Spatial and temporal trends in polychlorinated naphthalenes in sediment from industrialized coastal environments of Korea: Potential sources and ecotoxicological concerns

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Abstract

Few studies have been conducted on spatial and temporal trends in polychlorinated naphthalenes (PCNs) in coastal environments. Here, we describe 18 PCN congeners found in surface and dated sediment samples collected from highly industrialized bays of Korea. Measurable levels of PCN congeners were detected in all sediment samples, suggesting concurrent and historical contamination. The highest PCN concentrations were observed in sediment from rivers, streams, and the inner portions of the bays, which are surrounded by industrial complexes and commercial harbours. CNs 73, 66/67, and 52 were dominant in surface and dated sediment samples. Congener patterns and diagnostic ratios revealed that PCN contamination is originated from combustion processes and the use of polychlorinated biphenyl (PCB) technical mixtures. PCN concentrations in dated sediment increased from the 1980s to the mid 2000s and then decreased to 2015. Although the toxic equivalent (TEQ) levels of PCNs in our study did not exceed sediment quality guidelines proposed by international authorities, the cumulative risks from the TEQ concentrations of polychlorinated dibenzo-p-dioxins, furans, PCBs, and PCNs can be expected for benthic organisms.

Introduction

Polychlorinated naphthalenes (PCNs), which are chlorinated aromatic hydrocarbons with a naphthalene skeleton, comprise 75 congeners from mono- to octa-CN depending on the number and position of the chlorine atoms. Beginning in the 1970s, PCNs were produced for use as flame retardants in electrical devices, waterproofing materials for wood, paper, and textiles (Agunbiade et al., 2020). The representative technical mixtures of PCNs in industrial markets are Halowax, Seekay, Wako-PCN, and Clonacire waxes (Falandysz et al., 2006, 2008, 2014). The global production of PCNs was estimated to be approximately 150,000 to 400,000 tons based on statistical calculations of the consumption of the largest companies (Li et al., 2021). Although production and use of PCNs is now banned worldwide, PCNs have been detected in multiple environmental and biotic samples (Bidleman et al., 2010; Fromme et al., 2015; Liu et al., 2018; Waheed et al., 2020; Pagano & Garner, 2021). Earlier studies reported that the presence of PCNs in environmental compartments is associated with impurities in technical mixtures of PCNs and polychlorinated biphenyls (PCBs) and the combustion processes of waste incinerators and metal plating manufacturing (Wang et al., 2012; Hu et al., 2013; Falandysz et al., 2014; Hu et al., 2021; Shen et al., 2021).

As dioxin-like contaminants that can cause adverse health effects by binding with aryl hydrocarbon (AhR) receptors, toxicities of PCNs are similar to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and PCBs (Falandysz et al., 2014). Laboratory animal studies have found that PCN congeners elicit neurotoxicity, carcinogenicity, genotoxicity, and reproductive and developmental toxicities (Behnisch et al., 2003; Falandysz et al., 2014; Suzuki et al., 2020). Ecotoxicological data on PCNs have been also reported for several species at different trophic levels, including algae, aquatic plants, invertebrates, fish, and birds (Noma et al., 2005; Gu et al., 2021). Based on the greater potential for persistence, bioaccumulation, long-range transport, and health effects, PCNs were listed as persistent organic
pollutants (POPs) under the Stockholm Convention by the United Nations Environmental Programme in 2015 (United Nations Environmental Programme, 2015).

Sediment has been used as an indicator matrix for hydrophobic contamination in coastal environments (Liu et al., 2018; Dat et al., 2019; Lee et al., 2020). Sediment can also serve as a secondary source of organic contaminants to water-borne environments and marine species (Lundgren et al., 2002; Wang et al., 2012; Li et al., 2017). Dated sediment cores have been utilized to assess the depositional history of various organic contaminants in coastal environments (Kannan et al., 2000; Moon et al., 2009; Lee et al., 2018; Shen et al., 2018). Previous studies of dated sediments found that emissions, consumption, and regulatory actions are crucial factors in historical trends of targeted contaminants (Kannan et al., 2000; Moon et al., 2009; Lee et al., 2018; Shen et al., 2018). Although PCNs never produced in Korea, measurable levels of PCNs have been reported in the country’s for air, soil, biota, and human serum (Fromme et al., 2015; Kim et al., 2019; Park et al., 2021). No data are available on PCNs in coastal environments and limited information is available on historical trends for PCNs around the world (Kannan et al., 2000).

Ulsan and Onsan Bays, in the southeastern part of Korea, are surrounded by large industrial complexes and commercial harbors. Rapid industrialized development around the bays beginning in the 1970s resulted in severe contamination by POPs such as PCDD/Fs, PCBs, polybrominated diphenyl ethers (PBDEs) (Moon et al., 2007, 2008a; Lee et al., 2020), and emerging contaminants, such as siloxanes and alternative plasticizers (Lee et al., 2018; Kim et al., 2021). Comprehensive surveys of spatial and temporal distributions of PCNs were conducted in response to this trend. In the present study, surface and dated sediment samples were collected for the determination of 18 PCN congeners to assess the contamination, historical trends, and potential sources using congener-specific analysis. Ecotoxicological assessments were performed using sediment quality guidelines (SQGs) proposed by regulatory agencies.

Materials And Methods

Study area and sample collection

Ulsan and Onsan Bays are surrounded by large industrial complexes devoted to petrochemical production, iron and non-ferrous industries, automobiles, and shipyards (Fig. 1). These “National Industrial Complexes” produce approximately 32% of all commercial and industrial products consumed in the country (Lee et al., 2020). Surface sediment samples were collected from 42 locations in November 2014 using a Van Veen Grab sampler. A dated sediment core was collected in July 2015 from the central part of Ulsan Bay by scuba divers using an acryl tube 80 cm in length with an internal diameter of 11 cm. The collected core was immediately sliced at intervals of 2 to 5 cm using a stainless-steel plate. Surface and sliced core samples were wrapped with aluminum foil washed by a solvent and the samples were then transported to the laboratory.

Experimental procedures
The experimental procedures applied to all sediment samples were based on methods used for PCB and PBDE preparations (Jin et al., 2016; Lee et al., 2020). In brief, sediment samples (~10 g) were extracted using an accelerated solvent extractor (ASE 350, Dionex, Sunnyvale, CA, USA) with a mixture of dichloromethane (DCM; ultra-trace residue grade, J.T. Baker) and hexane (Ultra-trace residue grade, J.T. Baker) after spiking surrogate standards (CBs 103, 198, and 209). Activated copper (pesticide-analysis grade; Sigma-Aldrich) was added to the extracts to remove sulfur and the extracts were then concentrated to 5 mL by TurboVap LV (Biotage, Uppsala, Sweden). Mass-labeled PCN congeners (1 ng each of $^{13}$C$_{10}$-CNs 27, 42, 52, 67, 73, and 75; ECN-5102, Wellington Laboratories, Guelph, ON, Canada) were spiked into the extractor as internal standards, and the purification was conducted using a column of multi-layer silica gel (pesticide analysis grade; Kanto Chemical, Tokyo, Japan) containing H$_2$SO$_4$ and KOH-impregnated silica gels. The cleanup columns were eluted with a mixture of 15% DCM and hexane, and concentrated for instrumental analysis.

**Instrumental analysis**

Previous studies have measured PCN congeners in environmental samples using high-resolution mass spectrometry (HRMS) (Liu et al., 2018; Park et al., 2021). Due to the need for enhanced sensitivity, a gas chromatograph coupled with a tandem mass spectrometer (GC-MS/MS) has been recently introduced to measure PCN concentrations in sediment samples (Li et al., 2016a; Wu et al., 2018). GC-MS/MS analysis can provide more cost-effective and comprehensive monitoring compared with the HRMS. In our study, 18 PCN congeners (CNs 2, 6, 13, 27, 36/28, 46, 48, 50, 52, 53, 54, 63, 64/68, 66/67, 69, 72, 73, and 75; Cambridge Isotope Laboratories, Andover, MA, USA) were measured with a GC-MS/MS (7890GC/7000B, Agilent Technologies, Wilmington, DE, USA). A DB-5MS UI capillary column (60 m length, 0.25 mm inner diameter, 0.25 µm film thickness; J&W Scientific, Palo Alto, CA, USA) was used to separate the congeners. Some congeners, such as CNs 36/28, 64/68, and 66/67, were co-eluted in analytical conditions similar to those described previously (Wu et al., 2018). The oven temperature was programmed to increase from 90°C (1 min) to 160°C at 10°C/min (for 10 min), and then to 300°C (for 2 min). Inlet and ion source temperatures were maintained at 270°C and 330°C, respectively. Helium was used as a carrier gas at a constant flow rate of 1 mL/min. The MS/MS conditions were optimized for accurate quantitation of PCN congeners in the multiple reaction monitoring (MRM) mode. Detailed MS conditions of quantification and confirmation m/z for the MRM mode and retention time of PCN congeners are summarized in Table S1.

**Quality control**

Procedural blanks (n = 10) were processed as real samples after every 10th sample to check for background contamination. Trace levels (0.1 to 0.3 pg/g) of CNs 2, 6, 13, 36/28, 46, and 48 were detected in blank samples, which were subtracted from the measured concentrations in sediment samples. To check for crossover contamination of PCNs during GC-MS/MS analysis, hexane was used before and after the injections every 15 samples. No crossover contamination was observed in our samples. The instrumental limit of quantifications (iLOQs) for the PCN congeners were calculated as 10 times the standard deviation for seven replicate injections of the lowest acceptable PCN concentration (0.1 ng/mL), which ranged from 0.1 to 1.4 pg/g dry weight (wt) for all PCN congeners. Recovery of surrogate
standards spiked into all sediment samples ranged from 88–102% (mean: 95%), 87–103% (mean: 96%), and 84–110% (mean: 99%) for CBs 103, 198, and 209, respectively.

Measurement of sedimentation rate and sediment characteristics

Two radioactive isotopes, $^{210}\text{Pb}$ and $^{226}\text{Ra}$, were measured in sediment core samples to calculate the sedimentation rate using a well-type purity germanium detector. Measurements were taken at the Korea Basic Science Institute in Daejeon, Korea. The sedimentation rate calculated in our study was estimated to be 0.54 cm/year (Lee et al., 2018). Total organic carbon (TOC) and the grain size of sediment samples were measured using an elemental analyzer (Flash 2000 series, Thermo Scientific, MA, USA) and a particle size analyzer (Mastersizer 2000; Malvern Instruments, Malvern, UK), respectively.

Statistical analysis and calculation of TEQ concentrations

Individual PCN congeners detected > 60% of all sediment samples and total PCN concentrations ($\Sigma$PCN; the sum of 18 PCNs detected in sediments) were subjected to statistical analyses. An individual PCN congener level < iLOQ was treated as half the iLOQ for statistical purpose. When calculating the $\Sigma$PCN concentrations, the individual PCN congeners < iLOQ were treated as zero to avoid overestimation of the results. All data revealed the log-normal distributions of PCNs by the Kolmogorov-Smirnoff and Shapiro-Wilk tests and were log-transformed. Independent sample $t$-tests were used to assess significant differences in the sedimentary concentrations of PCNs depending on the sampling locations. Pearson correlation analysis was used to gauge the strength of relationships between the concentrations of PCNs and TOC in sediment. All statistical analyses were performed using SPSS 18.0 with a significance level of $p<0.05$.

To calculate toxic equivalent (TEQ) concentrations of PCNs, the toxic equivalent factors (TEFs) of individual congeners proposed by Falandysz et al. (2014) and commonly utilized for other studies were employed (Park et al., 2021; Pagano & Garner, 2021). TEQ concentrations were calculated by multiplying the actual concentration of individual PCN congener and its corresponding TEF.

Results And Discussion

Occurrence and concentrations of PCNs in surface sediment

Sample characteristics and PCN concentrations in surface sediment samples collected from Ulsan and Onsan Bays and their inflowing streams and rivers are summarized in Table 1. The TOC contents and grain size in all sediment samples ranged from 0.34–6.86% (mean: 1.55%) and 3.23 to 6.6 µm (mean: 12.8 µm), respectively. Sediment from Gosa Stream, which is surrounded by Onsan industrial complexes, had the highest TOC content (mean: 2.82%). This indicates the transport of organic matters from industrial complexes. In contrast, sediment from Taehwa River, which passes through an urbanized
region, had the lowest TOC levels (mean: 0.65%), indicating a limited contribution from household activities to organic contamination.
Table 1
Sediment characteristics and the concentrations of PCN congeners in sediments collected from Ulsan and Onsan Bays and their inflowing streams and rivers, Korea

<table>
<thead>
<tr>
<th>Detection rate (%)</th>
<th>Min–Max</th>
<th>Average ± SD&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TEQ&lt;sup&gt;c&lt;/sup&gt; (Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment characteristics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total organic carbon (%)</td>
<td>0.34–6.86</td>
<td>1.55 ± 1.25</td>
<td></td>
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<tr>
<td>Grain size (µm)</td>
<td>3.23–26.6</td>
<td>12.8 ± 4.78</td>
<td></td>
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<tr>
<td>Polychlorinated naphthalene (PCN) congeners (pg/g dry weight)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN 2</td>
<td>33</td>
<td>&lt;iLOQ–11.6</td>
<td>1.46 ± 2.86</td>
</tr>
<tr>
<td>CN 6</td>
<td>10</td>
<td>&lt;iLOQ–4.43</td>
<td>0.11 ± 0.68</td>
</tr>
<tr>
<td>CN 13</td>
<td>26</td>
<td>&lt;iLOQ–21.2</td>
<td>0.92 ± 3.33</td>
</tr>
<tr>
<td>CN 27</td>
<td>83</td>
<td>&lt;iLOQ–6.15</td>
<td>1.16 ± 1.15</td>
</tr>
<tr>
<td>CN 36/28</td>
<td>100</td>
<td>&lt;iLOQ–8.40</td>
<td>1.16 ± 1.29</td>
</tr>
<tr>
<td>CN 46</td>
<td>88</td>
<td>&lt;iLOQ–15.6</td>
<td>0.91 ± 2.38</td>
</tr>
<tr>
<td>CN 48</td>
<td>36</td>
<td>&lt;iLOQ–14.9</td>
<td>2.16 ± 3.97</td>
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<tr>
<td>CN 50</td>
<td>45</td>
<td>&lt;iLOQ–20.7</td>
<td>2.69 ± 4.93</td>
</tr>
<tr>
<td>CN 52</td>
<td>100</td>
<td>1.02–52.8</td>
<td>7.67 ± 11.8</td>
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<tr>
<td>CN 53</td>
<td>80</td>
<td>&lt;iLOQ–54.4</td>
<td>6.20 ± 9.94</td>
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<tr>
<td>CN 54</td>
<td>38</td>
<td>&lt;iLOQ–19.2</td>
<td>2.46 ± 4.75</td>
</tr>
<tr>
<td>CN 63</td>
<td>64</td>
<td>&lt;iLOQ–15.8</td>
<td>2.11 ± 3.02</td>
</tr>
<tr>
<td>CN 64/68</td>
<td>70</td>
<td>&lt;iLOQ–27.7</td>
<td>5.38 ± 6.88</td>
</tr>
<tr>
<td>CN 66/67</td>
<td>74</td>
<td>&lt;iLOQ–27.9</td>
<td>5.40 ± 6.83</td>
</tr>
<tr>
<td>CN 69</td>
<td>67</td>
<td>&lt;iLOQ–26.6</td>
<td>5.24 ± 6.70</td>
</tr>
<tr>
<td>CN 72</td>
<td>70</td>
<td>&lt;iLOQ–22.0</td>
<td>4.18 ± 5.44</td>
</tr>
</tbody>
</table>

<sup>a</sup>SD = standard deviation.

<sup>b</sup>ΣPCN = sum of 18 PCN congeners detected in sediment samples.

<sup>c</sup>TEQ = toxic equivalent.
Measurable levels of PCNs were detected in all coastal sediment samples, indicating widespread contamination. Despite domestic and global regulations on the production and consumption of technical mixtures of PCNs, the detectable concentrations of PCNs in our samples suggest on-going contamination from industrial complexes. The $\Sigma$PCN and TEQ concentrations in all sediment samples ranged from 1.10 to 405 (mean: 75.4) pg/g dry wt and $4.34 \times 10^{-6}$ to 0.82 (mean: 0.09) pg/g dry wt, respectively. Among 18 PCN congeners, CNs 36/28 and 52 were detected in all sediment samples. CNs 27, 46, 53, 64/68, 66/67, 72, and 73 were also detected in > 70% of the total sediment samples. Penta-CN (CNs 50, 52, 53, and 54) was a dominant homologue group, where mono- to tri-CNs (CNs 2, 6, and 13) were detected in less than 30% of the sediment samples. For all PCN congeners, the highest concentration was observed for CN 73, ranging from < iLOQ to 230 (mean: 17.5) pg/g dry wt. CNs 75 (8.27 ± 15.2 pg/g dry wt) and 52 (7.67 ± 11.8 pg/g dry wt) also showed higher concentrations than other congeners. The congener patterns of PCNs observed in our study were different with those reported for Halowax technical mixtures, which were governed by predominantly mono- and di-CN congeners (Falandysz et al., 2006). This implies that PCN technical mixtures are not primarily consumed in industrial markets of Korea. The predominance of highly chlorinated congeners such as CNs 73 and 75 is likely due to their greater or preferential affinity to sedimentary particles (Moon et al., 2008b; Jin et al., 2016).

Measured PCN concentrations in sediment are compared with those reported for other locations and countries in Table S3. Limited data are available on sedimentary PCNs around the world, and the data from sediment collected after 2010 were only used to avoid the effectiveness of regulatory actions. The $\Sigma$PCN concentrations (1.10–404 pg/g dry wt) measured in our study were similar to those reported from Feitsui Reservoir, Taiwan (12.0–55.0 pg/g dry wt; Dat et al., 2019). However, in other reports from China (10–262,000 pg/g dry wt; Li et al., 2016b; Li et al., 2017; Lei et al., 2022), Pakistan (8,940–414,000 pg/g dry wt; Mahmood et al., 2014), Spain (350–5,000 pg/g dry wt; Ayla-Cabrera et al., 2021), and the US (400–28,500 pg/g dry wt; McGoldrick et al., 2018) the concentrations were one to three orders of magnitude higher those observed in our study.
The concentrations of PCN congeners in all sediment samples were significantly correlated ($r = 0.314–0.999$, $p < 0.05$) with each other (Table S4). This implies similar contamination sources and behavior of PCN congeners in the coastal environments. The concentrations of individual PCN congeners within a homologue group had higher correlation coefficients than those between homologues. This suggests that the environmental behavior of PCNs is dependent on physico-chemical properties. In our study, the highest correlation coefficients were found among hexa-CN congeners, such as CNs 63, 64/68, 66/67, 69, and 72 ($r = 0.909–0.999$, $p < 0.001$), following by penta-CN congeners, such as 52 and 54 ($r = 0.935$, $p < 0.001$). Less chlorinated CN congeners, such as CN 27, 36/28, and 48, had relatively lower correlation coefficients ($r = 0.477–0.615$, $p < 0.01$). A significant correlation was found between PCN concentration and TOC content ($r = 0.446$, $p < 0.001$) or grain size ($r = 0.406$, $p < 0.01$). This is likely due to increasing hydrophobicity and affinity, expressed as an organic carbon-water partitioning coefficient, with chlorination of PCNs. Our findings suggest that chemical properties and sediment characteristics are confounding factors for the sedimentary distribution of PCNs in coastal environments. Similar results were observed for the relationships between other hydrophobic contaminants in sediment (Moon et al., 2008b; Lee et al., 2018; Lee et al., 2020; Kim et al., 2021).

**Spatial distribution of PCNs in sedimentary environment**

Spatial distributions of $\Sigma$PCN and $\Sigma$TEQ concentrations in sediments from Ulsan and Onsan Bays and their inflowing streams and rivers are presented in Fig. 2. The overall concentrations of $\Sigma$PCN and $\Sigma$TEQ in sediments gradually decreased from the inner portions of the bays, rivers, and streams to the outer coastal regions. This suggests that the PCNs originate in industrial complexes. The highest concentrations of $\Sigma$PCN (mean ± standard deviation; $239 \pm 89.0$ pg/g dry wt) and $\Sigma$TEQ ($0.22 \pm 0.08$ pg/g dry wt) were observed in sediment from Woihwang River, which is surrounded by iron and non-ferrous industries (Kim et al., 2021). Our findings suggest that these industries are potential sources of PCN contamination of coastal environments. Previous studies reported that copper smelting and steel industries are major sources of PCNs contamination (Shen et al., 2021; Lin et al., 2022). Similarly, sediment from Gosa Stream had higher $\Sigma$PCN and $\Sigma$TEQ concentrations, ranging from $196 \pm 178$ pg/g dry wt and $0.29 \pm 0.33$ pg/g dry wt, respectively. Gosa Stream is surrounded by automobile and petrochemical industrial complexes, which are potential sources of PCN contamination. Our previous studies reported severe contamination by siloxanes and plasticizers in sediment from Gosa Stream (Lee et al., 2018; Kim et al., 2021), indicating the consumption of various types of chemicals used in industrial complexes. Automobile and petrochemical industries could be consuming different types of chemicals during the manufacturing processes. However, sediment from Taehwa River had the lowest level of PCN contamination, ranging from $12.6 \pm 11.4$ pg/g dry wt and $0.01 \pm 0.01$ pg/g dry wt for $\Sigma$PCN and $\Sigma$TEQ, respectively. This suggests that PCN contamination is not a result of household activities but industrial activities. Similar results were found for other organic contaminants (Lee et al., 2018; Lee et al., 2020; Kim et al., 2021).

In our study, the concentrations of $\Sigma$PCN and $\Sigma$TEQ in sediment were significantly ($p = 0.003$) higher in Onsan Bay ($72.3 \pm 48.4$ pg/g dry wt and $0.09 \pm 0.05$ pg/g dry wt, respectively) compared with those in
Ulsan Bay (31.4 ± 39.2 pg/g dry wt and 0.04 ± 0.04 pg/g dry wt for ΣPCN and ΣTEQ, respectively). This finding can be explained by two factors. One is limited seawater circulation in Onsan Bay compared with Ulsan Bay (Lee et al., 2020; Kim et al., 2021). The other is the higher burden of PCN contamination from industrial complexes near Onsan Bay through Woihwang River, which was characterized by the highest level of PCN contamination in our study. Iron and non-ferrous industrial complexes could contribute to PCN contamination more than other types of industry. Iron and copper-making processes are the primary sources of PCNs in the environment (Shen et al., 2021; Lin et al., 2022). The PCN concentrations in sediment from the inner part of Ulsan Bay (U1–U11; 49.4 ± 47.9 pg/g dry wt and 0.05 ± 0.05 pg/g dry wt for ΣPCN and ΣTEQ, respectively) were significantly (p = 0.01) higher than those in the outer part of the bay (U12–U18; 11.0 ± 8.80 pg/g dry wt and 0.01 ± 0.01 pg/g dry wt for ΣPCN and ΣTEQ, respectively). A clear decreasing trend in ΣPCN and ΣTEQ concentrations was observed for sediment from Onsan Bay. The contamination patterns of PCNs found in our study were consistent with those reported for other organic contaminants, such as ame retardants and plasticizers (Lee et al., 2020; Kim et al., 2021). Collectively, these findings indicate that source proximity is a crucial factor in the spatial distribution of PCNs in coastal environments.

Compositional profiles and source tracking of PCNs

The congener profiles of PCNs in sediment from Ulsan and Onsan Bays and their inflowing streams and rivers are shown in Fig. 3. For actual PCN concentrations, the predominant congeners in all sediment samples were CNs 73 and 52, which accounted for 27% and 22% of ΣPCN concentrations, respectively. The next most highly contributed congeners were CNs 27, 66/67, 64/68, 69, and 36/28, collectively accounting for 38% of ΣPCN concentrations. Previous studies reported that CNs 73 and 52/60 were predominant in sediment from industrialized areas (Castells et al., 2008; Zhao et al., 2011), which is consistent with our findings. For homologue patterns, penta- and hexa-CN were major groups for ΣPCN concentrations, unlike those reported for PCN technical mixtures, such as Halowax (e.g., Halowax 1000) (Falandysz et al., 2006; 2008). This suggests that the PCN contamination found in our study can be associated with industrial activities. The predominance of highly chlorinated congeners of PCNs in sediments found in our study may be due to higher hydrophobicity, which results in fewer chlorinated PCN homologues being detected in sediment (Lin et al., 2022). For TEQ concentrations, CN 73 accounted for 57% of ΣTEQ concentrations, followed by CN 66/67 (mean: 19%). The concentrations and TEFs of these congeners appear to be higher than those for other congeners. Similar sediment profiles of TEQs for PCNs were reported by earlier studies (Dat et al., 2019; Lei et al., 2022).

Diagnostic ratios of selective PCN congeners have been employed to identify sources in the environment (Lee et al., 2007; Wang et al., 2012; Dat et al., 2019). In general, the major sources of PCNs are thermal-related emissions and the use of technical mixtures of PCNs and PCBs (Falandysz et al., 2008; Huang et al., 2015). The concentration ratios for CN 66/67 and 71/72 of > 2.5 and < 2.5, respectively, indicate thermal-related emissions and the use of technical mixtures of PCBs or PCNs (Dat et al., 2019). Lee et al. (2007) reported the major PCN congeners were CNs 13, 27, 36, 50, 52, 54, 66, 67, and 73, which are associated with thermal-related emissions. The concentration ratio of the sum of thermal-emission
related congeners and \( \Sigma \)PCN was therefore used to identify the contamination sources: > 0.5 for thermal-related emissions and < 0.11 for the use of technical mixtures, respectively (Lee et al., 2007). In this study, almost all sediment samples included a concentration ratio for CN 66/67 and 71/72 of < 2.5. This indicates that the sedimentary PCNs originated with the use of technical mixtures of PCBs or PCNs (Figure S1). For the concentration ratio of CN 66/67 and 71/72, only sediment from U2 (Ulsan Bay) near Ulsan Harbor exceeded 2.5, suggesting thermal-emission related sources. Moon et al. (2008a) reported severe contamination by dioxin-like PCBs in Ulsan and Onsan Bays. Because PCNs have never been produced and consumed in Korea (Park et al., 2021), this suggests that sedimentary PCN contamination originated with the use of technical mixtures of PCBs as impurities. However, the concentration ratio of sum of thermal-related congeners and \( \Sigma \)PCN exceeded 0.5 for half (23 of 42) of the sediment samples. Moreover, all of the remaining sediment samples also exceeded 0.3, with no samples reaching 0.11. Our findings suggest that PCN contamination is a result of combustion processes at industrial complexes. As shown by diagnostic ratios, the sediment samples investigated in our study were contaminated by PCNs produced by a combination of thermal-related emissions and the use of technical mixtures of PCBs.

**Historical trends of PCNs in dated sediment**

PCNs were detected in all dated sediment samples collected from Ulsan Bay, indicating longer-term contamination by PCNs. The concentrations of \( \Sigma \)PCN and \( \Sigma \)TEQ in all dated sediments ranged from 5.07 to 221 (mean: 62.8) pg/g dry wt and 0.002 to 0.27 (mean: 0.06) pg/g dry wt, respectively. CNs 28/36, 52, 13, 46, and 73 were detected in > 90% of all sediment core samples. CNs 6, 27, 63, 64/68, 66/67, 69, 72, and 73 were detected in > 50% of all sediment cores. Historical trends in actual and TEQ concentrations of PCNs in dated sediment samples are shown in Fig. 4. The actual and TEQ concentrations of PCNs increased from the 1980s to the mid 2000s. The onset of PCN contamination was consistent with the industrialization of Ulsan region, which was designated as a “National Industrial Complexes” in the 1970s (Moon et al., 2007, 2008a). Our findings suggest that local industrialization is a major contributor of PCN contamination in coastal environments. The concentrations of PCNs during the last decade (2006–2015) are decreasing, but TOC contents has increased over time, suggesting that organic matter recently released into the bay does not contain higher levels of PCNs compared to those in previous years. Our previous studies reported continuous contamination trends in siloxanes and plasticizers in dated sediment from Ulsan Bay (Lee et al., 2018; Kim et al., 2021), which differs from the result of this study, possibly due to different sources, behaviors, and the history of regulations governing contaminants.

**Sedimentary ecotoxicological concerns for TEQ concentrations**

SQGs have been developed to assess potential health risks of aquatic organisms exposed to dioxin-like contaminants. The Canadian Council of Ministers of the Environment has proposed interim SQGs (ISQGs; 0.85 pg TEQ/g dry wt) and probable effect levels (PELs; 21.5 pg TEQ/g dry wt) (Zhao et al., 2011; Canadian Council of Ministers of the Environment, 2014; Walker et al., 2015). In our study, \( \Sigma \)TEQ concentrations of PCNs (0.09 ± 0.16 pg TEQ/g dry wt) in all sediment samples were below the ISQGs and
PELs. Only a sediment sample collected from Gosa Stream (G2; 0.82 pg TEQ/g dry wt) had a concentration approaching the ISQG. A previous study reported that ΣTEQ concentrations of PCDD/Fs and dioxin-like PCBs in Ulsan Bay sediments were 3.01 ± 0.95 pg TEQ/g dry wt and 5.40 ± 8.11 pg TEQ/g dry wt, respectively (Moon et al., 2008a). Considering the cumulative risks posed by dioxin-like contaminants, ΣTEQ concentrations derived from dioxins, dioxin-like PCBs, and PCNs in all Ulsan Bay sediments could exceed the ISQGs, implying adverse health risks for aquatic species. Our findings suggest the need for a comprehensive survey of the ecological risks associated with a variety of organic contaminants in the bays surveyed (Lee et al., 2018; Lee et al., 2020; Kim et al., 2021).

Conclusions

PCNs were measured in surface and dated sediment samples from highly industrialized bays, streams, and rivers in Korea. All sediment samples showed measurable levels of PCNs, indicating continuous and long-term contamination. The highest PCN concentrations were observed in sediments close to both iron and non-ferrous industries. Congener patterns and diagnostic ratios suggest dual contamination sources; thermal-related emissions and the use of PCB technical mixtures. Time trends in PCN concentrations showed increases from the 1980s to the mid 2000s and declining levels for the last decade. The vertical distributions of PCNs were governed by the industrial history and TOC contents. Considering the simultaneous exposure by dioxin-like contaminants, a comprehensive ecological survey is required to protect the health of species inhabiting coastal environments.

Declarations

Authors contribution HL contributed to methodology, analysis, and writing-original draft. SL contributed to sample collection, analysis, methodology, and writing-review. ML contributed to project administration and funding acquisition. HM contributed to supervision, project administration, funding acquisition, and writing-reviewing and editing.

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Data availability All data generated or analyzed during the research conducted in this study are included in this article.

Conflict of interests The authors have no competing interests to declare that are relevant to the content of this article.

Ethical approval Not applicable in this article.

Consent to participate Not applicable in this article.
References


Figures
Figure 1. Sampling locations of sediment collected from Ulsan and Onsan Bays and their inflowing rivers and streams, Korea. T, G, U, W, and O indicate the sampling locations from Taehwa River, Gosa Stream, Ulsan Bay, Woihwang Stream, and Onsan Bay, respectively. A red circle (●) represents the sampling location for core sediment.

Figure 1

See image above for figure legend

Figure 2
Spatial distribution of (a) actual and (b) TEQ concentrations of PCNs in sediment collected from Ulsan and Onsan Bays and their inflowing rivers and streams, Korea.

Figure 3

Compositional profiles of PCN congeners for actual and TEQ concentrations in (a) surface sediment and (b) dated sediment from Ulsan and Onsan Bays and their inflowing rivers and streams, Korea. The
contribution of individual congeners was normalized to actual and TEQ concentrations of PCNs. Vertical bars represent the standard deviation.

**Figure 4**

Historical trends of (a) actual and (b) TEQ concentrations of PCNs and total organic carbon (TOC) in sediment core samples from Ulsan Bay, Korea.

**Supplementary Files**
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- Supplementarymaterials20220601.docx