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Decline in sediment contamination by persistent toxic substances from the outfall of wastewater treatment plant: Effectiveness of legislative actions in Korea

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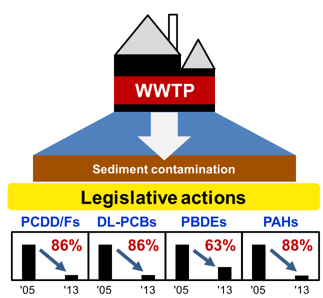
HIGHLIGHTS

- Clear decreasing trends in the POPs were observed with an increase in the distance from the WWTP outfall.
- Significant declines were found in the PCDD/Fs, dioxin-like PCBs, PBDEs, and PAHs during past years.
- Legislative actions were likely to be effective for reducing the POPs and PAHs in sediments.
- Current PCDD/F levels in the sediments near the WWTP outfall exceeded the sediment quality guidelines.

GRAPHICAL ABSTRACT



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ABSTRACT

Legacy and new persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) were measured in sediments near a wastewater treatment plant (WWTP) outfall in a semi-enclosed bay, to investigate the current contamination and temporal changes in these contaminants associated with regulation activities in Korea. The concentrations of most of the POPs showed clear decreasing trends with an increase in the distance from the WWTP outfall, indicating that the WWTP discharges greatly contributed to the sediment contamination by POPs. Highly significant correlations were found for most of the POPs, indicating a common source for sediment contamination. Significant declines were found in the concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (DL-PCBs), polybrominated diphenyl ethers (PBDEs), and PAHs in the sediments collected between 2005 and 2013. This result suggested that legislative actions (regulation of the PCDD/Fs in flue gas, total pollution load management, and whole effluent toxicity for WWTP discharges) and change of fuels, were likely to be effective at reducing the POP and PAH levels in sediments during the past several years. The different compositional profiles of the PCDD/Fs and PAHs between 2005 and 2013 implied changes in and/or additional sources of these contaminants. Despite a decline in the PCDD/Fs over time, the present levels of PCDD/Fs in the sediment exceeded some of the sediment quality guidelines suggested by the National Oceanic and Atmospheric Administration.

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1. Introduction

Persistent organic pollutants (POPs) are a group of ubiquitous and toxic man-made organic contaminants with the ability to withstand degradation processes, bioaccumulate in the fatty tissues of living organisms, and bio-amplify the POP levels in the food web (Conka et al., 2014). The United Nations Environment Programme (UNEP) designated 12 chemical groups as POPs, including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and some organochlorine pesticides (OCPs) such as DDTs, in 2001. Some other halogenated chemical groups, such as polybrominated diphenyl ethers (PBDEs) and perfluorinated compounds (PFCs), have been nominated for and regulated as new POPs since 2009. PBDEs, used as brominated flame retardants, are included in a variety of consumer products, such as electronic and electrical equipments and textiles (La Guardia et al., 2006). PFCs have been widely used for more than 50 years in industry and house with a variety of commercial applications, such as polymers, stain repellents, lubricants, paper coatings, and cosmetics (Giesy and Kannan, 2001). Based on these applications of PBDEs and PFCs, wastewater treatment plants (WWTPs) are known as a major environmental source of these contaminants (Lee et al., 2014a; Arvaniti and Stasinakis, 2015). Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants generated by the combustion of fossil fuels such as coal, petroleum, and wood (Moon et al., 2006; Ravindra et al., 2008). Unlike POPs, PAHs are not bioaccumulated in living organisms in a stable manner due to biotransformation processes (Huang et al., 2014). Nevertheless, the release of POPs and PAHs into the environment has resulted in adverse health effects in living organisms which include birth defects, cancer, endocrine disruption, immune modulations, neurological damages and reproductive disorders (Gassmann et al., 2010; La Merrill et al., 2013; Robledo et al., 2015).

WWTPs are one of the major sources of contaminants of emerging concern (CECs), since many chemicals used in consumer products are ultimately collected in municipal sewers, treated, and then released into aquatic environments (Lee et al., 2014a,b, 2015). The contamination of water bodies by WWTP effluents has been classified as an issue of global concern, based on the ecological and human health risks associated with exposure to toxic chemicals (Moon et al., 2008b; Lee et al., 2014a,b). Approximately 90% of wastewater effluent discharges undergo sedimentary burial into riverine and marine sediments, indicating that sediments are major pollution reservoirs for the POPs and related contaminants in the aquatic environment (Moon et al., 2012a,b).

Masan Bay, located in the southern part of Korea, is a representative semi-enclosed bay with a slow water exchange. The measured residence time of pollutants over a tidal cycle in Masan Bay ranged from 20 to 100 days with a mean of 40 days (Park et al., 2011). Approximately 1000 industrial complexes, such as petrochemicals, heavy metals, and electrical industries, surround Masan Bay. Several studies have reported severe contaminations of metals, POPs (e.g., PCDD/Fs and PCBs), and PAHs (Yim et al., 2014; Cho et al., 2015). Our previous studies confirmed that wastewater discharged from the WWTP is a significant contamination source of POPs, such as PCDD/Fs, PCBs, and nonylphenols, with evidence of benthic ecological risks in Masan Bay (Moon et al., 2008b, 2009). The Ministry of Ocean and Fisheries first applied the total pollution load management system (TPLMS) to Masan Bay in 2007, in order to improve the water quality, including such factors as chemical oxygen demand (COD), suspended solids (SS), total nitrogen (TN), and total phosphate (TP) (Chang et al., 2012). The Ministry of Environment also enforced water quality criteria, such as COD and TP, in WWTPs effluent, and also introduced a whole effluent toxicity (WET) management system using *Daphnia magna* in 2011 (Ministry of Environment (2012)). Chang et al. (2012) reported a significant reduction in the land-based levels of TN and TP into Masan Bay during the period of 2005–2010. In addition, the levels of PCDD/Fs in the atmosphere have declined due to the strict regulation of PCDD/Fs in flue gas from waste incinerators in Korea for the past decade (Lee et al., 2007). However, no reports are available on the temporal trends of POPs, such as PCDD/Fs in the marine environment associated with these legislative actions.

In the present study, we measured legacy (e.g. PCDD/Fs and PCBs) and new POPs (PBDEs and PFCs) as well as PAHs in sediments around the submarine outfall of the WWTP in Masan Bay, to evaluate the current contamination status, the potential sources, and the ecological implications of these contaminants. We also investigated temporal trends in the levels of POPs and PAHs in order to determine whether or not some legislative actions, such as TPLMS and WET, significantly reduced the POP and PAH levels in sediments from Korean coastal waters.

2. Materials and methods

2.1. WWTP and sample collection

The WWTP in Masan city was described in detail in a previous study (Moon et al., 2008b). The WWTP is located at Duckdong in Masan city and was established in 1994. The plant treats 260,000 tons/day of wastewater, about 90% domestic wastewater from approximately 1 million inhabitants and 10% from industries, and discharges the effluent into the Masan Bay through a submarine pipeline (Ministry of Environment (2012)). The plant uses sedimentation reservoirs and an activated sludge treatment process to purify the wastewaters.

Twenty surface sediments were collected using a Van Veen grab sampler in December 2013 at the same locations as in 2005 (Fig. 1). The sampling locations were chosen by the same lines of longitude and latitude using the global positioning system (GPS) on the research vessel, to remove the differences in the levels of target contaminants in sediment. The sampling points were selected based on the prediction of the movement of the effluent from the WWTP released into the bay. The area was divided into five transects (A to E lines) originating from the submarine outfall (Station OF). The Naval Base, which is located in the northern part of the bay from the WWTP outfall, was not included in the sampling regions. The surface sediments used for chemical analysis were wrapped in aluminium foil and then immediately frozen in a refrigerator on the research vessel. The samples were transported to the laboratory where they were kept in a freezer at −20 °C until further analysis.

2.2. Chemicals and reagents

The chemical groups measured in our study were PCDD/Fs, dioxin-like PCBs (DL-PCBs), non-DL-PCBs, OCPs, chlorobenzenens (CLBz), PBDEs, PFCs and PAHs. Seventeen toxic 2,3,7,8-substituted PCDD/F congeners; 12 toxic dioxin-like PCB congeners (DL-PCBs); 20 PCB congeners (IUPAC No. CBs 8, 18, 28, 29, 44, 52, 87, 101, 110, 128, 138, 153, 170, 180, 187, 194, 195, 200, 205, and 206); and 17 OCPs including dichloro-diphenyl-trichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), and chlordanes (CHLs), eight CLBz congeners (1,2,3-, 1,2,4-, 1,3,5-, 1,2,3,4-, 1,2,3,5-, 1,2,4,5-, penta-, and HCB), 22 PBDE congeners (BDEs 17, 28, 47, 66, 71, 85, 99, 100, 119, 126, 138, 153, 154, 183, 184, 190, 191, 196, 197, 206, 207, and 209), 16 PFCs [perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perflruorooctanoate (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic