Distribution of PCDD/Fs, PCBs, and PCNs in Coastal Sediments Collected from Major Industrial Bays in South Korea

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Introduction

Persistent organic pollutants (POPs) such as polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs) are known to bioaccumulate because of their persistence and lipophilicity [1]. Most of them are deposited from the air into soil, plants, surface water, or transferred into the food chain and affect human health [2]. In particular, POPs are highly accumulated in organic fraction of suspended particles and sediments [3]. They are chemically stable and thus persist for a long time [4]. Consequently, monitoring of POPs in surface sediments can provide information on recent pollution sources of the marine environment.

Major industrial bays in South Korea have been known to be contaminated with dioxin-like chemicals. For example, several studies reported on contamination of PCDD/Fs and PCBs in marine sediments, but the levels and patterns of PCNs and their correlation with PCDD/Fs and PCBs has rarely been investigated. Therefore, the purpose of this study was to investigate spatial variations and to evaluate the sources of 17 PCDD/Fs, 7 indicator and 12 dioxin-like PCBs (DL-PCBs), and 13 PCNs in coastal sediments collected from major industrial bays in South Korea.

Materials and Methods

Study areas and sample collection

Surface sediment samples were collected from 68 sites in four industrial bays, which are located in the southeast of South Korea (Busan: 18 sites, Ulsan: 14 sites, Jinhae: 20 sites, and Gwangyang: 16 sites) (Fig. 1). Sediment samples were collected by using a Van Veen grab sampler in March–April 2016. After collection, the samples were immediately frozen and stored at -20°C until analysis. In Ulsan, Jinhae, and Gwangyang Bays, industrial complexes such as petrochemical, shipbuilding, and heavy industries are located. In Busan Bay, the biggest international harbor of Korea is located. In addition, non-ferrous, shipbuilding, and heavy industries are located in the inner area of Busan Harbor. Namely, these four bays are the main industrial bays in the South-East region of Korea.

Instrumental Analysis

Freeze-dried sediment samples (10 g) were extracted with dichloromethane (DCM) using an Accelerated Solvent Extractor (ASE 350, Dionex, USA). Before the extraction, $^{13}C_{12}$-labeled surrogate standards were spiked into the samples. The extract was then concentrated to 2 mL by a nitrogen concentrator (TurboVap LV, Biotage, USA), and the solvent was exchanged into hexane. The extract was firstly cleaned up on a multi-layer silica gel column containing anhydrous Na_2SO_4 (0.5 g) (top), 10% $AgNO_3$-silica gel (2 g), silica gel (0.5 g), 22% H_2SO_4-silica gel (1.5 g), 44% H_2SO_4-silica gel (1.5 g), silica gel (0.5 g), and 2% KOH-silica (2 g), anhydrous Na_2SO_4 (0.5 g) (bottom). Then, the sample was further cleaned up on an activated alumina (10 g) column. For the multi-layer silica gel column, elution solvent was hexane (130 mL). For the activated alumina column, the target compounds were firstly eluted by 2% DCM in hexane (70 mL), followed by 50% DCM in hexane (80 mL). After the final concentration to approximately 50 µL, $^{13}C_{12}$-labeled internal standards were added to vial inserts prior to instrumental analysis. A gas chromatograph (GC, Agilent 7890A, USA) coupled with a high-resolution mass spectrometer (HRMS, Auto Spec Premier, Waters, USA) was used. The target analytes were separated on a capillary column (DB-5MS, 50 m × 0.25 mm × 0.25 µm film thickness).

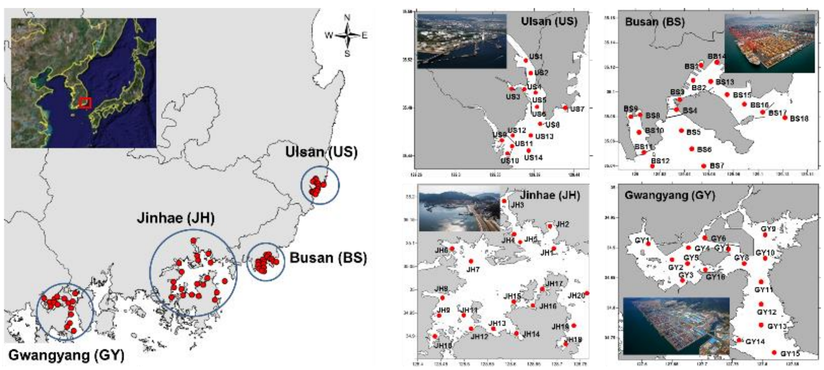

Figure 1. Location of sampling sites of coastal sediments from four major bays in South Korea.

Results and discussion

PCDD/Fs

In industrial bays, the levels and patterns of PCDD/Fs can be greatly influenced by various industrial activities, e.g., pulp and paper production, combustion processes, thermal reactions, iron and steel production, incineration, etc. The concentrations of Σ_{17} PCDD/Fs in Jinhae (JH) Bay were higher than those from the other bays (Fig. 2). The highest concentration was found at JH5 site (661.9 pg/g dry weight (dw)). The spatial distributions of PCDD/Fs and TEQ values in each bay were very similar. The higher concentrations of PCDD/Fs at the inner bays compared to those at the outer bays imply that major sources might be located near the bays.

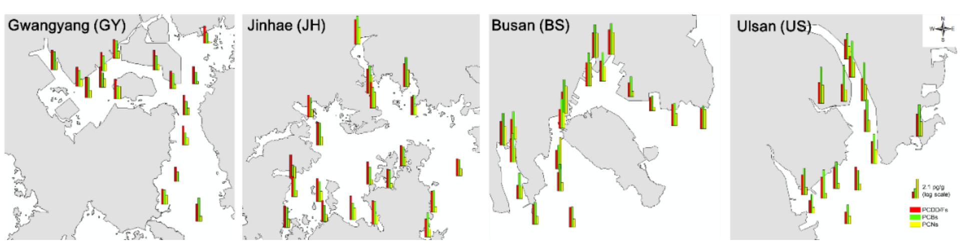

Figure 2. Concentrations of Σ_{17} PCDD/Fs, Σ_{19} PCBs, and Σ_{13} PCNs in coastal sediments from four industrial bays.

To understand the distribution pattern of PCDD/Fs and their regional characteristics, principal component analysis (PCA) was applied. The samples of Gwangyang (GY) were separated from the others and characterized by 1,2,3,4,6,7,8,9-OCDF and 2,3,7,8-TCDD (Fig. 3). The samples of Ulsan (US), Busan (BS), and JH are overlapped each other, located in the middle of the score plot, and characterized by 2,3,7,8-TCDD. This result suggests that the major sources of PCDD/Fs in GY are different from those in US, BS, and JH. Also, several sites in BS and JH in the right side of the score plot seemed to be influenced by similar emission sources. These specific potential sources are under investigation.

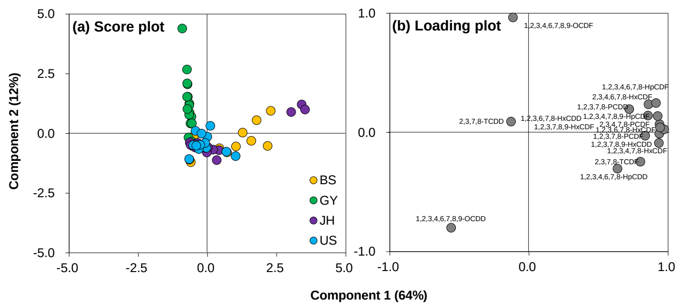

Figure 3. PCA results of PCDD/Fs: (a) score plot and (b) loading plot.

PCBs

Ulsan Bay showed the highest PCB concentrations among the four bays. In Ulsan Bay, the concentrations of DL-PCB and indicator PCB concentrations ranged from 5.6 to 7563.5 pg/g dw and from 42.3 to 6161.2 pg/g dw, respectively. The spatial distributions of indicator PCBs and DL-PCBs were very similar in each bay. Among the target congeners, PCB77 was a dominant congener, while PCB126 showed the highest TEQ because of a higher TEF value. The detection of PCB126 and PCB169, which are generally emitted from incinerators but are unlikely to occur in technical mixtures rare in PCB products, indicated the impact of incinerator emissions.

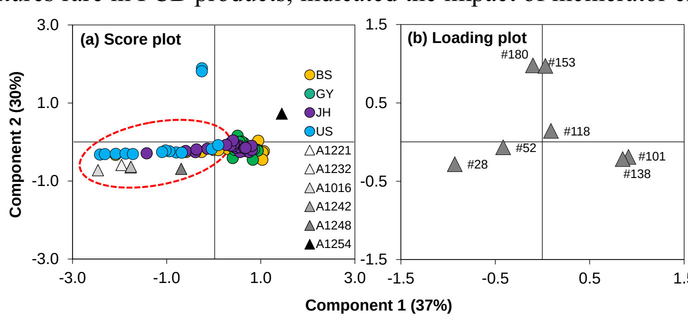

Figure 4. PCA results of indicator PCBs: (a) score plot and (b) loading plot.

According to the PCA result on the indicator PCBs (Fig. 4), sediment samples from BS, GY, and JH were mostly clustered together, referring the similar sources. Meanwhile, the sediment samples from Ulsan Bay (US) were generally separated from those of other bays, which was characterized by higher fractions of PCB 28 and 52. This congener pattern was also characterized for several Aroclor mixtures. The higher levels of PCBs in Ulsan were mostly attributed to lower chlorinated congeners, indicating the local contribution of the Aroclor mixtures. The higher levels of PCBs at sampling sites near shipbuilding industries and harbors demonstrate that technical mixtures are the main source of PCBs in coastal sediments.

PCNs

Unlike PCDD/Fs and PCBs, the concentrations of PCNs were significantly higher in Busan Bay than the other regions (Fig. 2). The PCN concentrations of sediments from the four bays ranged from <LOD to 620 pg/g dw, and they seemed to be mostly affected by local industrial activities, and thus gradients of concentrations from inner to outer bays were observed. PCN53/55 showed the highest concentration, whereas PCN73 with a higher TEF showed the highest TEQ concentration than other congeners.

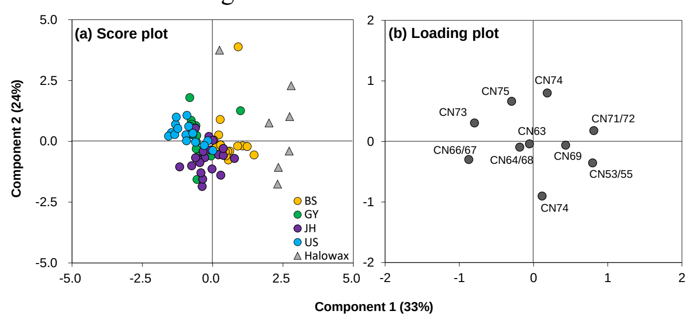

Figure 5. PCA results of indicator PCNs: (a) score plot and (b) loading plot.

The profiles of PCNs in the coastal sediments from the four bays were generally similar (Fig. 5), but there was a significant difference in the concentration, reflecting the location and strength of emission sources. In a score plot, the most coastal sediment samples were not associated with Halowaxes. Instead, the profiles of PCNs in this study are similar to those of combustion [5]. Especially, we suspect that PCNs in the study areas were significantly emitted from municipal solid waste incinerators (MSWIs) and industrial thermal processes.

Acknowledgements

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References

1. Oh J-E, Choi S-D, Lee S-J, and Chang Y-S, (2006) *Chemosphere*, **64**, 579-587.
2. Choi S-D, Baek S-Y, and Chang Y-S, (2008) *Atmospheric Environment*, **42**, 2479-2488.
3. Hong SH, Yim UH, Shim WJ, and Oh JR, (2005) *Environmental Science & Technology*, **39**, 7380-7388.
4. Moon H-B, Choi H-G, Lee P-Y, and Ok G, (2008) *Environmental Toxicology & Chemistry*, **27**, 323-333.
5. Xu Y, Li J, Zheng Q, Pan Q, Luo C, Zhu H, Nizzetto L, and Zhang G, (2015) *Environmental Pollution*, **204**, 124-132.