INTRODUCTION

In Korea, a wide variety of pesticides and chemicals have been used in agricultural and industrial production. Among various chemical contaminants, the issue related to emissions of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and exposure of humans has evoked great public concern. The PCDDs/DFs can be emitted from a number of activities, including industrial processes, municipal and industrial waste incineration, automobile exhaust, and natural events such as forest fires [1–5]. However, monitoring surveys on the extent of PCDDs/DFs contamination in Korea are limited. Thus, a need exists for monitoring environmental distribution and sources of PCDDs/DFs in the Korean environment.

Masan Bay is located in southeastern Korea and is a semi-closed estuary with an average depth of 10 to 20 m and a surface area of 16 km². Approximately 780,000 people reside around the bay, and several industrial complexes, including petrochemical, metal processing, electrical, and plastics manufacturing, are located in this region. Masan Bay was selected as a study area because the cities of Masan and Changwon are moderately urbanized and industrialized areas and because the bay and two cities represent diverse environments from which samples of sediments, soils, fish, shellfish, and air could be collected.

Because of their potential to cause carcinogenic and reproductive effects, PCDDs/DFs have been given priority for study in Korea as well as other countries [6–11]. Because sediments are a reservoir for hydrophobic contaminants like PCDDs/DFs [12–15], assessment of contaminants in sediments of estuaries has been a major research topic for several years. While research has focused on assessing exposure to and toxicity of PCDDs/DFs, little attention has been given to identification of sources in Asian countries like Korea. The objectives of this research were to measure concentrations of PCDDs/DFs in sediments of Masan Bay, to identify sources, and to determine the primary factors affecting concentrations of PCDDs/DFs in sediments.

MATERIALS AND METHODS

Masan Bay was divided into three regions for sampling, encompassing the near coastal area, the continental shelf, and the near open sea (Fig. 1). Sediments were collected from 11 locations in June 1992 using a stainless-steel Eckman dredge. Samples were placed in polyethylene bags and stored at 4°C until analysis. Analytical methods for PCDDs/DFs in sediments have been reported in detail elsewhere [12]. Briefly, sediment samples were air dried in a cool dark place and twigs and pebbles removed. Sediment samples were ground with a mortar and pestle, then sieved through 0.34-mm mesh. Sediments were Soxhlet extracted with 500 ml isopropanol for 24 h followed by 500 ml dichloromethane for 24 h. Known amounts of 13C-labeled PCDDs/DFs were added as internal standards. After Kuderna–Danish concentration, the solvent was transferred to hexane and treated with concentrated sulfuric acid. Before a series of silica gel, alumina, and activated carbon column cleanup, activated copper was used to remove elemental sulfur. A high-resolution gas chromatograph, interfaced with a high-resolution mass spectrometer, was used for...
and then increased at a rate of 20 °C/min to 180 °C, held for 1 min, and then increased at a rate of 2 °C/min to 240 °C. The mass spectrometer was operated under electron impact mode at 70 eV. The PCDD/DF isomers and congeners were determined by selected ion monitoring at the two most intensive ions of the molecular ion cluster. Recoveries of 13C-labeled internal standards ranged from 78 to 86%. Reported concentrations were corrected for the recoveries of internal standard. Identification and quantification of PCDDs/DFs were performed by means of internal and external standards. A fly ash sample containing known compositions of PCDD/DF congeners was used as a reference to identify individual PCDDs/DFs. Procedural blanks were analyzed for every five samples to check for interferences and laboratory contamination. Concentrations of PCDDs/DFs are reported as the sum of all the quantifiable isomers and congeners. Concentrations that were less than the method detection limits were assigned zero when calculating means.

RESULTS AND DISCUSSION

Almost all tetra- through octachlorinated PCDDs/DFs were present in all sediment samples (Table 1). Total concentrations of PCDDs/DFs and 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents in sediments ranged from 102 to 6,493 pg/g dry weight and from 1 to 76 pg/g dry weight, respectively. Although the concentrations varied considerably among the 11 sampling locations, a positive relationship was observed between concentrations of total PCDDs/DFs and concentrations of TEQs. Measured total concentrations of PCDDs/DFs in Masan Bay sediments (102–6,493 pg/g dry wt) were comparable to or slightly less than those found in other industrialized countries. The greatest concentrations observed in sediments of the Rhine and Humber Rivers along the estuarine and coastal North Sea ranged between 1,846 and 10,557 pg/g dry weight [16]. Concentrations of PCDDs/DFs in sediments of the Housatonic River in the United States ranged from 160 to 5,400 pg/g dry weight, except in one sample that contained a concentration of 82,000 pg/g dry weight [17]. Total concentrations of PCDDs/DFs in sediments from the United Kingdom rivers ranged from 446 to 9,310 pg/g dry weight [18] and in Japan ranged from 377 to 15,792 pg/g dry weight [19].

Total concentrations of PCDDs/DFs in sediments and the spatial gradient were used to determine potential point sources in Masan Bay (Fig. 2). Concentrations of PCDDs/DFs were widely distributed even to site 11, which is near the open sea and a productive fishing area. Maximum concentrations were observed in sediments from the most industrialized sampling locations, such as sites 1 and 6, then decreased along a spatial gradient away from the coast and out to the continental shelf. These results indicate that the point sources are in the vicinity of sites 1 and 6 and reflect the importance of urban discharges as sources of PCDDs/DFs to sediments. Previously, concentrations of PCBs at or near sites 1 and 6 have been reported to be greater than the other areas of Masan Bay [13,20]. These areas are urbanized and industrialized with chemical manufacturing, electrical processes, and steel production, all of which could have contributed for PCDDs/DFs. In addition, less flushing due to geographical characteristics, such as a long, narrow inlet, results in localized sedimentation of PCDDs/DFs in Masan Bay.

Different sources of PCDDs/DFs are characterized by different congeners and homologue patterns [21,22]. These differences in patterns can be used to discern possible sources. Although sediments at sites 1 and 6 were high in concentrations of PCDDs/DFs, the patterns of relative concentrations were different (Table 1 and Fig. 3). The total concentration of PCDFs was sevenfold greater than that of PCDDs at site 1, while the concentration of PCDFs was only 0.65 times the total concentration of PCDDs at site 6. The homologue composition of PCDFs was similar between these two locations. Tetrachlorinated dibenzofurans (TeCDFs) contributed the greatest proportions, accounting for 58 and 72% of the total PCDFs found in Kanechlor and PCB preparations such as Kanechls 300, 400, 500, and 600 [25]. These PCB preparations did not contain detectable amounts of PCDDs. The TeCDF homologue represented 58 and 72% of the total PCDFs found in Kanechls 300 and 400, followed in decreasing order by PeCDF, HeCDF, HpCDF, and OCDF. Both TeCDF and PeCDF homologues contributed between 80 and 93% of the total PCDFs.
Table 1. Polychlorinated dibenzo-\(p\)-dioxins and dibenzofurans (PCDDs/DFs) concentrations (pg/g, dry wt) of sediments from Masan Bay, Korea

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>TeCDD(^a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1368</td>
<td>34</td>
<td>22</td>
<td>19</td>
<td>18</td>
<td>44</td>
<td>110</td>
<td>54</td>
<td>8</td>
<td>13</td>
<td>15</td>
<td>9</td>
</tr>
<tr>
<td>1379</td>
<td>16</td>
<td>8</td>
<td>7</td>
<td>8</td>
<td>38</td>
<td>48</td>
<td>30</td>
<td>4</td>
<td>7</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>1378</td>
<td>13</td>
<td>0.3</td>
<td>0.9</td>
<td>0.4</td>
<td>2</td>
<td>6</td>
<td>4</td>
<td>0.6</td>
<td>1</td>
<td>&lt;0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>1247 + 1248 + 1369</td>
<td>35</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>10</td>
<td>8</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>0.9</td>
</tr>
<tr>
<td>1268</td>
<td>12</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>0.6</td>
<td>1</td>
<td>&lt;0.1</td>
<td>4</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.6</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>1478</td>
<td>6</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>4</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>2378</td>
<td>5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>1237</td>
<td>14</td>
<td>&lt;0.1</td>
<td>6.5</td>
<td>1</td>
<td>1.5</td>
<td>3</td>
<td>4</td>
<td>0.5</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1234 + 1246 + 1249 + 1238</td>
<td>24</td>
<td>&lt;0.1</td>
<td>10.5</td>
<td>2</td>
<td>2.5</td>
<td>6</td>
<td>6</td>
<td>1.3</td>
<td>1.4</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1279 + 1236</td>
<td>19</td>
<td>&lt;0.1</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>0.7</td>
<td>0.7</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>1278</td>
<td>4.5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>1469</td>
<td>4.5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
<td>&lt;0.1</td>
<td>0.3</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>1239</td>
<td>5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.7</td>
<td>3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>1269</td>
<td>9</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>1267</td>
<td>5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>1289</td>
<td>3</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Total</td>
<td>209</td>
<td>31.3</td>
<td>45.9</td>
<td>33.3</td>
<td>64.1</td>
<td>203</td>
<td>114</td>
<td>16.9</td>
<td>27.6</td>
<td>26</td>
<td>15.6</td>
</tr>
<tr>
<td>PeCDD(^a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12479 + 12468</td>
<td>72</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>10</td>
<td>40</td>
<td>22</td>
<td>4</td>
<td>8</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>12368</td>
<td>31</td>
<td>&lt;0.1</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>32</td>
<td>14</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>12478</td>
<td>13</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0.3</td>
<td>0.7</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>12379</td>
<td>15</td>
<td>&lt;0.1</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>&lt;0.1</td>
<td>10</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>12469 + 12347</td>
<td>23</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>1</td>
<td>2</td>
<td>11</td>
<td>4</td>
<td>0.6</td>
<td>2</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>12378</td>
<td>7</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.8</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>12369</td>
<td>8</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>4</td>
<td>1</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>12467</td>
<td>13</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.9</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>12489</td>
<td>10</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>2</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>1246 &lt;0.1</td>
<td>20</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>5</td>
<td>3</td>
<td>0.3</td>
<td>0.7</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>12389</td>
<td>6</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>5</td>
<td>3</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td>218</td>
<td>2.1</td>
<td>9.9</td>
<td>17</td>
<td>28.6</td>
<td>109</td>
<td>60</td>
<td>11.3</td>
<td>20.1</td>
<td>21.1</td>
<td>10.8</td>
</tr>
<tr>
<td>HeCDD(^p)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>124679 + 124689 + 123468</td>
<td>57</td>
<td>7</td>
<td>5</td>
<td>9.6</td>
<td>19</td>
<td>78</td>
<td>35</td>
<td>6</td>
<td>16</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>123679 + 123689</td>
<td>37</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>38</td>
<td>16</td>
<td>2</td>
<td>7</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>123478</td>
<td>7</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0.3</td>
<td>1</td>
<td>&lt;0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>123678</td>
<td>9</td>
<td>0.4</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
<td>7</td>
<td>4</td>
<td>0.6</td>
<td>2</td>
<td>2</td>
<td>0.7</td>
</tr>
<tr>
<td>123469</td>
<td>5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.5</td>
<td>5</td>
<td>1</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>123789</td>
<td>10</td>
<td>0.3</td>
<td>0.4</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>12346 &lt;0.1</td>
<td>2</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>1</td>
<td>8</td>
<td>5</td>
<td>0.3</td>
<td>0.7</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Total</td>
<td>127</td>
<td>10.7</td>
<td>6.9</td>
<td>17</td>
<td>30.5</td>
<td>143</td>
<td>62</td>
<td>9.6</td>
<td>27.8</td>
<td>30.7</td>
<td>11.5</td>
</tr>
<tr>
<td>HpCDD(^p)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1234679</td>
<td>33</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>8</td>
<td>115</td>
<td>24</td>
<td>4</td>
<td>29</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>1234678</td>
<td>26</td>
<td>3</td>
<td>1</td>
<td>7</td>
<td>8</td>
<td>73</td>
<td>27</td>
<td>4</td>
<td>20</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Total</td>
<td>59</td>
<td>7</td>
<td>3</td>
<td>13</td>
<td>16</td>
<td>188</td>
<td>51</td>
<td>8</td>
<td>49</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>OCDD(^p)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12346789</td>
<td>207</td>
<td>8</td>
<td>1</td>
<td>7</td>
<td>5</td>
<td>547</td>
<td>96</td>
<td>134</td>
<td>81</td>
<td>23</td>
<td>46</td>
</tr>
<tr>
<td>Total PCDDs</td>
<td>820</td>
<td>59.1</td>
<td>66.7</td>
<td>87.3</td>
<td>144.2</td>
<td>1,190</td>
<td>383</td>
<td>179.8</td>
<td>205.5</td>
<td>135.8</td>
<td>93.9</td>
</tr>
</tbody>
</table>

\(^a\) Concentrations are given in pg/g, dry wt.

\(^p\) Concentrations are given in pg/kg, dry wt.
Table 1. Continued

<table>
<thead>
<tr>
<th>TeCDF³</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1368</td>
<td>102</td>
<td>0.7</td>
<td>1</td>
<td>0.9</td>
<td>3</td>
<td>10</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>1</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>1378 + 1379</td>
<td>84</td>
<td>0.7</td>
<td>0.9</td>
<td>1</td>
<td>4</td>
<td>17</td>
<td>4</td>
<td>0.7</td>
<td>2</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>1347</td>
<td>102</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>2</td>
<td>10</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>0.9</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>1468</td>
<td>127</td>
<td>0.4</td>
<td>0.6</td>
<td>0.7</td>
<td>2</td>
<td>10</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>0.9</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>1247 + 1367</td>
<td>212</td>
<td>0.9</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>22</td>
<td>4</td>
<td>0.7</td>
<td>2</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>1348</td>
<td>91</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>2</td>
<td>8</td>
<td>0.3</td>
<td>0.7</td>
<td>0.4</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>1346</td>
<td>118</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
<td>8.5</td>
<td>2</td>
<td>0.4</td>
<td>1</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>1246 + 1268</td>
<td>181</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>2</td>
<td>8.5</td>
<td>2</td>
<td>0.3</td>
<td>1</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>1237 + 1369 + 1478</td>
<td>257</td>
<td>1.5</td>
<td>1.5</td>
<td>0.8</td>
<td>4</td>
<td>30</td>
<td>2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>1234 + 1678</td>
<td>203</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>2</td>
<td>20</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>1238 + 1467 + 1236</td>
<td>300</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>20</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>1246 + 1279</td>
<td>60</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>20</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>1236 + 1279</td>
<td>135</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>2</td>
<td>10</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>1247</td>
<td>10</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>1</td>
<td>15</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>2347</td>
<td>181</td>
<td>0.4</td>
<td>1</td>
<td>0.6</td>
<td>4</td>
<td>11</td>
<td>3</td>
<td>0.6</td>
<td>2</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>1239</td>
<td>70</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>1</td>
<td>5</td>
<td>0.1</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>1237</td>
<td>53</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>1269</td>
<td>10</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>3</td>
<td>3</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>1237</td>
<td>37</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>3</td>
<td>5</td>
<td>0.1</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>1234 + 1278</td>
<td>116</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>3</td>
<td>8</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>1236 + 1278</td>
<td>175</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>2</td>
<td>5</td>
<td>0.3</td>
<td>1.5</td>
<td>0.4</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>2347</td>
<td>155</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
<td>0.1</td>
<td>3</td>
<td>0.7</td>
<td>2</td>
<td>0.9</td>
</tr>
<tr>
<td>1239</td>
<td>111</td>
<td>0.3</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>2</td>
<td>4</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>0.7</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>1236 + 1279</td>
<td>12</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Total</td>
<td>3,269</td>
<td>13.8</td>
<td>16.8</td>
<td>20.1</td>
<td>69.4</td>
<td>330</td>
<td>65</td>
<td>21.2</td>
<td>31.9</td>
<td>17.1</td>
<td>8.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PeCDF³</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>13468</td>
<td>77</td>
<td>0.5</td>
<td>0.6</td>
<td>0.8</td>
<td>3</td>
<td>9</td>
<td>4</td>
<td>0.4</td>
<td>2</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>12468</td>
<td>82</td>
<td>0.8</td>
<td>11</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>9</td>
<td>4</td>
<td>0.4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>13678</td>
<td>46</td>
<td>0.5</td>
<td>0.5</td>
<td>0.6</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>0.3</td>
<td>1</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>13479</td>
<td>55</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>2.5</td>
<td>11</td>
<td>5</td>
<td>0.5</td>
<td>1.5</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>13478 + 12368</td>
<td>70</td>
<td>0.7</td>
<td>0.7</td>
<td>1.2</td>
<td>3.5</td>
<td>14</td>
<td>4</td>
<td>0.6</td>
<td>1.5</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>12478</td>
<td>65</td>
<td>0.6</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>17</td>
<td>9</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>12479 + 13467</td>
<td>106</td>
<td>0.5</td>
<td>0.6</td>
<td>0.8</td>
<td>3</td>
<td>13</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>12467</td>
<td>99</td>
<td>0.3</td>
<td>0.6</td>
<td>0.8</td>
<td>3</td>
<td>18</td>
<td>4</td>
<td>0.5</td>
<td>2</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>12347</td>
<td>63</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>2</td>
<td>6</td>
<td>1.5</td>
<td>0.3</td>
<td>1</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>14678</td>
<td>63</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>2</td>
<td>6</td>
<td>1.5</td>
<td>0.3</td>
<td>1</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>13469 + 12368</td>
<td>19</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>8</td>
<td>0.7</td>
<td>0.1</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>12348 + 12378</td>
<td>69</td>
<td>0.6</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0.6</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>12346</td>
<td>40</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>1.5</td>
<td>5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>13479</td>
<td>40</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>1.5</td>
<td>5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>12367</td>
<td>48</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>2</td>
<td>8</td>
<td>2</td>
<td>0.3</td>
<td>1</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>12369 + 12678</td>
<td>79</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>8</td>
<td>0.7</td>
<td>0.1</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>12679</td>
<td>30</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>6</td>
<td>2</td>
<td>0.2</td>
<td>1</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>12369</td>
<td>7</td>
<td>0.2</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>1</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>23468</td>
<td>40</td>
<td>0.2</td>
<td>0.3</td>
<td>0.9</td>
<td>3</td>
<td>13</td>
<td>4</td>
<td>0.3</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Table 1. Continued

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>12349</td>
<td>7</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>12489</td>
<td>5</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>23478</td>
<td>70</td>
<td>0.3</td>
<td>0.5</td>
<td>0.9</td>
<td>2</td>
<td>20</td>
<td>4</td>
<td>0.7</td>
<td>0.9</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>12389</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>23467</td>
<td>143</td>
<td>0.2</td>
<td>0.6</td>
<td>0.5</td>
<td>3.7</td>
<td>13</td>
<td>4</td>
<td>0.5</td>
<td>2</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>Total</td>
<td>1,325</td>
<td>8.3</td>
<td>21.2</td>
<td>16.4</td>
<td>49.7</td>
<td>205</td>
<td>62.7</td>
<td>8.6</td>
<td>31.5</td>
<td>20.6</td>
<td>8.3</td>
</tr>
</tbody>
</table>

**HeCDFs**

<table>
<thead>
<tr>
<th></th>
<th>123468</th>
<th>85</th>
<th>0.9</th>
<th>2</th>
<th>3</th>
<th>9</th>
<th>23</th>
<th>6</th>
<th>0.9</th>
<th>4</th>
<th>2</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>134678 + 134679</td>
<td>132</td>
<td>0.6</td>
<td>3</td>
<td>4</td>
<td>11</td>
<td>27</td>
<td>9</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>124678</td>
<td>122</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>11</td>
<td>31</td>
<td>15</td>
<td>2</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>124679</td>
<td>16</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.8</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0.2</td>
<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>123478 + 123479</td>
<td>62</td>
<td>0.6</td>
<td>2</td>
<td>9</td>
<td>10</td>
<td>14</td>
<td>19</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>123678</td>
<td>59</td>
<td>0.6</td>
<td>2</td>
<td>6</td>
<td>11</td>
<td>10</td>
<td>11</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>124689</td>
<td>6</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.8</td>
<td>1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>2</td>
<td>0.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>123467</td>
<td>123</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>37</td>
<td>7</td>
<td>0.8</td>
<td>2</td>
<td>1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>123679</td>
<td>5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.8</td>
<td>12</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>123469 + 123689</td>
<td>16</td>
<td>0.3</td>
<td>0.3</td>
<td>0.6</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>123789</td>
<td>10</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>0.6</td>
<td>1</td>
<td>6</td>
<td>5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>123489</td>
<td>5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.6</td>
<td>2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>234678</td>
<td>66</td>
<td>0.3</td>
<td>0.9</td>
<td>2</td>
<td>5</td>
<td>13</td>
<td>4</td>
<td>0.7</td>
<td>1</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>707</td>
<td>6.6</td>
<td>16.2</td>
<td>37.8</td>
<td>64.4</td>
<td>183</td>
<td>78</td>
<td>11.2</td>
<td>29.2</td>
<td>17.1</td>
<td>16.5</td>
<td></td>
</tr>
</tbody>
</table>

**HpCDFs**

<table>
<thead>
<tr>
<th></th>
<th>123468</th>
<th>300</th>
<th>7</th>
<th>2</th>
<th>9</th>
<th>19</th>
<th>48</th>
<th>36</th>
<th>3</th>
<th>42</th>
<th>33</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>134679</td>
<td>56</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.3</td>
<td>5</td>
<td>2</td>
<td>12</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>2</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>124689</td>
<td>16</td>
<td>7</td>
<td>&lt;0.1</td>
<td>0.9</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>17</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>1234789</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>372</td>
<td>14</td>
<td>2</td>
<td>10.5</td>
<td>27</td>
<td>52</td>
<td>48</td>
<td>3.7</td>
<td>59</td>
<td>42</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

**OCDFs**

<table>
<thead>
<tr>
<th></th>
<th>123468</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
<th>&lt;0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total PCDDs</td>
<td>829</td>
<td>59</td>
<td>67</td>
<td>87</td>
<td>144</td>
<td>1,190</td>
<td>383</td>
<td>180</td>
<td>206</td>
<td>136</td>
<td>95</td>
</tr>
<tr>
<td>Total PCDFs</td>
<td>5,673</td>
<td>43</td>
<td>56</td>
<td>85</td>
<td>211</td>
<td>782</td>
<td>284</td>
<td>45</td>
<td>152</td>
<td>97</td>
<td>51</td>
</tr>
<tr>
<td>Total PCDDs + PCDFs</td>
<td>6,493</td>
<td>102</td>
<td>123</td>
<td>172</td>
<td>355</td>
<td>1,972</td>
<td>667</td>
<td>225</td>
<td>358</td>
<td>233</td>
<td>146</td>
</tr>
<tr>
<td>Quotient PCDFs/PCDDs</td>
<td>6.9</td>
<td>0.7</td>
<td>0.8</td>
<td>1</td>
<td>1.5</td>
<td>0.7</td>
<td>0.7</td>
<td>0.3</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>TEQs</td>
<td>76</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>5</td>
<td>21</td>
<td>9</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

* TeCDD = tetrachlorodibenzo-p-dioxin.
* PeCDD = pentachlorodibenzo-p-dioxin.
* HeCDD = hexachlorodibenzo-p-dioxin.
* HpCDF = heptachlorodibenzo-p-dioxin.
* OCDD = octachlorodibenzo-p-dioxin.
* TeCDF = tetrachlorodibenzofuran.
* PeCDF = pentachlorodibenzofuran.
* HeCDF = hexachlorodibenzofuran.
* HpCDF = heptachlorodibenzofuran.
* OCDF = octachlorodibenzofuran.
* TEQs = toxic equivalency quotients.
in Kanechlors 300 and 400. Greater proportions of TeCDF and PeCDF homologues in sediments at sites 1 and 6 correspond well with those reported for Kanechlors 300 and 400. Furthermore, significant linear correlations existed between PCDF homologue compositions in sediments at sites 1 and 6 and the Kanechlor preparations (Figs. 4 to 6).

The composition of PCDFs in sediments from site 1 was as follows: TeCDF (57.6%), PeCDF (23.4%), HeCDF (12.5%), HpCDF (6.6%), and OCDF (0%). For Kanechlor 300, the homologue composition of PCDFs is as follows: TeCDF (58.2%), PeCDF (21.4%), HeCDF (14.2%), HpCDF (4%), and OCDF (2.3%). A significant correlation was observed between sediment and Kanechlor 300 profiles of PCDFs (Fig. 4; r = 0.99). Similar to that for Kanechlor 300, a significant correlation (r = 0.99) existed between the PCDFs homologue distribution at site 1 sediments and Kanechlor 400 (Fig. 5). The proportion of PCDF homologues in Kanechlor 400 is TeCDF (72.3%), PeCDF (20.9%), HeCDF (5.1%), HpCDF (1.05%), and OCDF (0.77%), respectively. No significant correlation was observed between profiles of PCDFs in sediments from site 1 and those in Kanechlors 500 or 600. Similarly, when relative concentrations of individual isomers from each homologue group of PCDFs in sediments were compared with those in Kanechlores, few isomers were less in sediments than that in Kanechlors 300 and 400. This could be due to selective degradation of certain PCDF congeners in sediments. Despite this, the results suggest that technical PCB mixtures may be one of the possible sources of PCDFs in sediments at site 1. Concentrations of PCBs in sediment near sites 1 and 6 were in the range of 150 to 200 ng/g dry weight [12,13,20]. Although concentrations of PCDDs were greater than those of PCDFs at site 6, the PCDFs homologue pattern in sediments from site 6 was correlated with those in Kanechlor 300 (r = 0.93) (Fig. 6), 400 (r = 0.87), and 500 (r = 0.66). The greater concentrations of PCDFs than of PCDDs and the correlation of the PCDF homologue pattern in sediments with technical PCBs suggest sources originating from technical PCB preparations. Furthermore, the presence of a series of PCDD isomers at both
site 1 and site 6 suggest the occurrence of other sources as well. Among possible sources of PCDDs, thermal processes, such as municipal and chemical waste incineration (including uncontrolled trash burning), hospital waste incineration, and other combustion processes, can result in the production of a range of PCDD isomers [26–28]. Pentachlorophenol production also results in significant releases of OCDD [29]. A wide range of tetra- through octachlorinated PCDD isomers were identified in all samples from Masan Bay, and great concentrations of tetra- through octachlorinated PCDD isomers were identified in the industrial zone of Masan Bay. In addition, uncontrolled incineration of industrial wastes in open areas and the usage of pentachlorophenol preparations have contributed for the PCDDs/DFs and organochlorine pesticides in yellow-blotched map turtle from the Pascagoula River basin, Mississippi, USA. Arch Environ Contam Toxicol 38:362–370.


