,p' \)-DDE. If the ratios of (DDE + DDD)/DDTs were higher than 0.5, DDT can be regarded as historical residue instead of fresh input (Yu et al., 2011). As shown in Fig. 6, the ratios of (DDE + DDD)/DDTs in marine fish from the Natuna Island ranged from 0.01 to 1.0, with a mean value of 0.64. In addition, there were 41% samples having values of (DDE + DDD)/DDTs lower than 0.5. These results indicated the presence of new DDT inputs in the neighboring environment of the Natuna Island, SCS. Fresh inputs of DDTs were also reported in fish (Sun et al., 2014), sediments (Chen et al., 2006; Li et al., 2014), air and surface seawater (Zhang et al., 2007) from the northern SCS. The ratios of \( o,p' \)-DDT/\( p,p' \)-DDT in fish samples were less than 1 (except one DT sample, 1.32), suggesting that DDT was unlikely from dicofol.

Fig. 3. PBDEs congener profiles in marine fish from the Natuna Island.

Fig. 4. Distribution of PCBs congener in marine fish from the Natuna Island.

Fig. 5. Fractions of DDT and its metabolites in marine fish from the Natuna Island.


