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Sources and distribution of polychlorinated-dibenzo-*p*-dioxins and -dibenzofurans in soil and sediment from the Yellow Sea region of China and Korea

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PCDD/Fs in soils and sediments along the Yellow Sea indicated both point and non-point sources and their contribution to total TEQs differed among land uses and by regional activities.

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ABSTRACT

Polychlorinated-dibenzo-*p*-dioxins and -dibenzofurans (PCDD/Fs) were measured in soils and sediments from the Yellow Sea region. Korean soils and sediments mostly contained detectable PCDD/Fs and showed a widespread distribution among locations. Soil and sedimentary PCDD/Fs from China were comparable to or less than those in Korea. The patterns of relative concentrations of individual congeners in soils were different between the two countries, but similar in sediments. Sources of PCDD/Fs in China and Korea were found to be independent of each other and their distributions reflected matrix-dependent accumulation. Spatial distribution indicated some point sources in Korea while Chinese sources were more widespread and diffuse. PCDD/Fs measured in the coastal areas of the Yellow Sea were comparable to or less than those previously reported in for eastern Asia. However, ∑TEQs in soils and sediments were near to or, in some cases exceeded environmental quality guidelines.

1. Introduction

Polychlorinated-dibenzo-*p*-dioxins and -dibenzofurans (PCDD/Fs) are well-known toxic environmental contaminants that are released into the environment from numerous sources including municipal and industrial waste incineration, forest fires, as unwanted by-products from chlorinated chemical manufacturing, and from automobile exhaust (Lohmann and Jones, 1998; Kim et al., 2007). Some PCDD/Fs have been shown to be probable carcinogens, cause developmental toxicity, and disrupt normal endocrine function (Safe, 1990; White and Birnbaum, 2009). Due to their physical–chemical properties, PCDD/Fs are hydrophobic and in the absence of UV light, resistant to both environmental and biological breakdown, and as a result tend to accumulate in both soils and sediments (Hilscherova et al., 2003).

The Yellow Sea, together with nearby coastal and riverine areas, is a major commercial artery and has undergone significant urbanization and industrialization (Luo et al., 2010; Naile et al., 2010). Its proximity to Beijing, the capital of China, and other major Chinese and Korean cities including Seoul, the capital of South Korea, makes it one of the busiest seaways in the world. Benefiting from its rich resources and convenient transportation, the economic contribution of the Yellow Sea amounts to one tenth of the gross national product of China, and economists call the zone around the Bohai Sea "the golden necklace" of Northern China. Several rivers including the

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Table 1
Sample details including geographical descriptions and surrounding activities of all sampling locations from the Yellow Sea.

Sampling				Samples		Land uses				Remark
Country	Province or city	Region	Sites	Soil	Sediment	Agricultural	Industrial	Municipal	Others	Geographical description
South Korea	Gyeonggi	Lake Shihwa	LS1	O	O		O	O		Coastal area, outside of lake, Gyeonggi Bay
			LS2	NC[a]	NC		O	O		Coastal area, outside of lake, Gyeonggi Bay
			LS3	NC	NC		O	O		Inside of lake
			LS4	NC	NC		O	O		Inside of lake
	Chungnam	Asan	AS1	NC	O	O				Inside of lake
			AS2	O	O	O				Coastal area, outside of lake, Asan Bay
		Sapgyo	SG1	O	O	O				Inside of lake
			SG2	O	O	O				Coastal area, outside of lake, Asan Bay
		Taean	SD	O	O				O	Coastal area (beach), Sinduri
			ML	O	O				O	Coastal area (beach), Manlipo
			AM	O	O				O	Coastal area (beach), Anmyundo
	Chonbuk	Geum River	GG1	O	O	O				River, inside of dam
			GG2	O	O	O				Coastal area, outside of dam
	Chonnam	Yeongsan River	YS1	O	O			O		Coastal area, outside of dam
			YS2	O	O			O		River, inside of dam
	Total		15	11	12					
China	Tangshan	Dou River	TS1	O	O	O				Small river
		Qing Long River	TS2	O	O	O				Small river
		Shuang Long River	TS3	NC	O	O				Downstream of river
			TS4	O	O	O				Upstream of river
		Luanhe River	TS5	O	O				O	Coastal area (harbour), river mouth
			TS6	O	O	O				Downstream of river
			TS7	O	O	O				Upstream of river
	Qinhuangdao	Bohai Sea	QH1	NC	O				O	Coastal area (beach)
			QH2	O	O	O				Upstream of tidal flat
			QH3	NC	O	O				Coastal area (tidal flat)
			QH4	NA[b]	O				O	Coastal area (beach)
	Huludao	Tian Ma Lake	QH5	NA	O				O	Lake
		Bohai Sea	HL1	NC	O				O	Coastal area (beach)
		Liugu River	HL2	O	O	O				Small river
			HL3	O	O	O				Small river
	Jinzhou	Wu Li River	HL4	O	NA		O			Small river
		Bohai Sea	HL5	O	O				O	Coastal area (beach)
		Wuli River	JZ1	O	NC			O		Small river
		Xiaoling River	JZ2	O	O			O		Small river
		Daling River	JZ3	O	O	O				Upstream of river
			JZ4	O	NA		O			Midstream of river
			JZ5	O	O	O				Downstream of river
	Panjin	Shuangtaizi River	PJ1	O	O	O				Large river
		Bohai Sea	PJ2	NC	O				O	Coastal area (tidal flat)
	Yingkou	Daliao River	YK1	O	NA			O		Midstream of river
		Bohai Sea	YK2	O	NA		O	O		Coastal area (tidal flat)
			YK3	O	NA				O	Coastal area (beach)
	Dalian	Fuzhou River	DL1	NA	NA					Small river
			DL2	O	O				O	Small river
		Bohai Sea	DL3	NC	NC					Coastal area (rock beach)
			DL4	NC	O				O	Coastal area (beach)
	Dandong	Bilia River	DL5	O	O	O				Downstream of river
		Bohai Sea	DL6	O	O				O	Coastal area (tidal flat)
		Dayang River	DD1	O	O	O				Downstream of river
		Yalu River	DD2	O	O	O				Upstream of river
			DD3	O	NA		O			Downstream of river
			DD4	O	O				O	Midstream of river
	Total		37	27	28					

[a] NC: Not collected.
[b] NA: Not analyzed.

Yellow River, Liaohe River, Haihe River, Luanhe River and Dalinhe River from China and Han River, Geum River, and Yeongsan River from South Korea are major fresh water sources discharging directly into the Yellow Sea. The drainage areas of these rivers are important to both the agricultural and chemical production in the area. Rapid social and economic development has caused the area to become increasingly urbanized but also has lead to the area being contaminated with persistent organic pollutants (POPs). Because the Yellow Sea is a semi-enclosed system, water exchange with the Pacific Ocean is relatively slow; and as a result, persistent pollutants tend to accumulate. Thus, the Bohai Sea and West Sea of Korea are considered to be one of the most polluted marine environments in East Asia (Kim et al., 2007; Hu et al., 2010; Luo et al., 2010).

There have been studies of PCDD/Fs in other parts of China (Zheng et al., 2008) and Korea (Kim et al., 2007), but few studies have reported concentrations of these compounds from north coastal and riverine regions of the Yellow Sea, particularly the Bohai Sea area of China. Therefore, baseline information on concentrations of PCDD/Fs in soils and/or sediments was urgently needed to fully understand the present environmental quality, and whether there is any environmental risk to the area. Finally, the Chinese government has developed and implemented a program to meet obligations as

a signatory to the Stockholm Convention to control releases of POPs (Lu and Giesy, 2005). Specifically, the Chinese government has taken a number of actions to reduce releases of PCDD/Fs to the environment (Geng et al., 2010) so it was critical to have baseline information against which to assess the efficacy of these measures, both in China and in more remote regions such as Korea.

As part of an ongoing study to determine the current status and extent of organic contaminants, as well as the potential for detrimental environmental effects in the Yellow Sea region of China and Korea, soil and sediment samples were collected along the northeastern coast of China and western coast of South Korea during the spring of 2008. Locations were chosen to detect possible point sources, and determine distribution characteristics throughout the region. Concentrations of PCDD/Fs in soil and sediment samples, collected from estuarine and coastal areas of China and South Korea, were determined to assess the potential risk of these compounds pose to both humans and wildlife. Also the concentrations and distributions of soil and sedimentary PCDD/Fs were reviewed from previously reported data for China, South Korea, and Japan to provide a current understanding of PCDD/F pollution in East Asia.

2. Materials and methods

2.1. Sample collection

Soils and sediments collected from 38 and 40 locations, respectively, with different land uses, along the coastal areas of China and Korea during the spring of 2008 (Table 1 and Fig. 1) were analyzed for PCDD/Fs. Eleven soil and twelve sediment samples were collected from the western coast of Korea in April 2008. In the Bohai Sea area, twenty seven soil and twenty eight sediment samples were collected in May, 2008. Individual soil samples consisted of approximately 15 cm of top soil from a central point and 15 cm of top soil from each of four additional points located 10–20 m in the four primary directions (N, E, S, W) from the central point. Sediments were collected from rivers, lakes, or costal locations along the Yellow Sea using a stainless steel scoop at a depth of 0–10 cm. After collection, pebbles and twigs were removed. All samples were transported on ice at 4 °C to the laboratory and were frozen at −20 °C until analyses. Samples were freeze-dried and ground with a mortar and pestle, prior to analysis.

2.2. Sample preparation

Concentrations of PCDD/Fs were determined by isotope-dilution following EPA method 1613 (USEPA, 1994; Wan et al., 2010). Samples were freeze-dried and approximately 10 g dry weight (dw) were fortified with a mixture of ^{13}C-labeled PCDD and PCDF surrogates (Wellington Laboratories, Guelph, ON, Canada). Samples were then Soxhlet extracted with 400 ml of 1:1 hexane/dichloromethane (Omni-Solv grade, EMD Chemicals Gibbstown, NJ, USA) for 16 h and were rotary evaporated to ~10 ml. After extracts were treated with activated copper to remove sulfur then concentrated to near dryness at 35 °C. Extracts were then dissolved in 100 ml hexane, and treated with 20 ml of concentrated sulfuric acid three times in a separatory funnel. The retained upper hexane layer was then rinsed with two 20 ml aliquots of nanopure water before being dried by passage through anhydrous sodium sulfate. The extract was then concentrated to approximately 2 ml and sequentially subjected to silica gel, neutral alumina, and activated carbon-impregnated silica gel column chromatography as described in the EPA methods. The silica gel packed glass column was packed with 2 g of silica gel, 2 g of silica gel impregnated with sulfuric acid (60% w/w), 2 g of silica gel, in that order. After the application of the sample the column was eluted with 150 ml hexane. The hexane eluate was concentrated and passed through a neutral alumina column (4 g sodium sulfate, 4 g neutral alumina, 4 g sodium sulfate), eluted with 20 ml hexane and then with 25 ml 60% dichloromethane in hexane. The second fraction was concentrated and passed through an activated carbon-impregnated silica gel column (in the order of 0.5 g of activated carbon dispersed silica gel), and eluted with 100 ml of hexane, 100 ml 20% dichloromethane in hexane and 100 ml toluene. The final eluent of the carbon column was concentrated and fortified with ^{13}C-1,3,6,8-TeCDF and ^{13}C-1,2,3,4,6,8,9-HpCDF for analysis of PCDD/Fs.

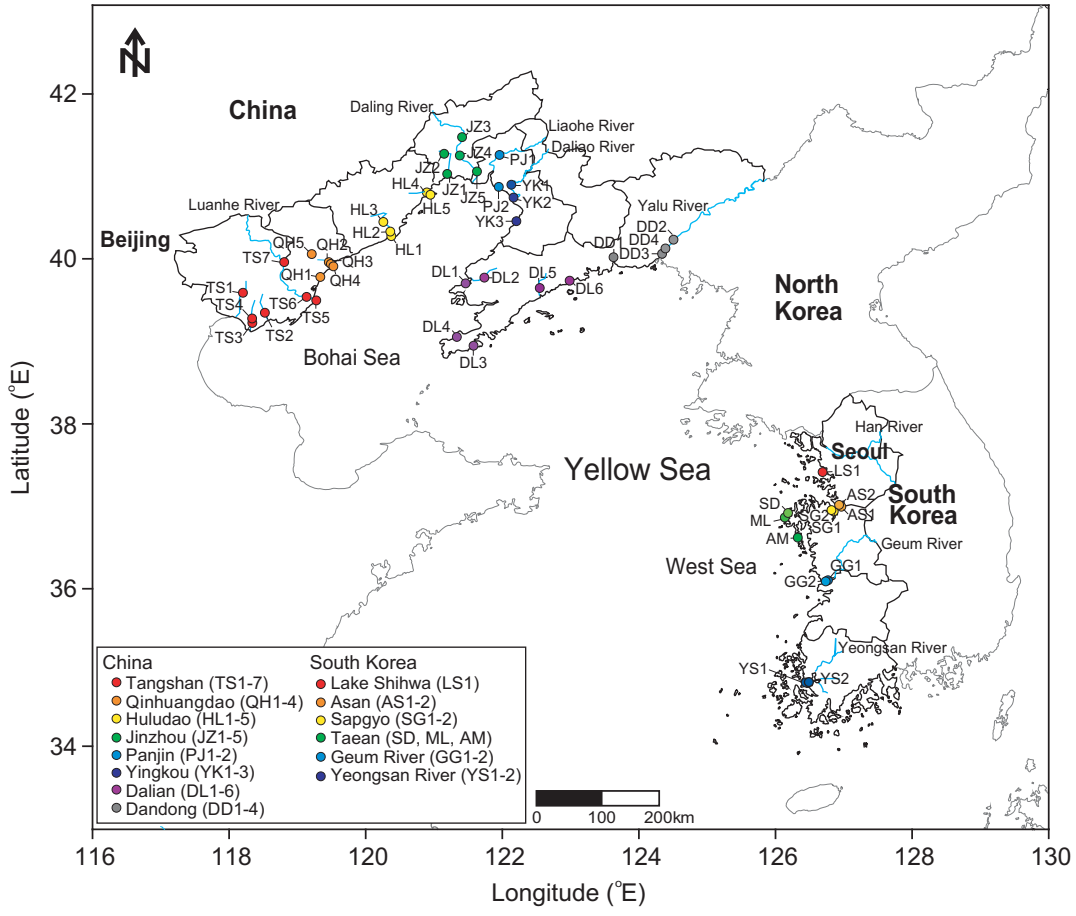

Fig. 1. Location map of soil and sediment samples collected from the rivers, lakes and coastal areas of the Yellow Sea.

Table 2
Overview of PCDD/Fs results for soil and sediment samples collected from the Yellow Sea.

Analytes	South Korea										China									
	Soil ($n = 11$)					Sediment ($n = 12$)					Soil ($n = 27$)					Sediment ($n = 28$)				
	Detected		Mean[a]	Max.	Max.	Detected		Mean	Max.	Max.	Detected		Mean	Max.	Max.	Detected		Mean	Max.	Max.
	n	(%)	(pg/g dw)	(pg/g dw)	Site	n	(%)	(pg/g dw)	(pg/g dw)	Site	n	(%)	(pg/g dw)	(pg/g dw)	Site	n	(%)	(pg/g dw)	(pg/g dw)	Site
2,3,7,8-TCDD	0	0	–	–	–	0	0	–	–	–	0	0	–	–	–	0	0	–	–	–
1,2,3,7,8-PeCDD	0	0	–	–	–	0	0	–	–	–	0	0	–	–	–	1	4	2.45	2.45	DD1
1,2,3,4,7,8-HxCDD	0	0	–	–	–	0	0	–	–	–	0	0	–	–	–	0	0	–	–	–
1,2,3,6,7,8-HxCDD	1	9	0.860	0.860	LS1	1	8	0.080	0.94	GG1	0	0	–	–	–	0	0	–	–	–
1,2,3,7,8,9-HxCDD	0	0	–	–	–	0	0	–	–	–	0	0	–	–	–	0	0	–	–	–
1,2,3,4,6,7,8-HpCDD	8	73	3.74	11.5	LS1	8	67	2.47	8.03	GG2	5	19	3.62	7.17	DD3	7	25	1.06	2.38	TS2
OCDD	10	91	26.6	75.9	GG2	7	58	27.2	117	GG2	23	85	17.4	50.5	DD2	21	75	13.1	42.4	DD4
∑PCDDs	11	100	27.0	78.6	GG2	8	67	29.8	125	GG2	23	85	12.3	50.5	DD2	22	79	8.14	42.4	DD4
2,3,7,8-TCDF	3	27	1.67	2.87	LS1	1	8	0.070	0.82	AS2	5	19	3.29	7.93	DL6	5	18	2.73	10.3	JZ2
1,2,3,7,8-PeCDF	3	27	1.49	2.58	LS1	2	17	0.150	1.09	AS2	1	4	2.08	2.08	HL4	3	11	0.480	0.656	QH3
2,3,4,7,8-PeCDF	3	27	2.15	4.30	LS1	0	0		–	–	3	11	1.78	3.96	HL4	2	7	0.660	0.650	QH3
1,2,3,4,7,8-HxCDF	5	45	1.95	5.16	LS1	2	17	0.300	2.18	AS2	4	15	2.15	4.38	HL4	4	14	0.510	0.440	TS1
1,2,3,6,7,8-HxCDF	1	9	4.01	4.01	LS1	2	17	0.150	1.09	AS2	3	11	1.53	2.71	HL4	1	4	0.310	0.310	TS3
2,3,4,6,7,8-HxCDF	5	45	2.12	6.59	LS1	1	8	0.060	0.710	GG1	2	7	1.26	1.67	HL4	3	11	0.660	0.960	QH1
1,2,3,7,8,9-HxCDF	1	9	1.72	1.72	LS1	1	8	0.070	0.800	YS1	1	4	1.25	1.25	HL4	0	0	–	–	–
1,2,3,4,6,7,8-HpCDF	9	82	5.23	25.0	LS1	7	58	1.66	5.44	AS2	11	41	4.69	22.3	HL4	11	39	2.04	5.20	JZ2
1,2,3,4,7,8,9-HpCDF	2	18	2.83	4.59	LS1	3	25	0.190	0.800	YS1	2	7	1.89	3.13	HL4	0	0	–	–	–
OCDF	9	82	6.80	39.6	LS1	9	75	2.81	10.6	GG2	8	30	16.8	59.8	YK1	10	36	3.41	15.4	TS3
∑PCDFs	10	91	14.2	96.4	LS1	9	75	5.45	17.1	AS2	12	44	6.78	104	HL4	14	50	2.21	15.5	JZ2

[a] Mean: average values of detected PCDD/Fs.

2.3. Instrumental conditions

Identification and quantification of PCDD/Fs were performed using a Hewlett–Packard 5890 series high-resolution gas chromatography interfaced with a Micromass® Autospec® high-resolution mass spectrometer (HRGC–HRMS) (Micromass®, Beverly, MD). Chromatographic separation was achieved on a DB-5MS fused silica capillary column (60 m length, 0.25 mm ID, 0.1 μm film thickness, Agilent, CA). After an initial hold of 2 min the oven temperature was raised to 150 °C at a rate of 15 °C/min, then to 270 °C at a rate of 3 °C/min, and then at 40 °C/min to 300 °C followed by a final 5 min hold. The mass spectrometer was operated in a Selected Ion-Monitoring (SIM) mode. The resolution for all reference gas peaks in all time windows was more than 10,000 for PCDD/Fs. The injector temperature was held at 285 °C and the ion source was kept at 285 °C. The electron-impact ionization energy was 37 eV and the trap current was 750 μA.

Table 3
Concentrations (pg/g dw) of PCDD/Fs in soil samples reported in the Far East Asia including China, South Korea, and Japan.

Sampling location	Year	n	PCDDs[a]			PCDFs[b]			References
			Mean	Min	Max	Mean	Min	Max	
China									
Daliao River Basin	2005	17	224	3.20	2070	606	6.40	7980	Zhang et al., 2008
Taizhou	–	4	188	66.8	362	40.1	6.98	66.1	Liu et al., 2007
Tangshan	2008	6	17.0	ND[c]	44.5	1.13	ND	5.60	This study
Qinhuangdao	2008	1	10.1			ND			This study
Huludao	2008	4	13.0	8.50	19.6	33.1	5.30	104	This study
Jinzhou	2008	5	15.9	5.20	27.3	2.09	ND	5.20	This study
Panjin	2008	1	ND			ND			This study
Yingkou	2008	3	11.0	ND	22.6	22.8	ND	68.4	This study
Dalian	2008	3	15.0	4.20	27.6	4.55	ND	11.9	This study
Dandong	2008	4	22.1	ND	50.5	0.179	ND	0.720	This study
South Korea									
Masan and Changwon Cities	1994	23	1280	19.0	20300	1830	2.50	38000	Im et al., 2002
Bucheon City	1997	11	249	6.90	840	273	9.00	1160	Oh et al., 2006
Pyungtak City	–	4	131	10.1	427	193	9.32	736	Kim et al., 2005
Lake Shihwa	2008	1	50.2			96.3			This study
Asan	2008	1	7.70			5.10			This study
Sapgyo	2008	2	6.80	ND	13.6	5.80	0.81	10.7	This study
Taean	2008	3	22.0	3.47	53.3	4.00	ND	7.54	This study
Geum River	2008	2	43.3	7.95	78.6	4.00	2.05	6.05	This study
Yeongsan River	2008	2	36.1	35.1	37.2	11.5	4.10	18.9	This study
Japan									
Tokyo Bay	1996	1	1110			499			Sakurai et al., 2000
Akita	2002	9	71900	1830	490000	719	53.1	3370	Kiguchi et al., 2007
Niigata	2004	10	33900	5890	145000	1430	407	2870	Sakai et al., 2008

[a] PCDDs = 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.
[b] PCDFs = 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.
[c] ND: not detected.

2.4. Quality assurance and quality control (QA/QC)

The QA/QC was conducted following EPA methods (USEPA, 1994). Concentrations of all congeners were quantified by the internal standard isotope-dilution method using mean relative response factors determined from standard calibration runs. All equipment rinses were carried out with acetone and hexane to avoid sample contamination and a laboratory blank, a matrix spike and a certified reference material (Wellington Laboratories) were incorporated in the analytical procedure for every batch of 20 samples. Co-elution of non-2,3,7,8-substituted congeners were checked with a resolution testing mixture standard (Wellington Laboratories) after injections of standards, and no interference was found in all samples. Recoveries of ^{13}C-labeled PCDD/F internal standards were within ranges specified by the EPA methods. The limits of quantification (LOQ) were defined as the least concentration that can be detected with signal-to-noise ratio of 3:1 in samples. The LOQ were generally 0.1–0.2 pg/g dw for TeCDD/Fs, PeCDD/Fs, HxCDDs/Fs and HpCDD/Fs, 0.2–0.4 pg/g dw for OCDD and OCDF.

2.5. Data analysis

To be comparable to the previous reports, concentrations of PCDD/Fs in soils and sediments are reported on a dry weight basis (Tables 2–4) and compared to those reported for China, South Korea, and Japan. A total of 17 reports were available to which the results reported here could be compared. To further evaluate the potential risk of PCDD/Fs in soils and sediments, the toxic equivalents (TEQs) for PCDD/Fs were calculated as the sum of the products of concentrations of individual congeners multiplied by their respective 2005 World Health Organization (WHO) toxic equivalency factors (TEF_{WHO}) (Van den Berg et al., 2006). Since no guidelines have been suggested in China or South Korea, the resulting 2,3,7,8-TCDD Equivalents (TEQ_{WHO}) were compared to currently available soil and sediment quality guidelines from various other Asian countries (Table 5). Patterns of relative concentrations of individual PCDD/Fs and their TEQs in soils and sediments were also utilized to identify potential sources and influences of different land uses (Figs. 2–4). Principal component analysis (PCA; SPSS for Windows 6.0.1) was performed to identify specific sources of PCDD/Fs in Yellow Sea soils and sediments. Finally, the overall spatial distribution of TEQ concentrations of PCDD/Fs in soils and sediments was evaluated to demonstrate a geographical distribution in Far East Asia including the Yellow Sea region.

3. Results and discussion

3.1. PCDD/Fs concentrations in the Yellow Sea

Both soils and sediments collected in China contained detectable concentrations of PCDDs (80%) and PCDFs (50%) (Table 2). The mean concentration of ∑PCDDs (sum of 7 congeners measured) in soil was 12.3 pg/g dw with individual concentrations as great as 50.5 pg/g dw at location DD2. The mean concentration of ∑PCDFs (sum of 10 congeners measured) in soil was 6.78 pg/g dw with a maximum concentration of 104 pg/g dw at location HL4. Concentrations of PCDD/F in sediments were less than those in soils. The mean concentrations of ∑PCDD and ∑PCDF in sediments were 8.14 pg/g dw and 2.21 pg/g dw, respectively. There was

Table 4
Concentrations (pg/g dw) of PCDD/Fs in sediment samples reported in the Far East Asia including China, South Korea, and Japan.

Sampling location	Year	*n*	PCDDs[a]			PCDFs[b]			References
			Mean	Min	Max	Mean	Min	Max	
China									
Haihe River	2008	10	1660	38.8	10100	139	24.6	705	Liu et al., 2007
Daliao River Basin	2008	13	220	11.6	1780	405	8.50	1900	Zhang et al., 2008
Taizhou	2008	6	128	21.8	240	141	8.30	515	Liu and Liu, 2009
Qingdao	2008	1	7.23			4.67			Pan et al., 2010
Rizhao	2008	1	19.9			7.49			Pan et al., 2010
Yantai	2008	1	4.61			1.58			Pan et al., 2010
Liaohe river	2008	15	22.6	1.80	102	14.2	1.40	64.8	Zhang et al., 2010
Tangshan	2008	7	8.34	ND[c]	21.0	4.61	ND	20.5	This study
Qinhuangdao	2008	5	8.71	ND	18.0	2.70	ND	12.1	This study
Huludao	2008	4	5.97	ND	12.5	0.221	ND	0.900	This study
Jinzhou	2008	3	10.7	ND	26.4	5.61	ND	15.5	This study
Panjin	2008	2	5.45	5.20	5.70	1.25	ND	2.50	This study
Dalian	2008	4	13.9	ND	37.8	ND	ND	6.29	This study
Dandong	2008	3	22.7	2.50	42.4	1.65	ND	4.96	This study
South Korea									
Yeongil Bay	2000–2002	20	3.38			4.04			Moon et al., 2008
Ulsan Bay	2000–2002	20	1.25			1.76			Moon et al., 2008
Busan Bay	2000–2002	21	2.57			3.72			Moon et al., 2008
Jinhae Bay	2000–2002	26	2.52			4.24			Moon et al., 2008
Gwangyang Bay	2000–2002	35	0.630			0.630			Moon et al., 2008
Hyungsan River	2001	6	279	2.60	1150	190	2.20	633	Koh et al., 2004
Han River	2006	18	71.5	44.0	82.6	28.5	17.3	56.0	Kim et al., 2009
Masan Bay	2006	5	620	229	1590	728	31.0	3100	Hong et al., 2009
Lake Shihwa	2008	1	ND			ND			This study
Asan	2008	2	32.1	1.00	63.1	9.84	2.50	17.1	This study
Sapgyo	2008	2	24.8	22.1	27.5	4.23	3.20	5.20	This study
Taean	2008	3	ND			0.431	ND	1.30	This study
Geum River	2008	2	113	101	125	15.2	14.6	15.8	This study
Yeongsan River	2008	2	9.12	8.40	9.90	2.77	1.00	4.50	This study
Japan									
Tokyo Bay	1995	7	7290	2030	14100	874	375	1560	Sakurai et al., 2000
Toyano lagoon	2003	5	12300	253	12800	426	9.10	1160	Sakai et al., 2008
Yoneshirogawa River	2003	7	228	12.9	1210	6.57	0.700	38.5	Kiguchi et al., 2007
Omonogawa River	2003	9	157	11.0	1290	4.78	0.200	37.4	Kiguchi et al., 2007
Koyoshigawa River	2003	5	133	11.5	304	6.06	2.80	11.9	Kiguchi et al., 2007
Osaka	2004	8	3650			3090			Kishida et al., 2010
Ariake Bay	2005	2	7070	3920	10200	897	450	1340	Kim et al., 2008

[a] PCDDs = 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.
[b] PCDFs = 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.
[c] ND: not detected.

Table 5
Soil and sediment quality guidelines (pg TEQ_{WHO}/g) for PCDD/Fs currently being used in various countries and number of samples associated with corresponding guidelines for the reported data in the Far East Asian countries (China, South Korea, and Japan) including this study.

Guidelines				China			South Korea			Japan
Matrix	Country	PCDD/Fs pg TEQ_{WHO}/g	Remark	This study	Previous study	Total	This study	Previous study	Total	Previous study
				$n = 27$	$n = 21$	$n = 48$ (%)	$n = 11$	$n = 38$	$n = 49$ (%)	$n = 20$ (%)
Soil	Canada[a]	<4	All land uses	27	11	38 (79)	10	15	25 (51)	0 (0)
	Germany[b]	<5	Target concentration	27	12	39 (81)	11	16	27 (55)	0 (0)
		5–40	Control of products if dioxin transfer	0	8	8 (17)	0	16	16 (33)	3 (15)
		40–100	Children playgrounds	0	1	1 (2)	0	4	4 (8)	5 (25)
		100–1000	Residential soils	0	0	0 (0)	0	1	1 (2)	11 (55)
		1000–10000	Industrial soils	0	0	0 (0)	0	1	1 (2)	1 (5)
	Japan[c]	<1000		27	21	48 (100)	11	37	48 (98)	19 (95)
	New Zealand[d]	<10	Agricultural	27	19	46 (96)	11	23	34 (69)	0 (0)
		10–1500	Residential	0	2	2 (4)	0	14	14 (29)	19 (95)
		1500–18000	Industrial (unpaved)	0	0	0 (0)	0	1	1 (2)	1 (5)
		18000–21000	Industrial (maintenance)	0	0	0 (0)	0	0	0 (0)	0 (0)
		21000–90000	Industrial (paved)	0	0	0 (0)	0	0	0 (0)	0 (0)
	Sweden[e]	<10	Sensitive uses	27	19	46 (96)	11	23	34 (69)	0 (0)
		10–250	Non-sensitive uses	0	2	2 (4)	0	14	14 (29)	17 (85)
	The Netherlands[f]	<1	Agricultural farming	27	6	33 (69)	9	3	12 (24)	0 (0)
		1–10	Dairy farming	0	13	13 (27)	2	20	22 (45)	0 (0)
	United Kingdom[g]	<8	Residential, allotment	27	17	44 (92)	11	18	29 (59)	0 (0)
		8–240	Commercial	0	4	4 (8)	0	19	19 (39)	16 (80)
	United States[h]	<50	Screening level	27	20	47 (98)	11	33	44 (90)	6 (30)
		50–1000	Evaluation level	0	1	1 (2)	0	4	4 (8)	13 (65)
		>1000	Actionable level	0	0	0 (0)	0	1	1 (2)	1 (5)
				$n = 28$	$n = 54$	$n = 82$ (%)	$n = 12$	$n = 29$	$n = 41$ (%)	$n = 35$ (%)
Sediment	Canada[i]	<0.85		27	13	40 (49)	9	1	10 (24)	15 (43)
	United States[j]	0–10	Possessing no	28	37	65 (79)	12	24	36 (88)	23 (66)
		10–20	Lowest possible	0	5	5 (6)	0	1	1 (2)	1 (3)
		20–30	Possible	0	6	6 (7)	0	0	0 (0)	2 (6)
		30–50	Possible/probable	0	3	3 (4)	0	1	1 (2)	3 (9)
		50–80	Definite risk to aquatic organisms	0	0	0 (0)	0	0	0 (0)	4 (11)
	Japan[c]	<150		28	52	80 (98)	12	26	38 (93)	34 (97)

[a] CCME, 2002.
[b] Fiedler, 2003.
[c] MOE Japan 2003.
[d] Müller et al., 2004.
[e] UNEP, 1999.
[f] UNEP, 1999.
[g] Environmental Agency, 2009.
[h] De Rosa et al., 1999.
[i] CCME, 2001.
[j] Zhang et al., 2009.

a positive association between concentrations of PCDD/Fs soils and sediments within a region.

In Korea, concentrations of PCDDs (100%) and PCDFs (91%) were detectable in most soils (Table 2). The percent-occurrence of PCDD/Fs in sediment was 70%, which was comparable to the rate of detection in soils from China. In general, concentrations of PCDD/Fs in Korean soils and sediments were greater than those in China. The mean concentration of ∑PCDDs in soils was 27.0 pg/g dw with individual concentrations as great as 78.6 pg/g dw at location GG2, The mean concentration of ∑PCDFs in soils was 14.2 pg/g dw with a maximum of 96.4 pg/g dw at location LS1. Concentrations of ∑PCDDs in sediment were similar to corresponding soil concentrations with a mean of 29.8 pg/g dw, while the mean concentration of ∑PCDFs in sediment (5.45 pg/g dw) was approximately three-fold less than the corresponding concentrations in soils.

Several consistent trends in patterns of concentrations of PCDD/Fs were observed in terms of matrix (soil versus sediment) or sampling area (China and Korea). First, concentrations of PCDDs were greater than those of PCDFs in both soils and sediments. Second, only selected PCDD congeners (mostly more chlorinated) were detected in either soils or sediments, but all *tetra*- through *octa*-chlorinated PCDFs were detected in all soils and sediments. These trends were consistent regardless of sampling area and/or locations, and were the same in China and Korea. Third, soils contained relatively greater (or at least comparable) concentrations of PCDD/Fs than corresponding sediments within a location. Fourth, maximum concentrations of individual congeners in soils were found in limited areas or locations, but those in sediment were found in various sampling locations. The last two trends were observed in samples from both China and Korea. Overall, concentrations of PCDD/Fs were greater in soils and sediments from Korea than those from China.

3.2. PCDD/Fs composition in the Yellow Sea

Patterns of relative concentrations of PCDD/Fs in soils and sediments were investigated relative to geography and surrounding human activities (Fig. 2). The patterns of relative concentrations were different between China and Korea. While relative proportions of individual PCDD/Fs in soils from China and Korea were similar in terms of geographical types, such as rivers or coastal areas variations were found when comparing their composition in terms of nearby activities (Fig. 2).

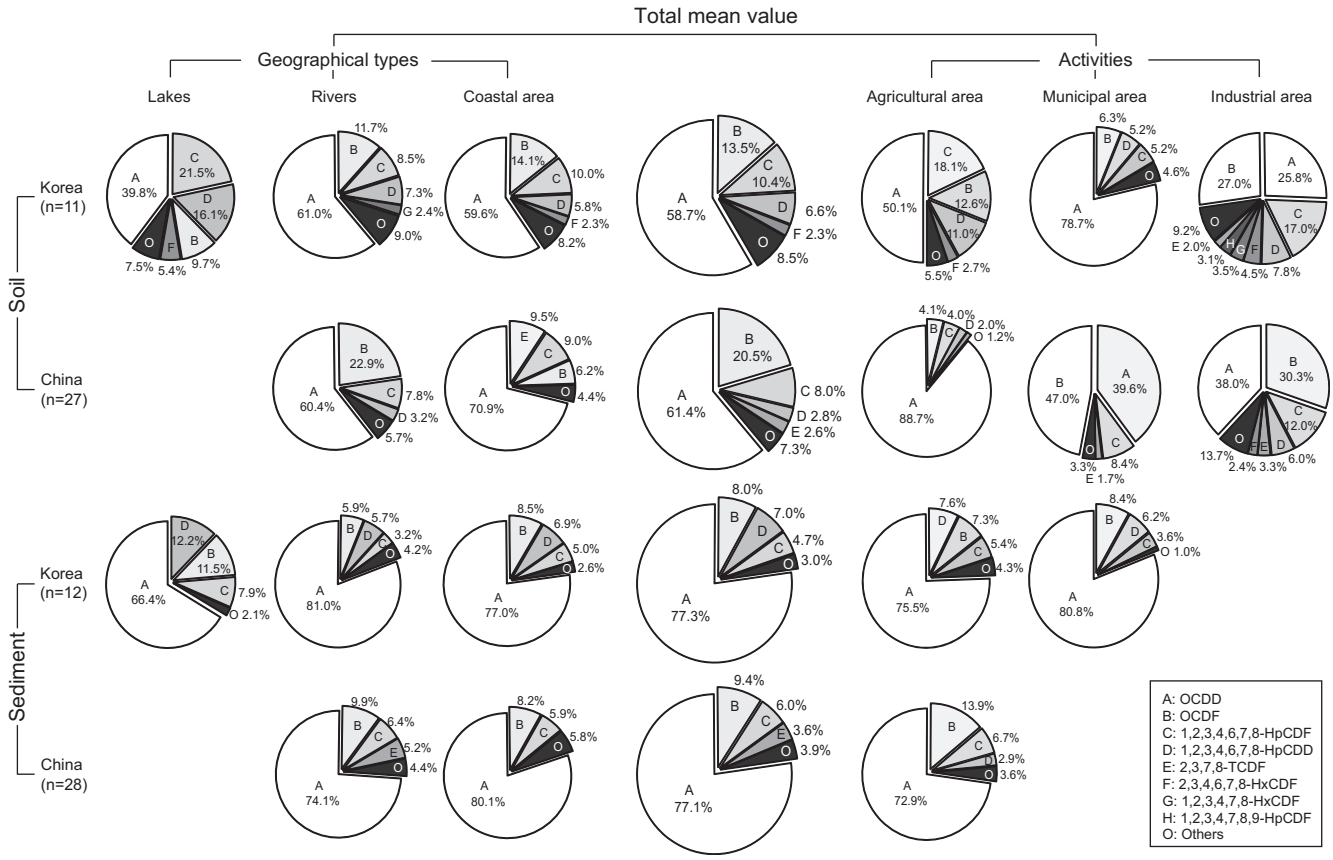

Fig. 2. Relative percentage of individual PCDD/Fs congeners in soil and sediment samples according to geographical types and activities (see Table 1) of the Yellow Sea.

Patterns of relative concentrations of PCDD/Fs in sediment were similar among geographical or land use types. The homologue composition(s) of PCDDs and PCDFs can be affected by factors other than source, such as physicochemical properties (mobility and solubility) and biological characteristics (biodegradation and bioaccumulation) (Lohmann and Jones, 1998; Hilscherova et al., 2003). Thus, the composition of PCDD/Fs even under similar land use activities would not necessarily be expected to be similar in China and Korea. However, the patterns of relative concentrations of PCDD/F congeners were similar in sediments from China and Korea. Considering the differences in local activities between the two countries, sources of PCDD/Fs were expected to be different between China and Korea (Table 1). The similar pattern of relative concentrations of PCDD/F of sediments observed in the present study may indicate the result of redistribution of PCDD/Fs after exposure. Such a result could be due to weathering, transportation followed by deposition of PCDD/Fs into air, water column followed by sedimentation (Lohmann and Jones, 1998).

Patterns of relative concentrations of individual PCDD/Fs between matrices, viz., in soils and sediments, were somewhat different in their accumulation. For example, concentrations of OCDD and HpCDD were greater in sediment than soil and OCDF and HpCDF concentrations were less in sediment than soil. The lesser proportion of more chlorinated PCDFs in sediment could be explained by the

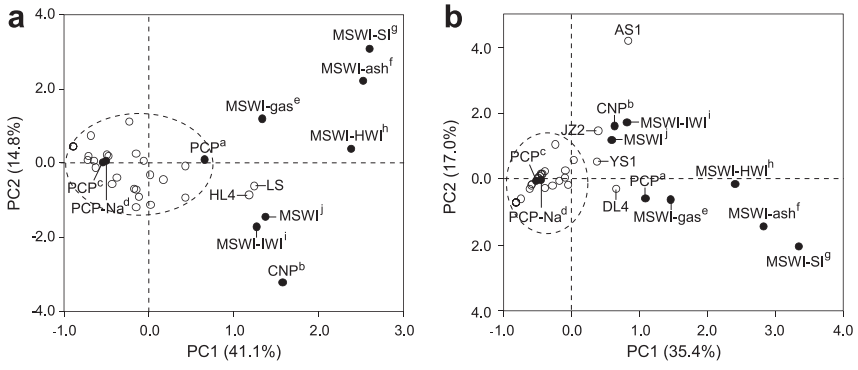

Fig. 3. Result of principal component analysis of individual PCDD/Fs in (a) soil and (b) sediment samples (○) collected from Yellow Sea regions and in representative sources (●) ([a]PCP: pentachlorophenol; [b]CNP: chloronitrophen (Masunaga et al., 2001a); [c]PCP: pentachlorophenol; [d]PCP-Na: sodium pentachlorophenate (Zhang et al., 2010); [e]MSWI-gas: municipal solid waste incinerators in China, flue gas; [f]ash: fly ash in China (Xu et al., 2008); [g]SI: small size incinerator in Korea; [h]HWI: hospital waste incinerator in Korea; [i]IWI: industrial waste incinerator in Korea; [j]MSWI in Korea (Oh et al., 1999)).

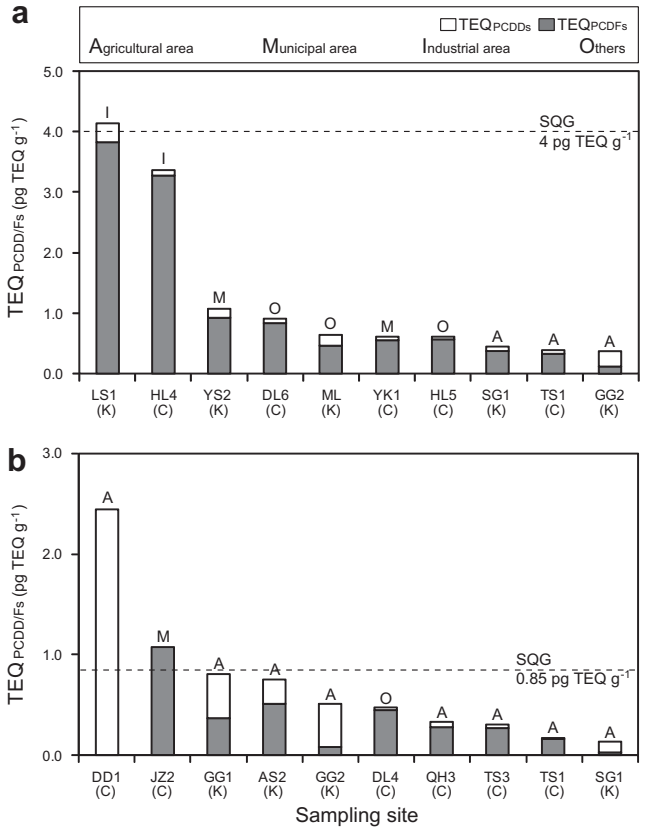

Fig. 4. Top ten greatest TEQs of PCDD/Fs and locations from (a) soils and (b) sediments analyzed in the present study (K: South Korea; C: China; dotted line: Canadian soil/sediment quality guidelines (CCME, 2001, 2002)).

slow mobility compared to less chlorinated PCDFs such as TeCDF and HxCDF (Kannan et al., 1998). While, the larger proportion of more chlorinated dioxins in sediment could have resulted from continuing sources and/or the use of some precursor compounds such as chlorophenols (Masunaga et al., 2001b). Also, lesser water solubility and greater affinity to fine particles of highly chlorinated dioxins, such as OCDD, could result in relatively long term accumulation, particularly in organic rich sediment, explaining the greater proportion of OCDD to total PCDDs (Sinkkonen and Paasivirta, 2000).

To clearly understand the more specific information on the sources of PCDD/Fs in the Yellow Sea, the profiles of individual PCDD/Fs from Yellow Sea regions were compared with those of known sources reported from earlier literature. The source profiles compared in this study include, some herbicides (pentachlorophenol (PCP), chloronitrophen (CNP), and sodium pentachlorophenate (Na-PCP)) and combustion gases (municipal solid waste incinerators (MSWI)) of China and Korea. The plot of principal components could cluster the locations into one major group and some scattered group locations both for soil and sediment data (Fig. 3). The major group of locations was clearly associated with PCP and NA-PCP both for soil and sediment data, indicating common PCDD/Fs sources of Yellow Sea samples from mainly herbicides. Some other locations for soil allocated in a separate group were LS (Korea) and HL4 (China), of which locations were near the industrial areas of Korea and China, respectively. Likewise several of locations such as YS1 (Korea), JZ2 and DL4 (China) situated near municipal regions reflected combustion sources rather than herbicides, which shows a good agreement between local activities and PCDD/Fs congener composition.

Such differences in composition of PCDD/Fs between soil and sediment would be expected in aquatic and terrestrial environments, thus critical identification of sources and understanding of physicochemical and biological processes in target areas would be necessary. Overall, the present study indicated that the sources of PCDD/Fs in China and Korea are independent of each other and their distributions reflected local activities and matrix-dependent accumulation.

3.3. PCDD/Fs distributions in the Yellow Sea

In general, concentrations of PCDD/Fs in Korean soils were greater than those in China with the concentration of TEQ_{WHO} from one location in South Korea (LS1) exceeding the Canadian soil quality guideline of 4 pg TEQ_{WHO}/g dw. Of the 11 Korean locations studied, 5 locations (LS1, YS2, ML, SG1, and GG2) were ranked within the top ten locations of greatest concentrations of TEQs while only 5 of 28 locations from China were found to be within the top ten locations of greatest concentrations of ∑PCDD/F (Fig. 4a). The spatial distribution of PCDD/Fs in Korean soils indicated some point sources contributing both ∑PCDDs (50.2 pg/g dw) and ∑PCDFs (96.3 pg/g dw) at location LS1 (Lake Shihwa), situated near the industrialized and populated coastal cities of Ansan and Shiheung in the Seoul region. However, concentrations of ∑PCDDs or ∑PCDFs (<100 pg/g dw) from the surveyed locations in Korea were as much as 100-fold less than previously reported concentrations in soil (several hundred ppb or ppm) from the inland cities of Pyungtak, Bucheon, and Masan (Table 3). Meanwhile spatial distribution of soil PCDD/Fs in China did not indicate identifiable point sources, but rather indicated widespread distribution but lesser degrees of contamination across the northern coasts of China. The greatest proportion of TEQs was contributed by PCDFs in soils in Korea and China, and was not clearly associated with known information on land uses at this time.

Relatively great concentrations of ∑PCDD/Fs in sediments from both South Korea and China were observed, but only two Chinese locations exceeded the Canadian sediment quality guideline of 0.85 pg TEQ_{WHO}/g dw. However, concentrations of PCDD/Fs in Chinese sediments collected in the present study were less than those previously reported in China (Table 4), which suggests a relatively small accumulation in river or coastal sediments along the northern coasts of China. The contribution of PCDDs and/or PCDFs to TEQ_{WHO} in sediment differed among land uses, some sources were associated with agricultural activities (Fig. 4b) and general combustion would be the major sources in China. Generally, concentrations of PCDD/Fs in sediments were related to industrial and/or agricultural activities around the sampling locations or areas in the Yellow Sea.

3.4. Comparison to other studies

Although PCDD/Fs are one of the classic POPs and have been of concern in Asian countries, their concentrations and distribution in soils have not been fully documented. Since the 1990s, only a few studies have reported concentrations of PCDD/Fs in soils of east Asian countries, including China, South Korea, and Japan (Table 3). The present study reports for the first time concentrations of PCDD/Fs for many areas of interest along the coastal areas of the Yellow Sea. Overall, concentrations of PCDD/Fs were found to be least in the order of China, South Korea, and Japan. These results are in agreement with the magnitudes and durations of industrialization among these three countries. However, the maximum concentrations reported in each country were comparable which indicated comparable sources to the environment in these countries. Although there are limited data available for comparison, a positive correlation between concentrations of PCDDs and PCDFs in soil

among countries is suggestive of common sources. Overall, concentrations of TEQ_{WHO} for PCDD/Fs in soil from the Yellow Sea region were less than current concentrations in other locations in South Korea and Japan (Fig. 5).

While limited studies of soil pollution are available, there are considerably more studies addressing concentrations of PCDD/F in sediment of China, South Korea, and Japan. A total of 14 previous reports and the present study cover many of coastal areas in the three countries for sediment PCDD/Fs. Thus, spatial comparisons of concentrations of sediments among countries and locations can be made (Table 4). For sediment, relatively large variations in concentrations of PCDD/Fs were found in China and South Korea with a few areas of greater concentrations (ppb levels) near more industrialized cities such as Tianjin City, China (Liu et al., 2007) and Masan City, Korea (Hong et al., 2009) (Fig. 6). Japanese sediments contained greater concentrations of PCDD/Fs, particularly the greatest concentrations found in Tokyo Bay, which is known as one of the most polluted bays in Asia (Sakurai et al., 2000). However, when expressed as TEQ_{WHO}, sediment from the Hyeongsan River contained the greatest concentration of 204 pg TEQ_{WHO}/g dw (Koh et al., 2004), which was far above the Canadian sediment quality guideline of 0.85 pg TEQ_{WHO}/g dw. Overall, most of the previously surveyed locations in the three countries exceeded the corresponding quality guidelines, which demonstrate the existence of locations with severe and continuing pollution with PCDD/Fs in the east Asia.

3.5. Potential for biological and ecological effects

Currently in South Korea and China, there are no environmental quality guidelines established for PCDD/Fs. Therefore, our results were compared to soil and sediment guidelines from various other countries. Available soil and sediment guidelines from various countries including Japan were compiled to evaluate the current status of PCDD/Fs pollution in the Yellow Sea (Table 5).

When compared to Canadian guidelines, which are one of the more stringent guidelines, 51% of Korean soils ($n = 49$) and 79% of Chinese soils ($n = 48$) did not exceed corresponding guidelines, but all Japanese soils ($n = 20$) exceeded the Canadian guidelines. However, when concentrations of TEQ_{WHO} were compared to the Japanese guideline (1000 pg TEQ_{WHO}/g dw), >95% of soils from China, South Korea, and Japan did not exceed the guideline. Several soil quality guidelines from European countries including Germany, New Zealand, Sweden, the Netherlands, and United Kingdom, were suggested and these guidelines are more specific in terms of target or activities compared to Canadian or Japanese guidelines. Compared with one of the most recent European guidelines from the United Kingdom, only 8% of Chinese soils ($n = 4$) exceeded residential levels (8 pg pg TEQ_{WHO}/g dw), while 39% of Korean soils ($n = 19$) and all of Japanese soils ($n = 20$) exceeded the corresponding guideline.

Few quality guidelines are available for sediment, which include Canada, United States, and Japan. Similar to soil, more than half of the sediment from the three countries exceeded the strictest guideline from Canada (0.85 pg TEQ_{WHO}/g dw), but more than 90% of sediments from China, Korea, and Japan did not exceed the Japanese sediment quality guideline (150 pg TEQ_{WHO}/g dw). None of sediment samples from China or Korea exceeded the US guideline of definite risk to aquatic organisms, but 11% of Japanese sediments exceeded the guideline indicating high degree of dioxin-like contamination in Japan.

Although soil and/or sediment guidelines are not presently available for China or Korea, the comparison with guidelines from many countries including Japan gave overall contamination status and potential risk posed by Asian soils and sediments including Yellow Sea samples. For site-specific evaluation of PCDD/Fs contamination, it would be necessary to establish the most

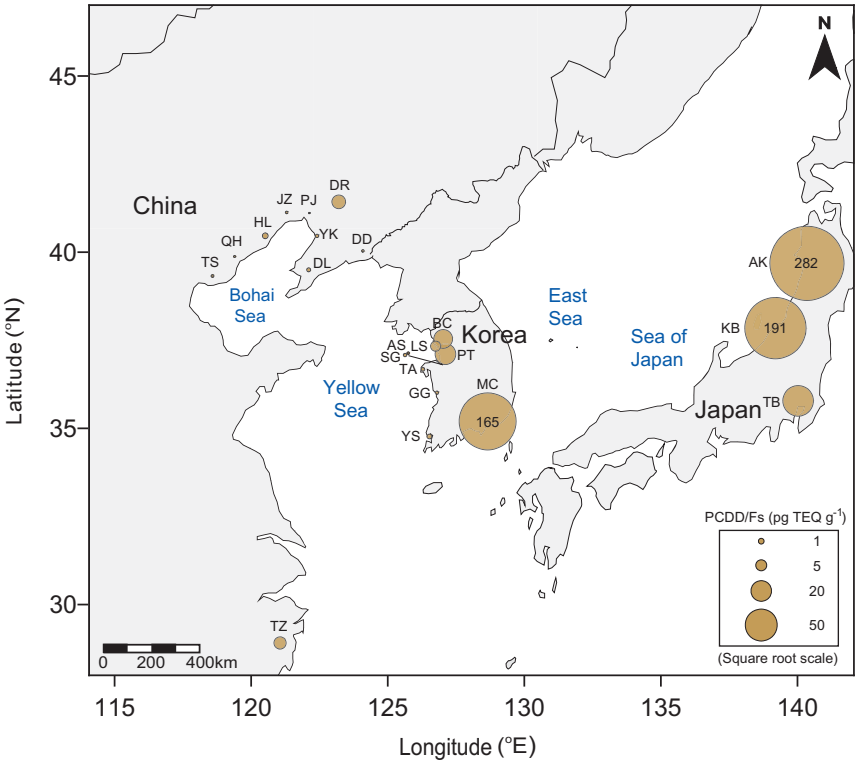

Fig. 5. Comparison of TEQs of PCDD/Fs in soil samples from this study and previous reports in South Korea, China and Japan (TB: Tokyo Bay, $n = 1$ (Sakurai et al., 2000); MC: Masan and Changwon City, $n = 23$ (Im et al., 2002); PT: Pyungtak City, $n = 4$ (Kim et al., 2005); BC: Bucheon City, $n = 11$ (Oh et al., 2006); AK: Akita, $n = 9$ (Kiguchi et al., 2007); DR: Daliao River, $n = 17$ (Zhang et al., 2008); KB: Kameda Basin, $n = 10$ (Sakai et al., 2008); TZ: Taichou, $n = 4$ (Liu and Liu, 2009)).

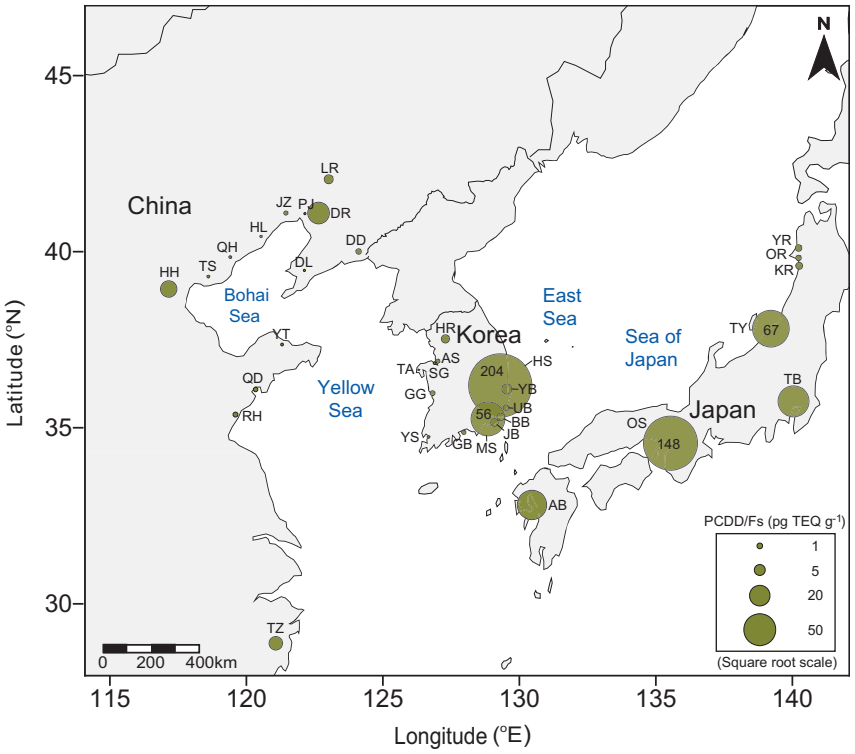

Fig. 6. Comparison of TEQs of PCDD/Fs in sediment samples from this study and previous reports in South Korea, China and Japan (TB: Tokyo Bay, $n = 7$ (Sakurai et al., 2000); HS: Hyeongsan River, $n = 6$ (Koh et al., 2004); YR: Yoneshirogawa River, $n = 7$; OR: Omonogawa River, $n = 9$; KR: Koyoshigawa River, $n = 5$ (Kiguchi et al., 2007); HH: Haihe River, $n = 10$ (Liu et al., 2007); AB: Ariake Bay, $n = 2$ (Kim et al., 2008); YB: Yeongil Bay, $n = 20$; UB: Ulsan Bay, $n = 20$; BB: Busan Bay, $n = 21$; GB: Gwangyang Bay, $n = 35$; JB: Jinhae Bay, $n = 26$ (Moon et al., 2008); TY: Toyano lagoon, $n = 5$ (Sakai et al., 2008); DR: Daliao River Basin, $n = 13$ (Zheng et al., 2008); MS: Masan Bay, $n = 5$ (Hong et al., 2009); HR: Han River, $n = 18$ (Kim et al., 2009); TZ: Taichou, $n = 4$ (Liu et al., 2007); OS: Osaka, $n = 8$ (Kishida et al., 2010); YT: Yantai, $n = 1$; QD: Qingdao, $n = 1$; RH: Rizhao, $n = 1$ (Pan et al., 2010); LR: Liaohe River, $n = 15$ (Zhang et al., 2010)).

appropriate guideline(s) to be used for accurate assessment of dioxin-like contaminants in China and/or South Korea in the near future.

4. Conclusion

Varying concentrations of PCDD/Fs were detected in soils and sediments from a field survey conducted in the Yellow Sea region along the north-eastern coast of China and western coast of South Korea. Concentrations of PCDDs were usually comparable or greater than those of PCDFs both in soils and sediments and this trend was consistent between China and Korea. More chlorinated compounds were dominant, particularly for dioxins, and the relative composition of PCDD/Fs was closely associated with land uses, such as agricultural, municipal, and industrial activities, rather than geographical locations. Concentrations of PCDD/Fs at the Korean locations were always greater than those from China, with elevated concentrations at some locations both in China and Korea, but both countries showed relatively small concentrations of PCDD/Fs compared to those in Japan. Soil and sediment PCDD/Fs in Korea indicated some point sources but those in China were rather low and relatively uniform indicating the presence of more diffuse sources in this region. Only a few sampling locations in China and Korea exceeded the Canadian soil and/or sediment quality guidelines, but widespread distribution and varying composition of PCDD/Fs suggested common and continuing sources of dioxins and furans in this region. Overall the present study indicated not only the residual characteristics of PCDD/Fs between matrices, soil versus sediment, but also suggested accumulation patterns into residue sinks between China and South Korea, which share and use the Yellow Sea ecosystem. Considering the current heavy and continuing industrial and municipal activities, and their inevitable increase, along the estuarine and coastal areas of China and South Korea, a monitoring effort followed by appropriate management and action plans, including development of site-specific environmental quality guidelines, would be highly recommended to ensure the sustainable use of this valuable and huge water body in the Yellow Sea eco-region.

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