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Instrumental and bioanalytical characterization of dioxin-like activity in sediments from the Yeongsan River and the Nakdong River estuaries, South Korea

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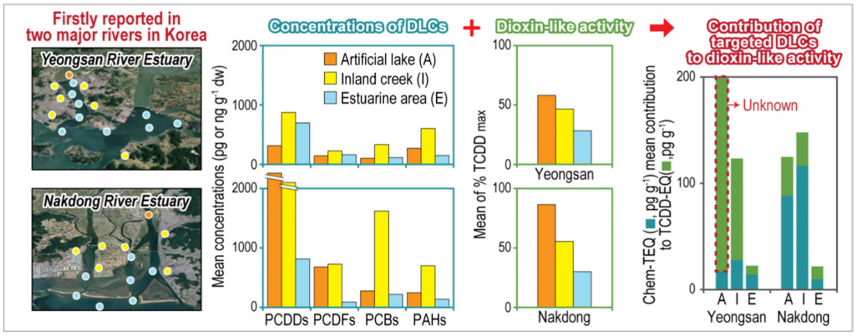
HIGHLIGHTS

- Contamination of PCDD/Fs, co-PCBs, and PAHs in sediments was investigated.
- PCA and PMF were used to identify the sources of PCDDs and PAHs, respectively.
- Contributions of the targeted dioxin-like chemicals in sediments were site-specific.
- 2,3,4,7,8-PeCDF was the major AhR agonist in sediments of the study areas.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, we investigated the contamination status of dioxin-like chemicals (DLCs) and potential toxic effects associated with river and coastal sediments from two large estuaries of South Korea. Sediments collected from the Yeongsan River and the Nakdong River estuaries were analyzed for several DLCs, including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), coplanar polychlorinated biphenyls (co-PCBs), and polycyclic aromatic hydrocarbons (PAHs). Greater concentrations of target DLCs (except for PCDDs in Nakdong River) were found in the inland creeks with decreasing trends towards estuarine and coastal areas in both regions. The result indicated that the elevated DLCs were attributable to the surrounding land use activities, such as point sources of industrial and municipal areas from the inland regions. Principal component analysis and positive matrix factorization model revealed that major sources of PCDD/Fs and PAHs in sediments were fly ash and dust, and petroleum and diesel emission, respectively. The dioxin-like activities of the sediments ranged from 0.98 to 88% of the maximal induction elicited by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, which generally explained the sedimentary contamination by the target DLCs. Dioxin-like activity in sediments from the artificial lake and inland creek of the Nakdong River Estuary was mostly explained by the targeted DLCs (~75%). However, the contribution of known DLCs from the sediments of the Yeongsan River Estuary was relatively low (~35%) compared to that of the Nakdong River Estuary, suggesting the presence of unknown DLCs in sediments. Overall, the distribution of DLCs quite varied by region, generally reflecting the difference in the surrounding land use activity. In the future, it is needed to study the distribution, sources, and potential ecological effects of unknown toxic substances in coastal sediments.

1. Introduction

A myriad of persistent toxic substances (PTSs) is introduced into an estuary as a transitional system via various pathways, including domestic

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sewage effluents, industrial wastewater, rivers, and atmospheric inputs (Baumard et al., 1998; Choi et al., 2011). Due to the hydrophobicity and persistence of PTSs, they ultimately accumulate in sediments of estuaries. The contamination of PTSs in sediments in rivers and estuaries may pose harmful effects on aquatic organisms and humans (Moore et al., 2002; Zeng and Venkatesan, 1999). Thus, sediment is considered as a suitable environmental matrix in monitoring programs assessing the coastal ecosystem health (Kelly et al., 2007; Skotvold and Savinov, 2003; Verta et al., 2007).

Bioassays are widely used to assess potential adverse effects of sediments, such as genotoxicity, mutagenicity, estrogenicity, aryl hydrocarbon receptor (AhR)-mediated activity, etc., because they can evaluate the overall potential toxic effects of chemicals in sediments (Hilscherova et al., 2000). The representative mechanism of toxicity for some PTSs, including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs), is dioxin-like activity (Hilscherova et al., 2000; Lee et al., 2017a, 2020; Takigami et al., 2005; Xia et al., 2014; Zhang et al., 2017). Dioxin-like chemicals (DLCs) induce a variety of toxic effects such as lethality, carcinogenesis, and tumor promotion by activating AhR (Giesy et al., 2002; Mitchell and Elferink, 2009). AhR is mainly activated by endogenous physiological ligands and is also activated by the environmental ligands of contaminants (Quintana, 2013). Thus, AhR-mediated potencies as dioxin-like responses are generally used to assess the exposure of DLCs in environmental mixture samples, such as sediments.

The Yeongsan and Nakdong rivers are two major rivers and are representative of an artificially manipulated estuary located southwestern and southeast of South Korea, respectively (Hong et al., 2013). The Yeongsan and the Nakdong watershed include large cities, such as Mokpo City and Busan City, respectively, and huge industrial complexes have been developed (Hong et al., 2013). These include chemical and textile facilities for plastics and rubber resin, and oil refining. The pollution of these two estuaries has been a long concern because of various effluents discharged from nearby cities, industrial, and municipal areas (Hong et al., 2013). Several studies continue to report that various DLCs are present in sediments from these regions and point out that potential toxicity might exist (Choi et al., 1999; Jeong et al., 2001; Lam et al., 2014). Despite the pollution by various contaminants of both rivers, the ecotoxicological potential of sediments from two estuaries and which substances contributed to the toxicity have not been investigated.

The research hypothesis is that contamination levels of DLCs and potential toxic effects of sediments in the Yeongsan and Nakdong River estuaries are associated with the surrounding land use activity. The objectives of the present study were to investigate the contamination status, sources, and potential dioxin-like activities of PCDD/Fs, co-PCBs, and PAHs in sediments from Yeongsan and Nakdong River estuaries. Total dioxin-like activities of sediments were measured using H4IIE-*luc* in vitro bioassay. In addition, the contribution of target DLCs to the total induced dioxin-like activity of sediments was estimated. We attempted a more detailed sediment pollution assessment using complementary instrumental and bioanalytical tools in this study.

2. Materials and methods

2.1. Sample collection and sample preparation

Surface sediments were collected from the artificial lakes ($n = 2$), inland creeks ($n = 12$), and estuarine area ($n = 16$) of Yeongsan River and Nakdong River estuaries in 2011 (Fig. 1). Detailed information for sampling sites is provided in Table 1. Sediment samples were transferred to pre-cleaned glass jars and were stored at −20 °C until freeze-drying. Detailed methods on sample extraction, clean-up, instrumental analysis, and bioassays are available in previous studies (Khim et al., 1999; Koh et al., 2004). In brief, 20 g freeze-dried sediments were extracted with 350 mL 1:1 hexane/dichloromethane (OmniSolv grade, EMD Chemicals Gibbstown, NJ) using a Soxhlet extractor for 16 h. After extraction, interfering substances, such as sulfur, present in the sediment extracts were removed using activated copper (Merck, Darmstadt, Germany). The organic extracts of sediments were concentrated and divided into three aliquots for use in bioassay, PCDD/Fs and co-PCBs analysis, and PAHs analysis. For PCDD/Fs and co-PCBs analyses, extracts were cleaned up using a multi-layer column chromatography packed with 4 g of silica gel (70–230 mesh; Sigma-Aldrich, Saint Louis, MO) and 2 g of silica gel impregnated with sulfuric acid (60% w/w). Samples were eluted with 150 mL hexane. For PAHs analysis, the organic extracts were cleaned up using silica gel column chromatography (8 g, activated). PAHs fraction was collected using 60 mL 20% dichloromethane in hexane. The sediment organic extracts for bioassay were substituted with dimethyl sulfoxide (DMSO, Burdick & Jackson, Muskegon, MI).

2.2. Instrumental analyses

Analyses of targeted DLCs in sediments were performed by the methods described elsewhere (United States Environmental Protection Agency (US EPA), 1994; Khim et al., 1999; Naile et al., 2011; Hong et al., 2014). Information on targeted compounds of 7 PCDDs, 10 PCDFs, 12 co-PCBs, and 16 PAHs are presented in Tables S1–S4. The concentrations of PCDD/Fs and co-PCBs were measured using high-resolution gas chromatography (HRGC, Hewlett-Packard 5890 series, Palo Alto, CA) coupled with a high-resolution mass spectrometer (HRMS, Micromass, Beverly, MD). Separation for PCDD/Fs and co-PCBs was performed using a DB-5MS column (60 m long, 0.25 mm i.d., 0.1 μm film thickness, Agilent, Palo Alto, CA). The 16 PAHs in the sediments were quantified using a GC-mass selective detector (Agilent 5975, Agilent Technologies). Method detection limits (MDL) for individual PCDD/Fs, co-PCBs, and PAH chemicals were 0.1–0.2 pg g^{-1}

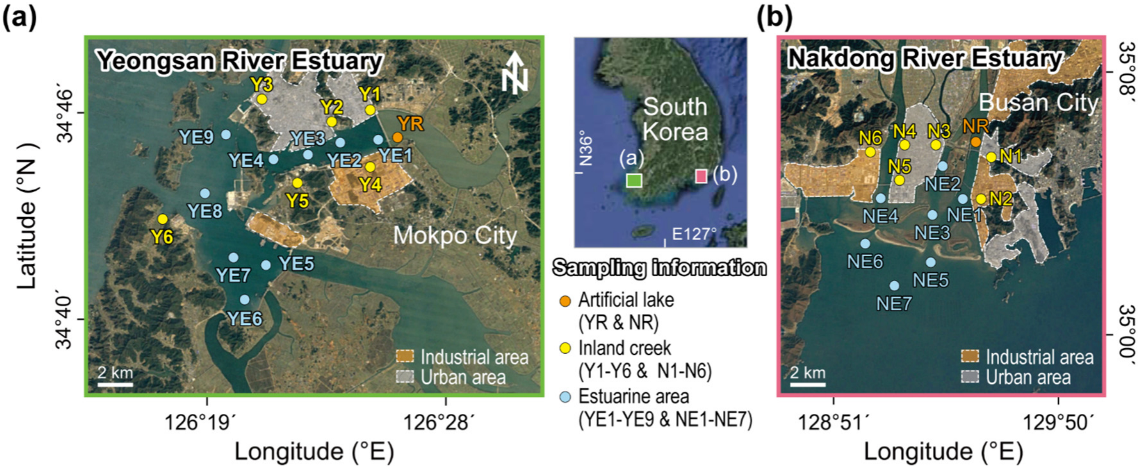

Fig. 1. Sampling sites of surface sediments from (a) Yeongsan River Estuary and (b) Nakdong River Estuary, South Korea.

Table 1
Description of sampling sites and summary of results for H4IIE-*luc* bioassay and instrumental analyses of sediments collected from the Yeongsan and Nakdong River estuaries, South Korea.

Sampling Region	Site	Sample type	Salinity (psu)	Organic carbon contents (%)	% $TCDD_{max}$	$TCDD\text{-}EQ_{bio}$ (pg g^{-1} dw)	TEQ_{chem} (pg g^{-1} dw)				Contribution (%)
							TEQ_{PCDDs}	TEQ_{PCDFs}	$TEQ_{Co\text{-}PCBs}$	TEQ_{PAHs}	
Yeongsan River											
Artificial lake	YR	Mud	0.52	1.6	87	200	2.4	12	0.21	2.4	8.6
Inland creeks	Y1	Mud	0.24	2.2	60	280	1.4	6.9	0.34	3.5	4.3
	Y2	Mud	0.42	4.3	46	170	15	14	0.11	6.8	21
	Y3	Mud	8.0	2.1	52	23	3.1	12	0.15	0.36	65
	Y4	Mud	0.0	1.5	48	55	7.7	29	1.8	5.6	81
	Y5	Mud	0.40	2.6	41	68	18	27	0.87	0.54	68
	Y6	Mud	1.8	2.0	88	140	2.2	8.4	0.14	0.81	8.1
Estuarine area	YE1	Mud	30	1.0	45	30	3.8	4.5	0.23	1.6	34
	YE2	Mud	31	1.2	38	22	3.5	4.6	0.28	1.3	44
	YE3	Mud	32	1.1	31	25	4.5	11	0.28	2.0	70
	YE4	Mud	33	0.93	2.0	9.1	2.7	4.8	0.21	1.4	100
	YE5	Mud	32	1.1	33	14	5.5	7.0	0.17	1.8	103
	YE6	Mud	32	0.43	1.0	2.0	0.41	0.7	0.07	0.24	70
	YE7	Mud	33	0.94	36	23	6.4	9.6	0.08	1.7	77
	YE8	Mud	32	0.90	46	43	11	14	0.08	1.7	60
	YE9	Mud	32	0.61	40	34	5.3	12	0.35	3.7	62
Nakdong River											
Artificial lake	NR	Mud	0.34	2.0	58	120	21	65	0.36	2.1	71
Inland creeks	N1	Mud	0.19	4.3	39	80	17	35	2.2	4.7	75
	N2	Mud	0.46	7.5	88	390	140	240	1.5	9.2	100
	N3	Mud/sand	0.82	2.0	17	8.3	1.7	3.2	0.16	0.04	61
	N4	Mud	1.9	0.95	54	290	46	62	5.2	9.3	43
	N5	Mud	1.8	1.9	29	69	24	41	0.04	0.6	96
	N6	Mud	0.12	4.0	54	55	13	37	1.5	1.9	99
Estuarine area	NE1	Mud	13	1.6	49	57	9.1	20	0.68	3.4	58
	NE2	Sand	15	0.48	31	9.1	1.7	2.4	0.2	0.30	51
	NE3	Mud	18	0.61	44	30	4.6	9.4	0.3	0.66	49
	NE4	Sand	22	0.14	6.7	2.1	0.28	1.0	0.08	0.25	77
	NE5	Sand	17	0.12	3.1	5.8	0.50	1.7	0.25	0.07	43
	NE6	Sand	30	0.14	2.6	0.89	0.03	0.07	0.04	0.07	24
	NE7	Mud	31	0.64	62	48	3.6	5.2	0.08	2.3	23

dw (dry weight), 0.1–0.3 pg g^{-1} dw, and 0.1–0.3 ng g^{-1} dw, respectively. MDL was calculated by multiplying the standard deviation of the results obtained by repeatedly measuring the lowest concentration of the standard by 3.14. Recoveries of ^{13}C-labeled surrogate standards of PCDD/Fs were within ranges specified by the US Environmental Protection Agency (EPA) methods (40–135%) (United States Environmental Protection Agency (US EPA), 1994). The recovery of surrogate standards for PAHs ranged from 72 to 111% (mean: 93%, Table S5).

2.3. H4IIE-luc bioassay

The dioxin-like activity of sediment organic extracts was determined using H4IIE-*luc* bioassays according to previously described methods (Khim et al., 1999; Hong et al., 2014). The cytotoxicity of sediment extracts was evaluated by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (MTT) assay (Yoo et al., 2006). Cell viability in the sediment organic extract was set as 80% of live cells compared to the control. Thus, cytotoxicity occurred when the percentage of live cells was <80%. A bioassay was performed with a sample diluted five times that of the existing sediment organic extract. H4IIE-*luc* cells in the culture plate were separated using trypsin, and were then seeded at a concentration of 7.0×10^4 cells mL^{-1} in a 96-well plate by 250 μL. H4IIE-*luc* cells were cultured for 24 h at 37 °C in a 5% CO_2 cell incubator. After 24 h, the culture medium was removed from the 96-well plates, and the organic extracts of sediments and controls were exposed. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) was used as a positive control, while 0.1% DMSO was used as solvent control, and culture medium was used as the negative control. The first concentration of the positive control was set at 300 pM (=100% $TCDD_{max}$). It was then diluted three times to obtain a total of six concentrations. Luciferase luminescence was measured at 72 h after exposing samples using a microplate reading luminometer (Tecan, Infinite 200, Mannedorf, Switzerland). Bioassay results were converted to the percentage of maximal TCDD response. Potency-based AhR-mediated activities were calculated from the dose-response relationship of six concentrations of sediment organic extracts.

2.4. Potency balance analysis

Bioassay-derived TCDD-equivalent concentrations (TCDD-EQs) and instrument-derived toxic equivalents (TEQs) were compared to determine the contribution of the targeted DLCs to the overall AhR-mediated potencies. The TEQs of AhR-active compounds were calculated by multiplying the concentrations of the compounds in sediments by individual RePs (Koh et al., 2004; Hong et al., 2014) (Eq. 1).

$$TEQ_s = \sum[(\text{concentrations of AhR agonist}_i) \times ReP_i] \quad (1)$$

where [concentrations of AhR agonist$_i$] are the concentrations of target DLCs in the sediment extracts, and ReP_i is the assay-specific RePs of the individual AhR agonists. AhR-mediated potency was assumed to be additive without any antagonistic/synergistic effects (Larsson et al., 2014). Assay-specific ReP values for PCDD/Fs, co-PCBs, and PAHs were reported previously (Behnisch et al., 2003; Lee et al., 2013; Van den Berg et al., 1998; Villeneuve et al., 2002). The ReP values of the targeted AhR-active compounds used in the present study are presented in Table S6.

2.5. Principal component analysis

Principal component analysis (PCA) was used to determine the major factors driving variability in PCDD/Fs, and to group sampling sites based on the relationships of the PCDD/Fs concentrations in the sediments of the two estuaries. PCA was performed using SPSS 24.0 (SPSS Inc., Chicago, IL) on concentrations of PCDD/Fs in the sediments of Yeongsan River and Nakdong River estuaries, along with various sources reported in previous studies (Masunaga et al., 2001; Xu et al., 2008; Oh et al., 1999; Kim et al., 2005). PCA was used by converting the contribution of variables into two main components to identify the sources of PCDD/Fs in the sediments of the two estuaries.

2.6. Positive matrix factorization receptor model

The US EPA positive matrix factorization receptor (PMF) model (Ver. 5.0) was used to determine the sources of PAHs in the sediments of the two estuaries. The PMF model is a type of factor analysis that is actively used to trace the sources of PTSs (Paatero and Tapper, 1993). The PMF model calculates the negative value obtained after factor analysis to generate a positive value using a mathematical algorithm and generates the least-squares value (Moon et al., 2008). The input data included 16 PAHs in sediments from 31 sites. The Q_{True}/Q_{Exp} values obtained by the PMF model were considered the most reliable when analyzing PAHs in sediments. Thus, the smallest Q_{True}/Q_{Exp} value was selected. The respective 3-factor was selected from the sediments of the two estuaries. The slope of the linear regression of the observed values in the Yeongsan River was 0.21–1.1, with an R^2 value of 0.98. For the sediments of the Nakdong River, the slope value was 0.12–1.21, with an R^2 value of 0.99. The PMF model results obtained from the present study were considered reliable.

3. Results and discussion

3.1. Concentrations and distributions of PCDD/Fs, co-PCBs, and PAHs

3.1.1. PCDD/Fs

PCDD/Fs were detected in all sediment samples from artificial lakes, inland creeks, and estuarine areas of the Yeongsan and Nakdong River estuaries (Fig. 2a and b). The mean concentration of ΣPCDDs (sum of seven measured congeners) in sediments from the Yeongsan was 920 pg g^{-1} dw in inland creeks and 720 pg g^{-1} dw in estuarine areas. The concentrations of ΣPCDDs in inland creeks were greater than those in estuarine areas. A similar pattern was found in Nakdong River, with the mean concentration of ΣPCDDs in the sediments of inland creeks and estuarine areas being 2200 pg g^{-1} dw and 560 pg g^{-1} dw, respectively. Greater concentrations of ΣPCDDs were detected in inland creeks, particularly in sites N4 (5100 pg g^{-1} dw) and N2 (4700 pg g^{-1} dw).

The distribution of ΣPCDFs (sum of 10 congeners) in sediments was similar to that of ΣPCDDs. Greater concentrations of ΣPCDFs were found in the sediments of inland creeks (mean = 220 pg g^{-1} dw and 740 pg g^{-1} dw in Yeongsan and Nakdong, respectively) compared to estuarine areas (mean = 170 pg g^{-1} dw and 91 pg g^{-1} dw in Yeongsan and Nakdong, respectively) (Fig. 2b). Like ΣPCDDs, ΣPCDF concentrations were greater in N2 and N4 compared to other sites. However, the greatest concentrations of ΣPCDFs were found in N2 (2300 pg g^{-1} dw), followed by N4 (920 pg g^{-1} dw). The TEQ concentrations of PCDD/Fs in Y2, Y4, and Y5 of the Yeongsan River Estuary and at all sites of the river and inland creeks of Nakdong River Estuary (except for N3) exceeded the predicted effects level (PEL, 21.5 pg TEQs g^{-1}) by Canadian Council of Ministers of the Environment (Canadian Council of Ministers of the Environment (CCME), 2001) (Table 1), signifying possible toxicological significance.

Out of the seven PCDDs, OCDD was predominantly distributed in all sites, which is consistent with the results of previous studies in Korea (Jin et al., 2016; Kim et al., 2019) (Fig. S1). Maximum concentrations of ΣPCDFs (sum of 10 measured congeners) were detected in N2, with relative concentrations differing to other sites. OCDF concentrations were highest at all other sites, whereas N2 had the highest 1,2,3,4,6,7,8-HpCDF concentration. In general, OCDD and OCDF in environmental matrices are produced from many combustion sources. The release of OCDD and OCDF from industrial complexes is assumed to be widely distributed in nearby sediments. OCDD/F tends to be dominant because of its higher hydrophobicity and lower degradation potential in the environment (Baker and Hites, 2000; Hong et al., 2014; Moon et al., 2009). Total PCDD/F concentrations have a significant positive correlation ($r = 0.07$ to 0.62, $p < 0.05$) with total organic carbon (TOC). In other words, great concentrations of PCDD/Fs were detected at the sites with a high TOC in the sediment of the study area (Fig. S2).

3.1.2. Co-PCBs

Concentrations of co-PCBs ranged from 27 to 7000 pg g^{-1} dw in sediments of the Yeongsan River and Nakdong River estuaries (Fig. 2c). The mean concentration of co-PCBs (790 pg g^{-1} dw) in Nakdong River Estuary ($n = 14$) was generally greater than that in Yeongsan River Estuary (200 pg g^{-1} dw, $n = 16$). In the Yeongsan River Estuary, co-PCB concentrations

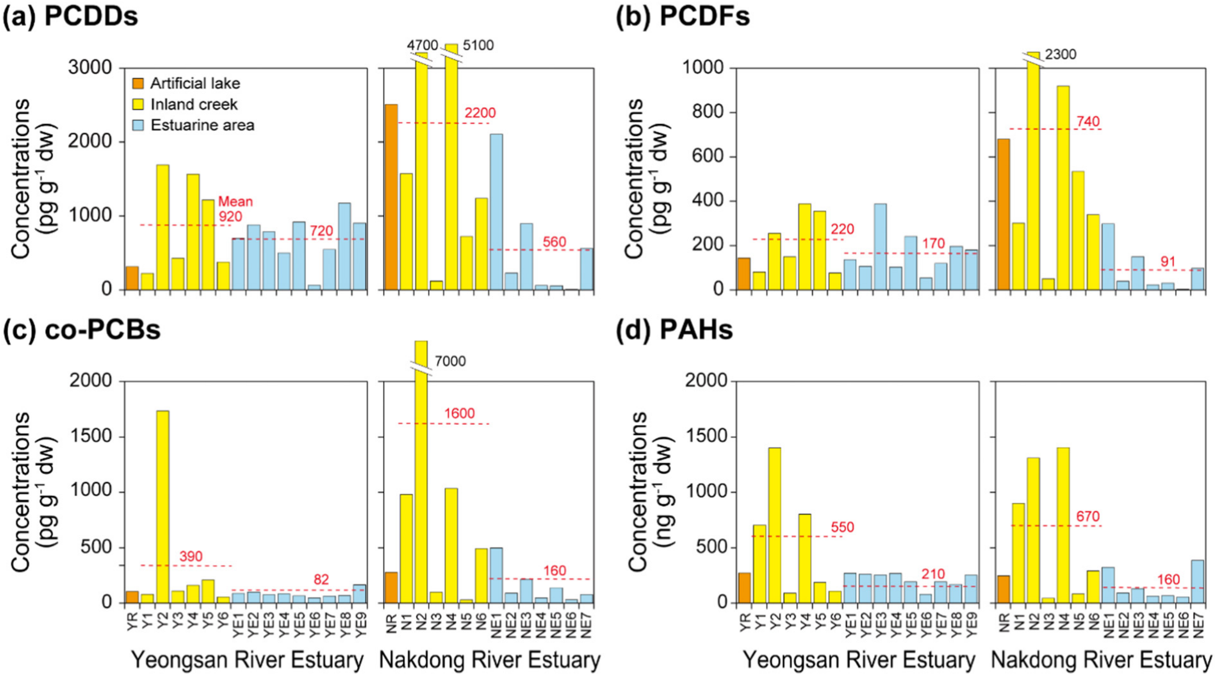

Fig. 2. Concentrations and distributions of (a) PCDDs, (b) PCDFs, (c) co-PCBs, and (d) PAHs in the sediments of the artificial lake, inland creek, and estuarine areas of Yeongsan and Nakdong River estuaries, South Korea.

were similar across sites, except for site Y2 (1700 pg g^{-1} dw). The high concentration at Y2 was attributed to it being located close to Daebul Pier in Mokpo Port and Daebul National Industrial Complex on the south side (Figs. 1 and 2). High PCB concentrations were found in N2, followed by N4. Co-PCB concentrations in N2 (7000 pg g^{-1} dw) were similar or slightly lower compared to those recorded in samples from highly industrialized regions, such as Gyeonggi Bay (1000–580,000 pg g^{-1} dw) and Yeongil Bay (1000–170,000 pg g^{-1} dw) (Hong et al., 2016). Despite the ban on the use of PCBs as dielectric fluid since 1995 in South Korea, hotspots of PCBs contamination still exist. The concentrations of Σco-PCBs in this study did not exceed the effects-range-low (ERL) guideline (Long et al., 1995). However, as the measured concentration of co-PCBs did not cover all compounds considered in the sediment quality guidelines, the direct comparison was difficult. In further studies, measurements involving more PCB congeners are needed.

Co-PCBs in sediments had compositional differences across sampling sites in the two estuaries (Fig. S1c). For instance, CB 105 was the highest in the artificial lake and inland creek of Yeongsan River, whereas CB 118 was highest in the estuary. CB 114 was high in the artificial lake of Nakdong River, whereas CB 77, CB 105, and CB 118 were high in the inland creeks and estuary. These results are generally consistent with the findings of previous studies, which suggested that commercially used CB 118 and CB 105 dominate most samples (Hui et al., 2009; Lee et al., 2017b; Li et al., 2012; Yang et al., 2020).

3.1.3. PAHs

Concentrations of PAHs in sediments of the Yeongsan River Estuary and Nakdong River Estuary were 77–1400 ng g^{-1} dw (mean: 340 ng g^{-1} dw) and 42–1400 ng g^{-1} dw (mean: 380 ng g^{-1} dw), respectively. The highest concentrations of total PAHs were found in Y2 and N4 (1400 ng g^{-1} dw) (Fig. 2d), which exceeded the interim sediment quality guidelines (ISQG, 768 ng g^{-1} dw) (CCME, 2001). These two sites had the highest concentrations (708 ng g^{-1} dw and 678 ng g^{-1} dw, respectively) of seven DL-PAHs, including benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno [1,2,3-*cd*]pyrene (IcdP), and dibenzo[*a,h*]anthracene (DbahA). Meanwhile, the concentration of pyrene (Py) was highest in sediments of both river estuaries, followed by phenanthrene (Phe) and fluoranthene (Fl) (Fig. S1d), indicating that the PAHs in the study areas were mainly originated from the vehicular emissions (May and Wise, 1984).

Overall, the concentrations of all targeted chemicals (except PCDDs in Nakdong River Estuary) in sediments exhibited land to estuarine area gradient in both rivers. These results were expected, as they reflect the environmental process in which contaminants generated from point and/or non-point sources, including industrial activities and wastewater treatment plants (WWTP) are transported to estuarine areas via inland creeks (Hong et al., 2013). For example, N2 and N4 sites were in the inland creeks of Nakdong River Estuary, where all target chemicals had high concentrations. N2 was located at the outflow of a WWTP that receives wastewater from dyeing, fabric, textile, and leather industrial complexes (Choi et al., 1999). In addition, N4 was located near a small wood-processing company, which seemed to be a potential source of target chemicals. Thus, in order to reduce pollution of DLCs in the estuarine areas, it is necessary to identify the sources and manage the inflow of pollutants into the estuary.

3.2. Identification of PCDD/F and PAH sources

The potential sources of PCDD/Fs were selected based on urban and industrial activities, such as residential areas, cement, pulp, paper, and dye factories in the two estuaries, which included stack gas (SG), fly ash (FA), small size incinerator (SI), municipal solid waste incinerator (MSWI), hazardous waste incinerator (HWI), house coal burning (CB), dust, and tetrachloro-isophthalonitrile 1993 (TPN 1993) reported previously (Masunaga et al., 2001; Xu et al., 2008; Oh et al., 1999; Kim et al., 2005). TPN 1993 is used as a fungicide, and it has been reported that small amounts of dioxins are released from these chemicals in a previous study (Masunaga et al., 2001). Since South Korea also used TPN 1993 fungicide, it was considered as a potential source of PCDD/Fs in sediments and included in PCA in this study (Lee et al., 2015). The results of PCA on Yeongsan River Estuary extracted two principal components (PCs), accounting for 63% (PC1) and 15% (PC2) of variability (Fig. 3a). Sediments from the artificial lake, inland creek, and estuarine area were separated in PC2, indicating different PCDD sources. Estuarine area sediments were associated with fly ash. The artificial lake and inland creek sediments of Nakdong River were on the positive axis of PC1, whereas the estuary was on the negative axis of PC1. Most estuarine sites in Nakdong River were grouped with documented known sources of PCDD/Fs.

As a result of PMF modeling for identification of PAHs sources in Yeongsan River Estuary, Factor 1 was dominated by Fl (65%), Py (55%), BaA (97%), and DbahA (57%), and could have been emitted from coal combustion (Yang et al., 2012) (Fig. 3b). The main components of Factor 2 were identified as naphthalene (Na; 61%), acenaphthylene (Acl; 75%), acenaphthene (Ace; 61%), fluorene (Flu; 62%), Phe (62%), Chr (83%), and benzo[*g,h,i*]perylene (BghiP; 88%). A high percentage of PAHs were of both low and high molecular weight. The source of PAHs in sediments was traced through low molecular weight PAHs, which were dominant in Factor 2. These PAHs likely originated from petroleum combustion (Hu et al., 2013). In Factor 3, BbF and BkF explained 57% and 69% variability, respectively, with diesel emission being confirmed as the source (Harrison et al., 1996). Sites Y2, Y4, and Y1 in the sediments of inland creeks had relatively high factor scores and were largely influenced by coal combustion and diesel emission sources (Fig. 3c). Y1 and Y2 sites were close to urban areas, while Y4 was close to industrial complexes; consequently, these sites were mainly affected by diesel emissions and coal combustion from nearby (non)point sources. The artificial lake site had lower factor scores, with similar levels among the three factors. The sediments of the estuarine area were mainly influenced by petroleum sources. Mokpo Port is located near the estuarine area and is directly associated with petroleum emissions from the operation of ships.

The PMF results on the sediments of Nakdong River Estuary showed that Na (63%), Acl (57%), Phe (54%), Chr (59%), and BghiP (54%) were the main components in Factor 1, and likely originated from petroleum sources (Hu et al., 2013). Py (63%), BbF (53%), BkF (71%), BaP (55%), IcdP (74%), and BghiP (100%) were the main components in Factor 2, and likely originated from diesel emissions (Harrison et al., 1996). In Factor 3, low molecular weight PAHs, including Ace (72%), Flu (59%), and Fl (52%) were dominant, with coal tar combustion, such as creosote, being the potential source (Wang et al., 2013). N1, N2, and N4 had relatively high factor scores in the sediments of the Nakdong River Estuary. N1 is located close to an urban area and industrial complexes, and might be associated with diesel emissions and coal tar combustion sources. N2 is close to an industrial area, and is likely affected by petroleum, diesel emission, and coal tar combustion sources. N4 is in an urban area, with high PAH contamination from diesel emission, and was mainly affected by automobile fuel emissions on nearby roads. The inland creek and estuarine sediments of Nakdong River were affected by petroleum & creosote sources and petroleum & diesel emissions, respectively, from nearby industrial areas. The PMF indicated that the sediments of both rivers were contaminated with PAHs originating from petroleum and diesel emissions. Thus, future studies need to investigate the occurrence, generation, and fate of PAHs originating from petroleum and diesel emissions in the sediments of both regions.

3.3. AhR-mediated potencies in sediment extracts

Fourteen of the 16 sediments from Yeongsan River Estuary and 12 of the 14 sediments in Nakdong River Estuary had detectable AhR-mediated potencies with $\%TCDD_{max}$ (Fig. S3). The AhR-mediated potencies of the sediment extracts varied depending on the sampling area. In both Yeongsan and Nakdong River estuaries, the artificial lake and inland creek sediments had greater AhR-mediated potencies, on average, than estuarine area sediments. Potency-based TCDD-EQs of organic extracts from the Yeongsan and Nakdong River estuaries ranged from 2.0 to 280 pg g^{-1} dw (mean =

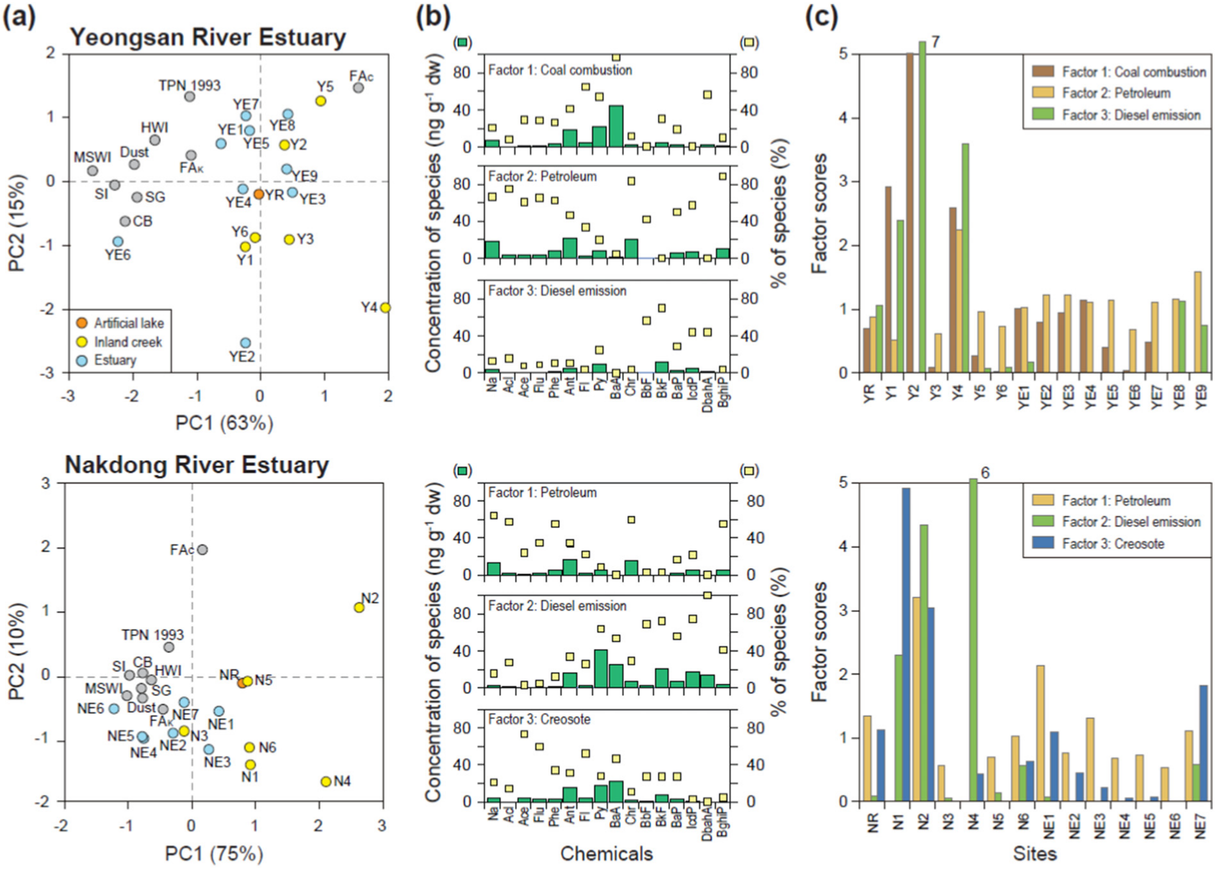

Fig. 3. (a) PCA based on PCDD/Fs concentrations and known sources based on previous literature. (b) Source identification of PAHs in the sediments analyzed in the present study. (c) Factor profiles and factor scores generated by the PMF model [stack gas (SG), fly ash (FA), small size incinerator (SI), municipal solid waste incinerator (MSWI), hazardous waste incinerator (HWI), house coal burning (CB), dust, and tetrachloro-isophthalonitrile 1993 (TPN 1993) (Masunaga et al., 2001; Xu et al., 2008; Oh et al., 1999; Kim et al., 2005)].

71 pg g^{-1} dw) and 0.89–390 pg g^{-1} dw (mean = 83 pg g^{-1} dw), respectively (Fig. 4a). Mean TCDD-EQ sediment concentrations in both regions were greater than those previously recorded on the west coast of Korea (n = 12, mean = 4.6 pg g^{-1} dw) and China (n = 34, mean = 4.9 pg g^{-1} dw), but were lower than those recorded in the inland creeks of Ulsan Bay (n = 11, mean = 1600 pg g^{-1} dw) and Hyeongsan River (n = 5, mean = 380 pg g^{-1} dw) (Hong et al., 2012) (Table 2).

The TCDD-EQ was greatest in Y1, followed by the Y2, which contrasted with concentrations of target AhR agonists. This result indicated that large amounts of untargeted AhR agonists likely exist in the Y1. In contrast, the AhR-mediated potency in the Nakdong River Estuary was great in N2 (390 pg g^{-1} dw) and N4 (286 pg g^{-1} dw), where concentrations of target compounds were also great. Detected TCDD-EQs in the sediments of both rivers seemed to be linked to regional human activities. For example, potential sources of TCDD-EQs include wastewater and runoff from factories, cities along rivers, and pollutants from ports (Jiao et al., 2012).

All TCDD-EQ concentrations in the artificial lake and inland creeks of both rivers (except for Y3 and N3) exceeded the sediment quality guidelines (>30 pg g^{-1}, possible-effect level; PEL) of the US for dioxin-like compounds (De Rosa et al., 1999; Zhang et al., 2009). In the estuarine area, YE8 and YE9 of the Yeongsan River and NE3 and NE7 of the Nakdong River exceeded PEL. Some sites along both rivers exceeded the Canadian Sediment Quality Guidelines (>0.85 pg g^{-1} for sediment) (CCME, 2001, 2002). Thus, dioxin-like chemicals likely have adverse effects on the aquatic ecosystems in both rivers. Complementary research, such as effect-directed analysis, could be used to identify causative toxic chemicals to implement appropriate countermeasures (Lee and Khim, 2022).

3.4. Potency balance analysis

Bioassay-derived TCDD-EQs and instrument-derived TEQs were compared to determine the contribution of targeted AhR agonists to total induced AhR-mediated potencies in sediments (Fig. 4). The mean concentration of TCDD-EQs in sediments was similar to the two river estuaries, but the identified proportion of TCDD-EQs by TEQs and major contributors differed. In Yeongsan River Estuary, TEQ contributed more to TCDD-EQs in estuarine areas (34–103%; mean: 69%) compared to artificial lakes and inland creeks (8.1–81%; mean: 37%) (Fig. 4b). In Nakdong River Estuary, TEQs contributed less to TCDD-EQs in estuarine areas (23–77%; mean: 46%) compared to artificial lakes and inland creeks (43–100%; mean: 78%). There was a significant difference in the contribution of the artificial lakes and inland creeks at the estuaries of Yeongsan River and Nakdong River, which may reflect the differences in surrounding activities. The industrial area of the Yeongsan River Estuary has cement, pulp, and paper factories, while the Nakdong River Estuary includes dyeing, leather, as well as municipal complexes. Most of the AhR active substances introduced through the (non)point source of the Nakdong River Estuary were the target DLCs (PCDD/Fs, co-PCBs, DL-PAHs) in this study.

In both regions, the main contributors to total dioxin-like activities were PCDD/Fs (mean: 48% and 56% in Yeongsan River and Nakdong River estuaries, respectively), followed by DL-PAHs (mean: 6.3% and 3.9%), and co-PCBs (mean: 1.1% and 2.0%) (Fig. 4a). The high contribution for the inland creeks of the Nakdong River Estuary was attributed to high concentrations of PCDD/Fs. In sediments from the west coast of Korea and the Liaohe River of China, PCDD/Fs were the dominant AhR agonists (Hong et al., 2012; Zhang et al., 2017) (Table 2). In contrast, DL-PAHs were the dominant AhR agonists in Tai Lake, China (Hong et al., 2012; Xia et al., 2014).

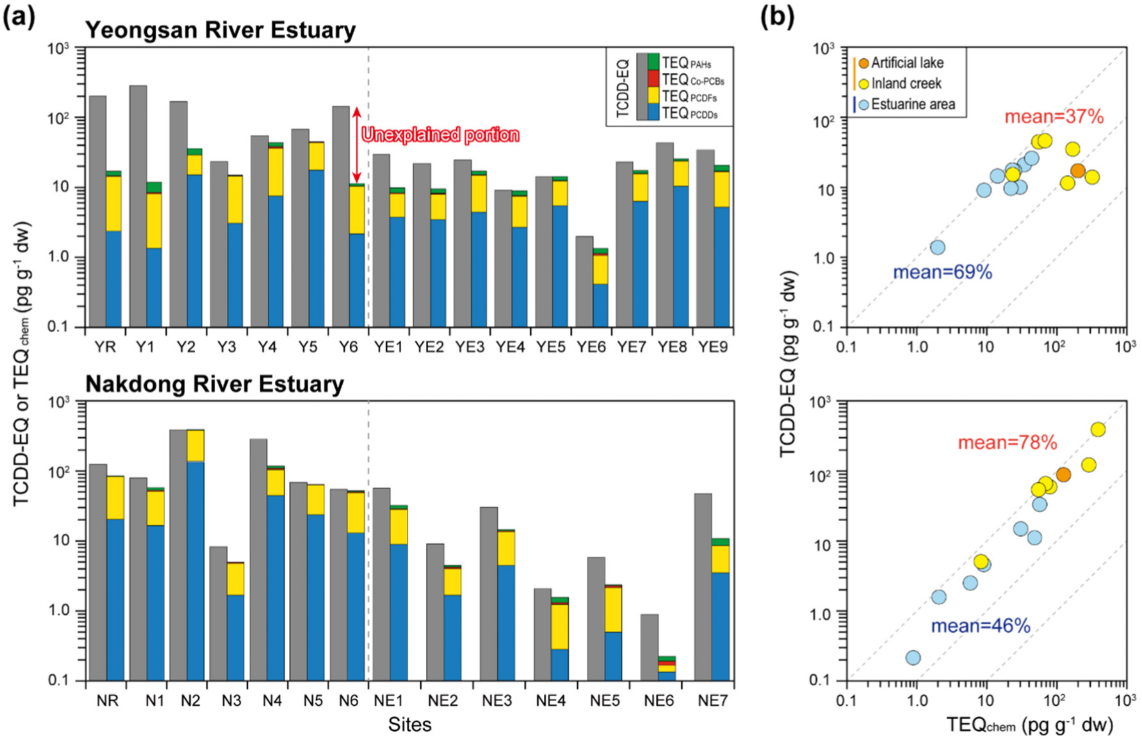

Fig. 4. (a) Bioassay-derived TCDD-EQs and instrument-derived TEQs from PCDD/Fs, co-PCBs, and DL-PAHs and (b) comparison of TCDD-EQs and $TEQ_{chem\ (PCDD/Fs + Co\text{-}PCBs + DL\text{-}PAHs)}$ concentrations in sediments of Yeongsan River Estuary and Nakdong River Estuary.

Thus, it is indicated that the chemical compositions and contributions of AhR agonists in sediments appear to be site-specific. Meanwhile, PCA results for sources of PCDD/Fs revealed that fly ash was identified as the main contributor in sediments of the Yeongsan River Estuary. Thus, the potential AhR-mediated activity in sediments in this area seemed to be mainly originated from the fly ash. To reduce the potential toxicity of sediments in this area, more accurate identification and management of sources of pollutants will be needed.

Among the PCDD/Fs, 2,3,4,7,8-PeCDF was found to be the major contributor in all sites of the study areas (Fig. S4), which result is similar to the previous study conducted in the Hyungsan River Estuary in South Korea (Hong et al., 2014). This is because 2,3,4,7,8-PeCDF concentrations are relatively high in sediments, with great RePs compared to other DLCs (Table S2) (Behnisch et al., 2003). Meanwhile, OCDD and OCDF concentrations were highest in the sediments of both river estuaries, but their ReP values were very small. Consequently, they did not have significant contributions to potential toxicity in sediments.

3.5. Comparison with previous studies

In the present study, targeted AhR-active compounds largely explained observed dioxin-like activities, particularly for the inland creeks of Nakdong River (Table 1). The contribution of targeted DLCs in the sediments was compared with that in sediments from previous studies (Table 2). Most previous studies showed that TCDD-EQs only explained a small portion of TEQs (<20%), because limited target DLCs were considered in potency balance

Table 2

Comparison of TCDD-EQ and TEQ_{chem} in the sediment samples from this study and previous studies.

Country	Region	TCDD-EQ (pg g^{-1} dw)	TEQchem (pg g^{-1} dw)				Contribution (%)	Reference
			$TEQ_{PCDD/Fs}$	TEQ_{PCBs}	TEQ_{PAHs}	$TEQ_{PBDD/Fs}$		
South Korea	Yeongsan River	2.0–280	1.1–45	0.07–1.8	0.24–6.8		4.3–100	This study
	Nakdong River	0.89–390	0.10–380	0.04–5.2	0.04–9.3		23–100	This study
	Hyungsan River	ND[a]–800	0.72–730	ND–6.2	0.24–22		ND–100	Hong et al. (2014)
	Lake Sihwa	47–3630			ND–5.9		ND–5.6	Lee et al. (2017b)
	Masan Bay	62.6–100			0.60–29		0.80–2.2	Lee et al. (2018)
	Taean Coast	8.3–250			1.3–120		15–56	Hong et al. (2016)
	West Coast	ND–4.6	ND–1.3		0.17–0.93		5.3–59	Hong et al. (2012)
China	Liaohe River	89–190	19–41	0.01–0.09	2.6–7.0		17–26	Zhang et al. (2017)
	Tai Lake	18–110		ND–0.28	0.15–2.9		0.70–8.7	Xia et al. (2014)
South Africa	Klip River	ND–820			0.6–9.7		ND–9.2	Pheiffer et al. (2019)
Brazil	Billing Reservoir	5100			72		1.4	Rocha et al. (2010)
	Pinheiros River	24,000			570		2.5	
	Barra Bonita Reservoir	340			23		6.8	
	Bariri Reservoir	6200			180		2.9	
	Promissao Reservoir	320			15		4.7	
	Tres Irmaos Reservoir	1100			17		1.5	
Japan	Osaka Bay	3.7–140	1.8–48	0.04–44		0.3–8.3	58–100	Takigami et al. (2005)

[a] ND: not detected.

analysis (Table 2). Takigami et al. (2005) showed high contributions of targeted AhR-active compounds; this study considered polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) as AhR agonists (Table 2). Although PBDD/Fs had great ReP values, they did not account for a large portion of TEQ values (Table S6). Because the presence of DLCs in sediments varies across regions, it is very important to consider various compounds to improve understanding of the potential toxic effects of sediments. In the future, the effect-directed analysis approach needs to be applied more to identify the causative agents of unknown toxicity in environmental samples (Lee and Khim, 2022).

Ultimately, it is difficult to explain all induced biological responses based on limited target compounds. In particular, unmonitored AhR-active compounds appear to be present in the sediments of Yeongsan River and Nakdong River estuaries. For example, emerging PAHs in sediments from South Korea have been reported as AhR agonists (ReP relative to BaP), including benzo[*j*]fluoranthene (1.7), 4,5-methanochrysene (1.0), and 11H-benzo[*a*]fluorene (1.2) (Cha et al., 2019; Kim et al., 2019). Although these substances were not considered in the current study, they have great AhR binding potency. Thus, it is necessary to elucidate the unknown AhR agonists in sediments and to extend the explanation of the potency balance analysis by obtaining the assay-specific RePs of those compounds.

4. Conclusions

The present study assessed the spatial distribution of DLCs and potential ecotoxicological effects of the sediments from the two major river estuaries in Korea. The concentrations of DLCs showed a gradient that decreased from inland creeks to the estuarine and coastal areas, primarily due to the distance from the source. A combined analysis of chemical measurements of 36 known AhR agonists and the bioanalytical results from in vitro bioassays revealed that targeted AhR agonists contributed a considerable portion of the determined AhR-mediated activities. Overall, this study provided baseline information on the occurrence, sources, and AhR-mediated activity of the major group of widespread DLCs in the sediments of two river basins in Korea. Continuing efforts on monitoring and determining spatiotemporal characteristics with sedimentary transport in the estuarine and coastal environment of Korea should be acknowledged to identify sources and manage the coastal contamination of DLCs in a long-term aspect.

CRediT authorship contribution statement

Junghyun Lee: Conceptualization, Investigation, Formal analysis, Data curation, Visualization, Writing - original draft, Writing - review & editing. **Jihyun Cha:** Investigation, Formal analysis, Data curation, Writing - original draft. **Seo Joon Yoon:** Investigation, Formal analysis, Visualization. **Seongjin Hong:** Conceptualization, Writing - original draft, Writing - review & editing, Project administration. **Jong Seong Khim**: Conceptualization, Methods development, Investigation, Writing – review & editing, Project administration, Funding acquisition, Supervision.

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.scitotenv.2022.154240.

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Supplementary Materials for

Instrumental and bioanalytical characterization of dioxin-like activity in sediments from the Yeongsan River and the Nakdong River estuaries, South Korea

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References

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Supplementary Tables

Table S1. Concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea.

Sampling Region/Site	**Compounds (pg g^{-1} dry weight)**						
	2,3,7,8 -TCDD	**1,2,3,7,8 -PeCDD**	**1,2,3,4,7,8 -HxCDD**	**1,2,3,6,7,8 -HxCDD**	**1,2,3,7,8,9 -HxCDD**	**1,2,3,4,6,7,8-HpCDD**	**OCDD**
Yeongsan River							
Artifical Lake							
YR	ND[a]	ND	2.1	4.0	2.4	29	280
Inland creeks							
Y1	ND	ND	ND	2.9	1.8	17	200
Y2	ND	9.1	3.9	7.5	5.5	140	1500
Y3	ND	ND	ND	6.5	6.0	38	380
Y4	ND	ND	ND	5.7	13	100	1400
Y5	ND	13	9.2	16	15	118	1000
Y6	ND	ND	ND	4.4	5.4	25	340
Estuarine area							
YE1	ND	2.1	1.0	3.1	3.5	30	660
YE2	0.6	ND	ND	ND	ND	41	840
YE3	ND	ND	2.0	4.2	6.1	57	720
YE4	ND	ND	1.5	2.9	3.8	34	460
YE5	ND	1.7	3.7	5.4	6.0	52	850
YE6	ND	ND	ND	ND	0.9	5.7	58
YE7	ND	4.3	4.0	6.0	7.4	41	480
YE8	ND	6.2	6.4	8.5	11	78	1000
YE9	ND	ND	4.0	4.5	8.8	64	820
Nakdong River							
Artifical Lake							
NR	3.8	13	6.2	15	11	110	2400
Inland creeks							
N1	ND	ND	8.0	17	15	130	1400
N2	10	120	49	110	65	650	3700
N3	ND	0.8	0.9	2.5	2.2	14	98
N4	ND	35	15	43	38	280	4700
N5	2.3	15	9.7	29	27	140	500
N6	ND	7.7	6.4	14	11	100	1100
Estuarine area							
NE1	1.0	3.7	3.4	7.2	7.5	64	2000
NE2	ND	1.5	0.5	1.0	1.1	9.4	210
NE3	ND	1.8	2.5	3.1	3.5	41	840
NE4	ND	ND	ND	ND	0.6	3.7	85
NE5	ND	ND	ND	0.7	ND	7.3	46
NE6	ND	ND	ND	ND	ND	0.5	4.8
NE7	0.5	1.3	1.6	2.1	2.5	26	530

[a] Not detected.

Table S2. Concentrations of polychlorinated dibenzofurans (PCDFs) in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea (ND: not detected).

Region/ Site	**Compounds (pg g^{-1} dry weight)**									
	2,3,7,8-TCDF	**1,2,3,7,8-PeCDF**	**2,3,4,7,8-PeCDF**	**1,2,3,4,7,8-HxCDF**	**1,2,3,6,7,8-HxCDF**	**2,3,4,6,7,8-HxCDF**	**1,2,3,7,8,9-HxCDF**	**1,2,3,4,6,7,8-HpCDF**	**1,2,3,4,7,8,9-HpCDF**	**OCDF**
Yeongsan River										
Artificial lake										
YR	9.6	6.7	11	7.9	7.2	2.1	9.4	30	3.8	56
Inland creek										
Y1	6.0	4.4	5.2	5.8	5.4	1.8	5.5	20	3.2	23
Y2	14	12	11	11	10	ND	8.4	63	ND	130
Y3	9.1	9.2	9.2	8.5	8.4	4.5	9.4	56	3.3	33
Y4	24	34	26	29	27	ND	15	91	12	130
Y5	21	38	21	34	23	4.1	11	88	9.1	110
Y6	5.9	6.9	9.0	4.8	3.1	1.6	5.0	18	2.2	20
Estuarine area										
YE1	1.7	3.8	2.5	4.9	3.2	2.3	5.2	21	2.0	90
YE2	2.1	3.2	3.0	7.2	3.7	ND	4.8	31	3.2	48
YE3	3.7	5.4	5.6	16	8.3	2.3	7.3	77	14	250
YE4	2.2	3.6	3.4	5.9	4.0	0.8	5.5	25	2.8	50
YE5	4.1	4.9	3.7	7.0	6.4	1.9	6.7	30	4.2	170
YE6	ND	0.5	0.4	0.8	0.9	ND	ND	2.7	ND	49
YE7	6.3	8.0	7.5	7.9	8.0	4.6	7.5	29	6.5	34
YE8	7.9	14	11	16	16	3.5	10	50	10	59
YE9	5.5	12	8.5	14	11	7.0	9.3	10	5.7	68
Nakdong River										
Artificial lake										
NR	46	16	70	35	38	9.1	36	140	18	250
Inland creek										
N1	25	22	32	30	26	7.3	34	8.1	17	99
N2	149	126	245	210	215	ND	260	740	ND	350
N3	1.6	4.8	2.0	6.9	3.3	0.6	1.3	14	1.3	14
N4	40	95	52	100	46	ND	21	218	16	330
N5	27	70	28	85	30	5.3	13	171	10	94
N6	26	28	41	24	20	4.4	18	79	8.7	89
Estuarine area										
NE1	15	11	18	14	11	5.2	14	59	9.7	140
NE2	1.7	1.5	1.8	2.3	1.1	0.9	1.8	7.0	1.2	19
NE3	5.8	4.9	8.4	8.0	5.7	2.7	5.8	28	4.8	75
NE4	0.6	0.8	0.9	1.0	0.8	ND	ND	3.7	1.1	14
NE5	ND	1.5	1.5	2.4	1.6	1.0	1.2	7.4	1.6	12
NE6	0.1	ND	ND	0.1	0.1	ND	ND	2.0	ND	ND
NE7	2.4	2.6	4.3	5.1	3.1	1.5	5.2	20	2.4	51

Table S3. Concentrations of coplanar polychlorinated biphenyls (co-PCBs) in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea (ND: not detected).

Region/	**Compounds (pg g^{-1} dry weight)**											
Site	**CB 77**	**CB 81**	**CB 105**	**CB 114**	**CB 118**	**CB 123**	**CB 126**	**CB 156**	**CB 157**	**CB 167**	**CB 169**	**CB 189**
Yeongsan River												
Artificial lake												
YR	11	ND	27	3.7	14	15	2.0	10	7.4	14	0.8	ND
Inland creek												
Y1	5.1	2.5	25	1.3	12	ND	3.4	9.7	6.8	12	ND	ND
Y2	16	ND	770	28	170	190	ND	270	8.2	250	34	ND
Y3	12	ND	35	ND	16	17	1.5	7.0	6.0	8.1	ND	4.5
Y4	2.9	2.4	52	2.9	28	ND	18	16	13	20	ND	4.7
Y5	9.5	4.5	51	93	1.2	ND	8.5	13	5.1	16	ND	5.2
Y6	0.8	2.1	15	2.6	8.5	9.0	1.3	5.0	2.8	5.2	0.5	ND
Estuarine area												
YE1	5.9	2.1	11	2.9	41	6.3	2.2	5.8	0.1	2.5	0.9	5.5
YE2	3.9	3.0	14	3.1	43	8.6	2.7	6.5	0.1	5.8	1.0	6.6
YE3	3.4	2.3	9.7	3.0	33	3.4	2.7	5.9	0.3	3.8	1.0	5.8
YE4	3.7	2.9	12	2.5	35	7.6	2.0	5.3	1.0	4.0	1.2	5.4
YE5	3.7	2.0	6.7	2.5	28	4.5	1.6	4.3	ND	3.1	0.9	6.3
YE6	2.0	2.1	6.1	1.9	20	2.9	0.6	3.3	0.03	1.9	0.6	3.6
YE7	3.0	1.9	7.5	2.5	28	4.4	0.7	4.3	0.2	2.8	0.8	5.4
YE8	4.2	2.1	7.8	3.3	28	4.7	0.8	4.2	0.2	2.7	0.9	7.2
YE9	24	4.5	14	6.7	62	8.9	3.3	19	4.3	9.3	1.0	5.3
Nakdong River												
Artificial lake												
NR	20	4.1	46	5.8	120	34	3.4	25	4.9	9.4	1.7	4.5
Inland creek												
N1	32	12	280	510	ND	ND	22	70	56	ND	ND	4.2
N2	97	140	5800	ND	34	ND	ND	ND	570	22	360	6.8
N3	11	ND	24	17	9.8	10	1.6	6.5	5.9	7.3	1.2	2.3
N4	410	6.1	140	120	72	ND	52	66	81	84	1.2	3.5
N5	3.6	ND	3.6	1.4	12	2.0	0.4	2.2	0.2	1.1	0.5	ND
N6	68	ND	160	3.9	47	50	14	50	52	66	8.7	ND
Estuarine area												
NE1	240	2.8	89	7.6	84	20	6.5	24	5.4	9.6	1.2	6.8
NE2	15	1.1	14	2.0	39	5.9	1.9	3.5	0.6	1.8	0.5	2.7
NE3	47	1.9	36	4.7	88	14	2.8	79	1.4	3.5	1.4	4.6
NE4	3.5	1.1	5.1	1.9	22	3.6	0.7	2.6	0.5	1.2	0.5	2.9
NE5	17	2.8	35	2.9	50	8.0	1.3	10	2.6	4.6	0.5	2.9
NE6	2.3	0.9	3.9	1.2	12	2.0	0.4	2.0	ND	0.9	0.5	2.1
NE7	13	1.7	11	2.1	31	5.5	0.7	4.4	0.6	1.9	0.5	3.0

Table S4. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea (ND: not detected).

Region/ Site	**Compounds (ng g^{-1} dry weight)**															
	Na	**Acl**	**Ace**	**Flu**	**Phe**	**Ant**	**Fl**	**Py**	**BaA**	**Chr**	**BbF**	**BkF**	**BaP**	**IcdP**	**BghiP**	**DbahA**
Yeongsan River																
Artificial lake																
YR	21	5.6	5.2	7.3	37	5.1	33	33	24	10	15	14	12	8.7	8.3	31
Inland creek																
Y1	71	4.5	5.7	16	82	19	141	119	49	59	40	19	17	15	8.3	37
Y2	55	11	20	39	126	16	169	240	88	330	120	33	38	18	17	78
Y3	14	5.1	4.3	9.5	16	1.9	6.1	ND	13	ND	ND	2.1	4.3	ND	4.6	7.2
Y4	64	14	26	44	125	19	81	99	44	48	79	32	36	4.2	18	67
Y5	23	9.2	10	19	28	2.2	10	5.4	21	ND	ND	3.2	7.7	ND	35	10
Y6	14	5.1	3.9	7.3	16	2.2	9.6	4.5	16	ND	1.9	5.1	6.1	ND	6.8	8.1
Estuarine area																
YE1	25	7.1	7.8	12	38	8.3	33	63	25	ND	3.5	10	8.7	ND	8.8	16
YE2	32	7.8	9.0	12	36	12	31	48	28	ND	0.8	8.4	8.3	ND	9.7	17
YE3	28	5.0	8.3	8.7	44	6.4	30	37	28	ND	5.8	13	8.7	ND	10	18
YE4	22	4.8	4.0	9.1	44	7.3	36	74	27	ND	ND	8.7	8.1	ND	9.5	15
YE5	25	4.1	3.7	8.0	30	5.7	24	17	25	ND	2.7	12	7.5	ND	9.5	18
YE6	16	3.5	2.1	5.0	16	1.9	6.1	1.3	15	ND	ND	1.3	5.1	ND	4.9	5.7
YE7	24	5.1	3.8	9.1	30	5.8	19	2.9	25	ND	23	10	8.0	ND	9.3	17
YE8	25	4.6	2.9	8.4	28	3.0	16	ND	25	ND	4.5	11	15	ND	9.4	16
YE9	34	7.7	8.6	11	35	2.1	22	8.0	34	ND	20	25	16	ND	10	18
Nakdong River																
Artificial lake																
NR	24	6.4	6.5	9.9	43	5.5	23	19	26	3.9	22	13	10	ND	9.1	26
Inland creek																
N1	37	5.0	19	27	110	15	90	190	57	78	93	21	27	34	12	79
N2	88	12	30	57	190	36	98	170	44	68	130	44	73	77	31	160
N3	6.8	1.9	ND	2.4	8.1	ND	2.5	ND	9.2	ND	ND	ND	4.0	ND	3.2	3.5
N4	17	7.2	3.0	6.4	97	26	250	290	150	120	110	45	86	86	28	78
N5	8.4	2.7	1.5	4.1	12	1.6	9.4	2.9	12	ND	2.2	3.8	6.1	ND	6.9	7.9
N6	24	4.7	3.8	7.8	36	6.7	40	28	26	17	25	11	16	ND	9.6	32
Estuarine area																
NE1	36	7.9	8.4	14	53	10	34	20	38	ND	14	22	14	3.1	14	33
NE2	12	2.9	2.6	5.5	16	1.7	8.7	12	12	ND	ND	1.7	3.9	ND	4.2	5.5
NE3	19	3.5	3.7	7.8	26	2.1	12	2.1	22	ND	1.6	3.9	7.5	ND	7.5	12
NE4	10	3.0	2.7	5.0	12	1.8	3.6	ND	11	ND	ND	1.5	3.3	ND	3.9	3.8
NE5	10	3.4	3.1	5.7	13	2.2	4.1	0.2	12	ND	ND	0.1	3.4	ND	4.2	4.0
NE6	11	3.5	3.1	5.4	9.9	1.2	2.2	ND	8.4	ND	ND	0.3	2.5	ND	3.0	2.8
NE7	16	4.9	9.6	14	71	28	68	61	28	ND	21	14	18	ND	8.5	21

Table S5. Recoveries of surrogate standards for PAHs.

Surrogate standards	**Abbreviation**	**Surrogate recovery (%, mean)**
Acenaphthene-d10	Ace-d10	96.5
Fluorene-d10	Flu-d10	101
Phenanthrene-d10	Phe-d10	102
Anthracene-d10	Ant-d10	91.7
Fluoranthene-d10	Fl-d10	111
Pyrene-d10	Py-d10	94.8
Benzo[*a*]anthracene-d12	BaA-d12	75.2
Chrysene-d12	Chr-d12	101
Benzo[*b*]fluoranthene-d12	BbF-d12	103
Benzo[*k*]fluoranthene-d12	BkF-d12	81.2
Benzo[*a*]pyrene-d12	BaP-d12	71.8
Indeno[*1,2,3-cd*]pyrene-d12	IcdP-d12	95.3
Dibenz[*a,h*]anthracene-d14	DbahA-d14	91.0
Benzo[*g,h,i*]perylene-d12	BghiP-d12	92.1

Table S6. Relative potency values of AhR-active compounds reported by previous studies.

Compounds	Relative potency value	Reference
PCDDs		
2,3,7,8-TCDD	1.0	Lee et al. (2013)
1,2,3,7,8-PeCDD	6.0×10^{-1}	
1,2,3,4,7,8-HxCDD	1.0×10^{-1}	
1,2,3,6,7,8-HxCDD	5.0×10^{-2}	
1,2,3,7,8,9-HxCDD	5.0×10^{-2}	
1,2,3,4,6,7,8-HpCDD	6.0×10^{-2}	
OCDD	5.0×10^{-4}	Behnisch et al. (2003)
PCDFs		
2,3,7,8-TCDF	3.0×10^{-1}	Lee et al. (2013)
1,2,3,7,8-PeCDF	2.0×10^{-2}	
2,3,4,7,8-PeCDF	5.0×10^{-1}	Behnisch et al. (2003)
1,2,3,4,7,8-HxCDF	1.3×10^{-1}	
1,2,3,6,7,8-HxCDF	3.9×10^{-2}	
2,3,4,6,7,8-HxCDF	1.8×10^{-1}	
1,2,3,7,8,9-HxCDF	1.1×10^{-1}	
1,2,3,4,6,7,8-HpCDF	1.0×10^{-2}	Lee et al. (2013)
1,2,3,4,7,8,9-HpCDF	4.1×10^{-2}	Behnisch et al. (2003)
OCDF	6.5×10^{-3}	
PBDD/Fs		
1,2,3,7,8-PeBDF	7.5×10^{-2}	Takigami et al. (2005)
2,3,7,8-TeBDE	6.5×10^{-1}	
2,3,4,7,8-PeBDF	6.9×10^{-2}	
DeBDE	5.4×10^{-6}	
Co-PCBs		
CB 77	1.0×10^{-4}	Van den Berg et al. (1998)
CB 81	3.0×10^{-3}	Lee et al. (2013)
CB 105	1.0×10^{-7}	
CB 114	5.0×10^{-6}	
CB 118	1.0×10^{-7}	
CB 123	1.0×10^{-5}	
CB 126	1.0×10^{-1}	
CB 156	2.0×10^{-5}	
CB 157	4.0×10^{-5}	
CB 167	1.0×10^{-9}	
CB 169	3.0×10^{-4}	
CB 189	1.0×10^{-9}	
DL-PAHs		
6-hydroxychrysene	2.9×10^{-5}	Villeneuve et al. (2002)
BaA	1.9×10^{-6}	
Chr	2.3×10^{-6}	
BbF	5.1×10^{-6}	
BkF	1.4×10^{-4}	
BaP	1.6×10^{-6}	
IcdP	1.5×10^{-5}	
DbahA	4.6×10^{-6}	
1-Methylchrysene	7.7×10^{-6}	Lee et al. (2015)
3-Methylchrysene	9.5×10^{-6}	
6-Ethylchrysene	8.0×10^{-7}	
Dibenzothiphene	1.1×10^{-8}	

Supplementary Figures

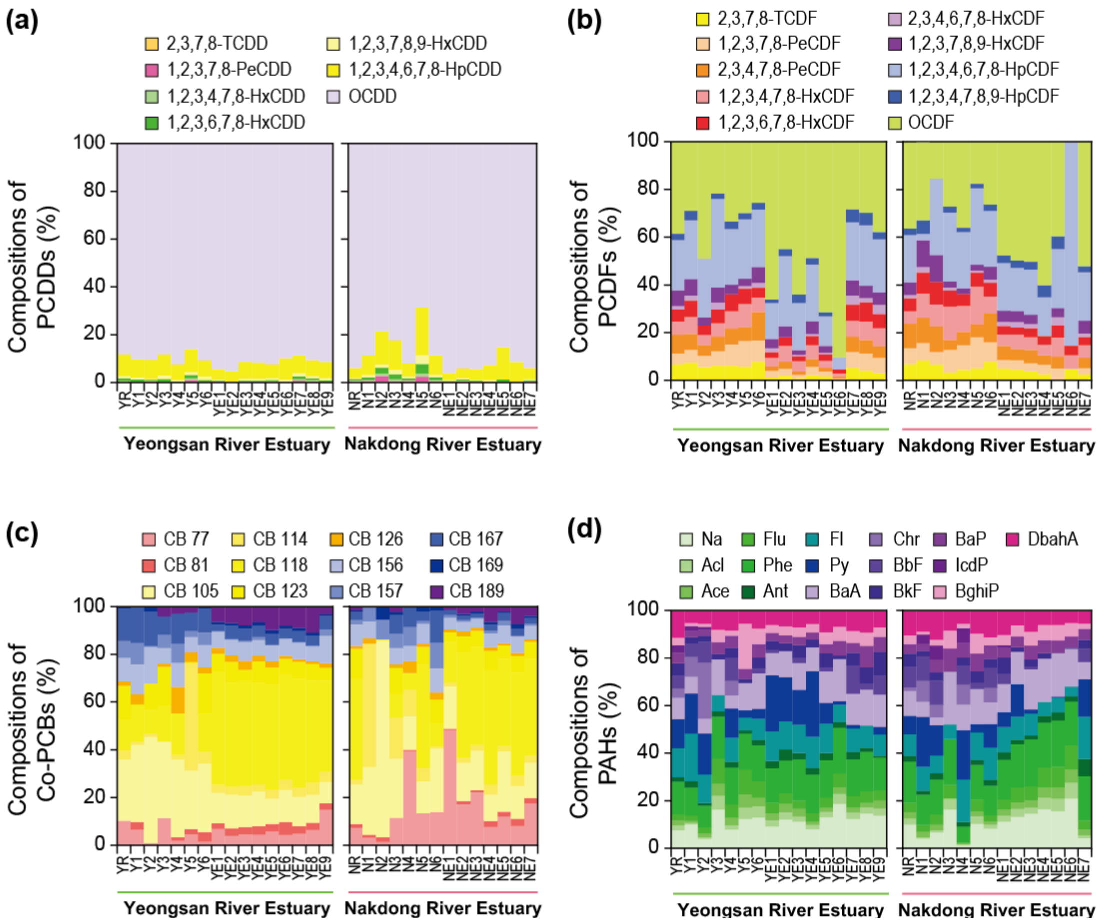

Fig. S1. Relative composition of individual PCDDs, PCDFs, Co-PCBs, and PAHs in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea.

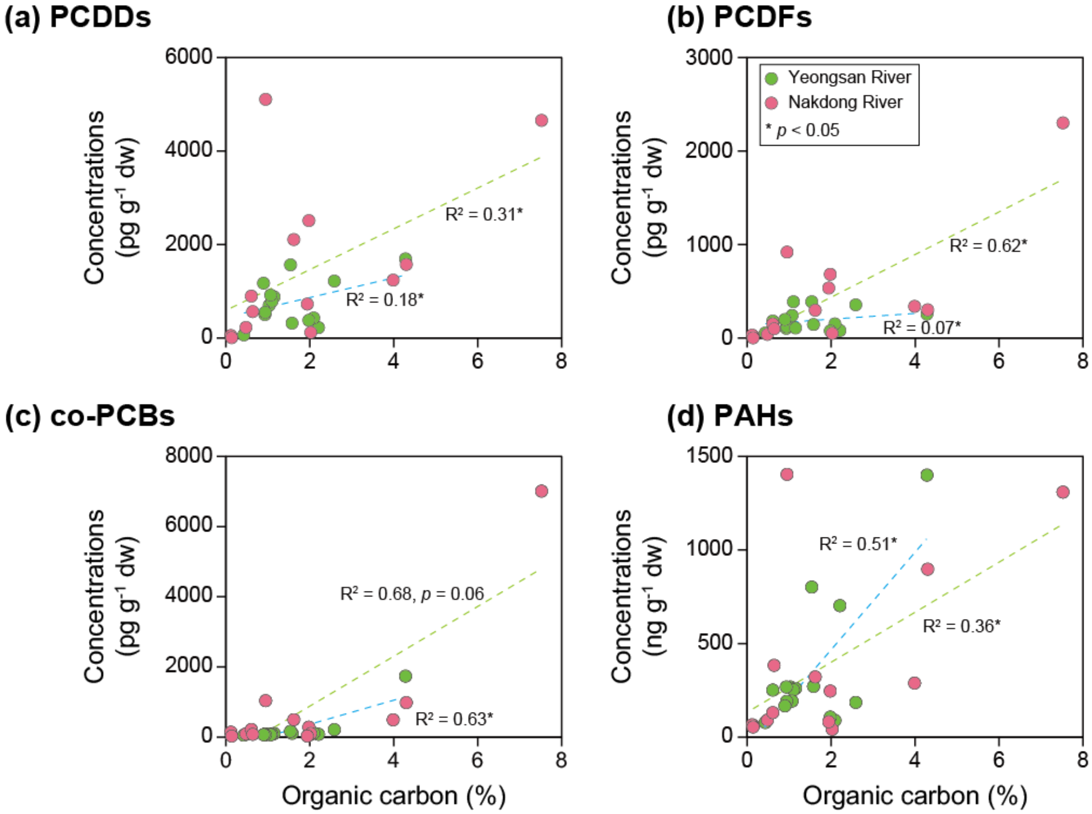

Fig. S2. Correlations between organic carbon content (%) and PCDDs, PCDFs, Co-PCBs, and PAHs in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea.

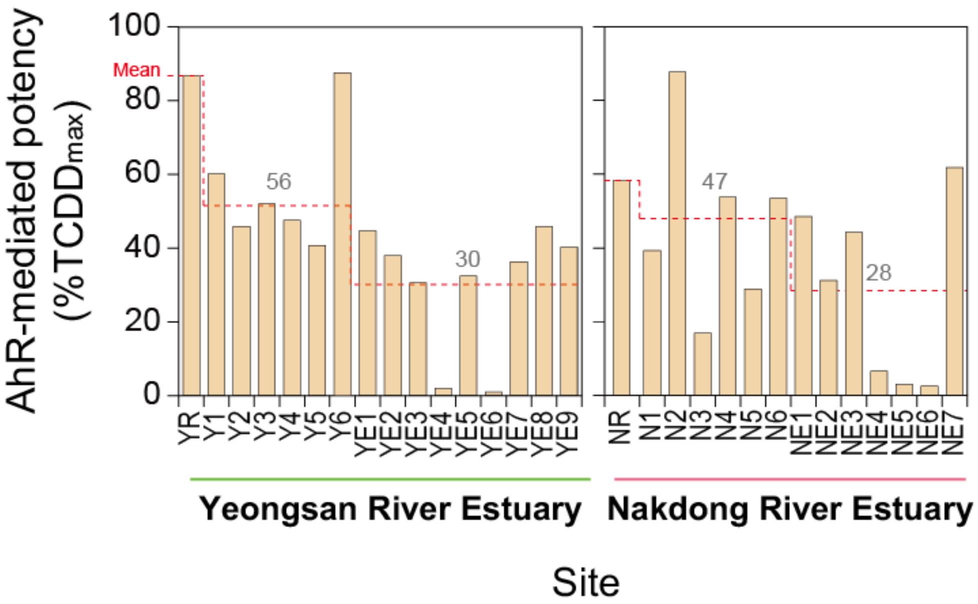

Fig. S3. Distributions of AhR-mediated potencies (%$TCDD_{max}$) in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea.

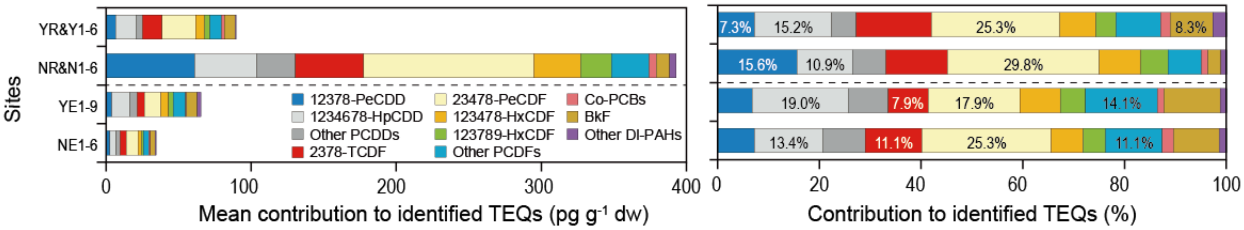

Fig. S4. Mean contribution of TCDD-EQs to identified TEQs (pg g^{-1} dw) and contribution to identified TEQs (%) in the sediments of the artificial lake, inland creeks, and estuarine areas in Yeongsan River and Nakdong River, South Korea.

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