

# HISTORICAL RECORDS OF PERFLUOROALKYL SUBSTANCES (PFAS) INCLUDING THEIR PRECURSORS AND REPLACEMENTS IN A SEMI-ENCLOSED BAY OF KOREA

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## Introduction

Perfluoroalkyl substance (PFASs) have been widely used in commercial applications such as textile, paper coating, electronics and firefighting foam (AFFF) due to their amphiphilic properties<sup>1</sup>. PFASs are ubiquitously persistent and have been found multi-matrices including water, sediment<sup>2</sup>, wildlife<sup>3</sup> and human<sup>4</sup>. Because of their persistent, bioaccumulative, and toxic properties, perfluorooctane sulfonic acid (PFOS), its salts, and perfluorooctane sulfonyl fluoride have been regulated under Stockholm Convention on the persistent organic pollutants (POPs) since 2009<sup>5</sup>. Perfluorooctanoic acid (PFOA), and perfluorohexane sulfonate (PFHxS), and its salts also nominated as POP candidate in 2018. Masan Bay is located on the southeast coast of Korea, which has been identified as one of the most polluted coastal area<sup>6,7,8</sup> by local discharges from industrial complexes and slow rate of water circulation because of narrow inlet of semi-closed bay. Masan and Changwon industrial complexes, including petrochemical, heavy metal, electrical, steel manufacturers dye houses, pulp factories, and a sewage treatment plant, as well as heavily populated cities<sup>7,9,10</sup>. Masan Bay has been listed as a Special Management Coastal Zone (SMCZ) by the Korean government since 2000, in association with overloads of pollution. In this study, the historical records and composition profiles of PFASs including their precursors and alternatives were determined in three sediment cores collected from Masan Bay.

## Materials and methods

### Sample collection

Three sediment core samples were collected from inner part of Masan Bay (Core 1), outfall of Dukdong wastewater treatment plant (WWTP) (Core 2), and Haengam Bay (Core 3) of Masan Bay in April 2018. The samples were obtained by scuba divers using acrylic tubes (length 150 cm, internal diameter 11 cm). The length of each sediment core were 108, 101 and 92 cm for Core 1, 2 and, 3, respectively. Collected cores were sliced at 2 cm intervals up to 30 cm and the remaining parts were sliced at 5 cm intervals. Measurements of <sup>210</sup>Pb and <sup>226</sup>Ra for each sediment core were conducted to obtain sedimentation rates, which were estimated to be 1.23, 0.68 and 0.84 cm/year for each sediment core.

### Chemicals and Instrumental analysis

Freeze-dried sediment samples (~5 g) were extracted by mechanical shaking (250 rpm) and sonicated with methanol, after spiking with mixture of internal standards (5 ng). The extracts were centrifuged at 3000 rpm and the supernatant was transferred into a polypropylene tube. This procedure was repeated twice, and extracts were combined and concentrated into 1 mL. The extracts were purified with a ENVI-Carb cartridge and were eluted with 5 mL of methanol. The samples were concentrated to 1 mL and filtered using a Nylon-filter for instrumental analysis. Twenty-four PFASs (16 PFAAs, 5 precursors and 3 alternatives) were analyzed by a high-performance liquid chromatography tandem mass spectrometer (LC-MS/MS; Agilent 1260/6470). A betasil C<sub>18</sub> column (2.1 mm i.d. × 100 mm length × 5 μm particle size) were used for the separation of the PFASs. The mobile phases were 2 mM ammonium acetate solution in methanol (A) and methanol (B). The gradient was increased from 10% to 100%

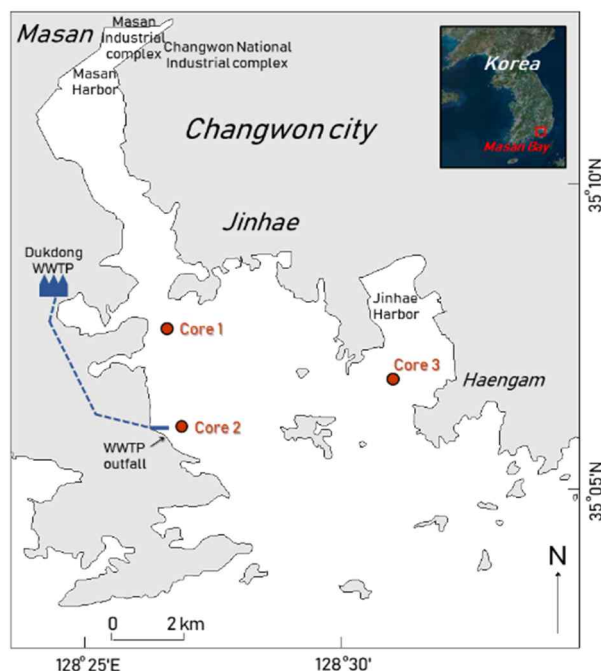


Figure 1. Sampling location of core sediment from Masan Bay, Korea

methanol over 15 min at flow rate of 300  $\mu\text{L}/\text{min}$  flow rate, decreased to 50% during 2 min and maintained at 10% methanol for 2 min.

## Results and discussion

### Occurrences and concentrations of PFASs

The  $\sum_{16}\text{PFAA}$  and  $\sum_6\text{precursor}$  concentrations were  $<\text{LOQ}$ –1.6 (mean: 0.22)  $\text{ng}/\text{g}$  dry weight (dw) and  $<\text{LOQ}$ –2.50 (mean: 0.28)  $\text{ng}/\text{g}$  dw, respectively. All of alternatives (ADONA, GenX and F-53B) were not detected in all sediment samples. The major compounds were PFOS, longer chain PFCAs (PFUnDA, PFDoDA, and PFTrDA) and PFOS precursors (N-EtFOSAA and N-MeFOSAA). The TOC contents and concentrations of PFASs (mean: 0.35  $\text{ng}/\text{g}$  dw) and their alternatives (0.73  $\text{ng}/\text{g}$  dw) were significantly higher in Dukdong region (ANOVA,  $p>0.001$ ) which is the location close to the outfall of a WWTP, suggesting a potential contamination source of PFASs of Masan coastal environment.

### Historical records of PFASs and HFRs

Historical records in TOC, PFASs and HFRs including PBDEs, NBFRs and DP were presented in Figure 2. TOC content showed the highest level in Dukdong region (mean: 1.97%) than Masan (1.73%) and Haengam (1.18%), indication that high input of organic carbon content from WWTP outfall.

The first appearance year (1950~60s) for PFASs at trace levels. The rapidly increasing trends of PFASs concentrations in Masan and Dukdong regions were began in the late 1980s, which is consistent with the history of production of PFASs globally<sup>11</sup>. In Haengam region, concentrations of PFASs were gradually increased from late 1980 to 2000s with lower levels than those of other core sediments, indicating that there is no specific sources related with PFASs in Haengam region. The highest concentrations of PFASs were found in 2000s (12–18 cm) and then dramatically decreased to the surface layers in Masan and Dukdong regions. The legislative action on the total pollution load management system (TPLMS) from Korean government has been applied to Masan Bay since 2007 to improve water quality<sup>12</sup>. The portion of longer-chain PFASs such as PFUnDA, PFDoDA and PFTrDA to total PFASs concentrations increased in Masan and Dukdong regions since 2000. This result indicates a shift in the usage pattern of PFASs to longer-chain PFASs in Korean industry.

Historical trends in PBDE concentrations showed a clear increase since 1980s and the highest peak in 1990s, and then decreased with increasing time. This was consistent with domestic and global consumption patterns of PBDEs. Similar trends in PBDEs were found for BTBPE and DP, suggesting contemporary consumption for these FRs. However, the concentrations of DBDPE gradually increased since 2000s and then slightly decreased to the present, implying consumption of DBDPE as alternatives for regulated FRs. Gradual increase in the ratio of DBDPE/BDE 209 indicates the effectiveness of regulation on PBDEs in Korea industries.

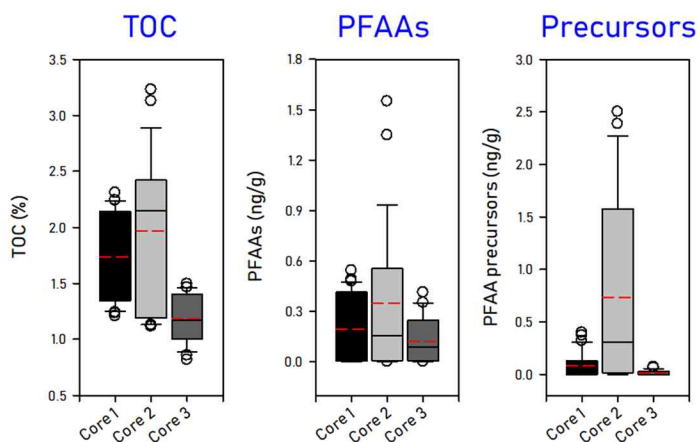
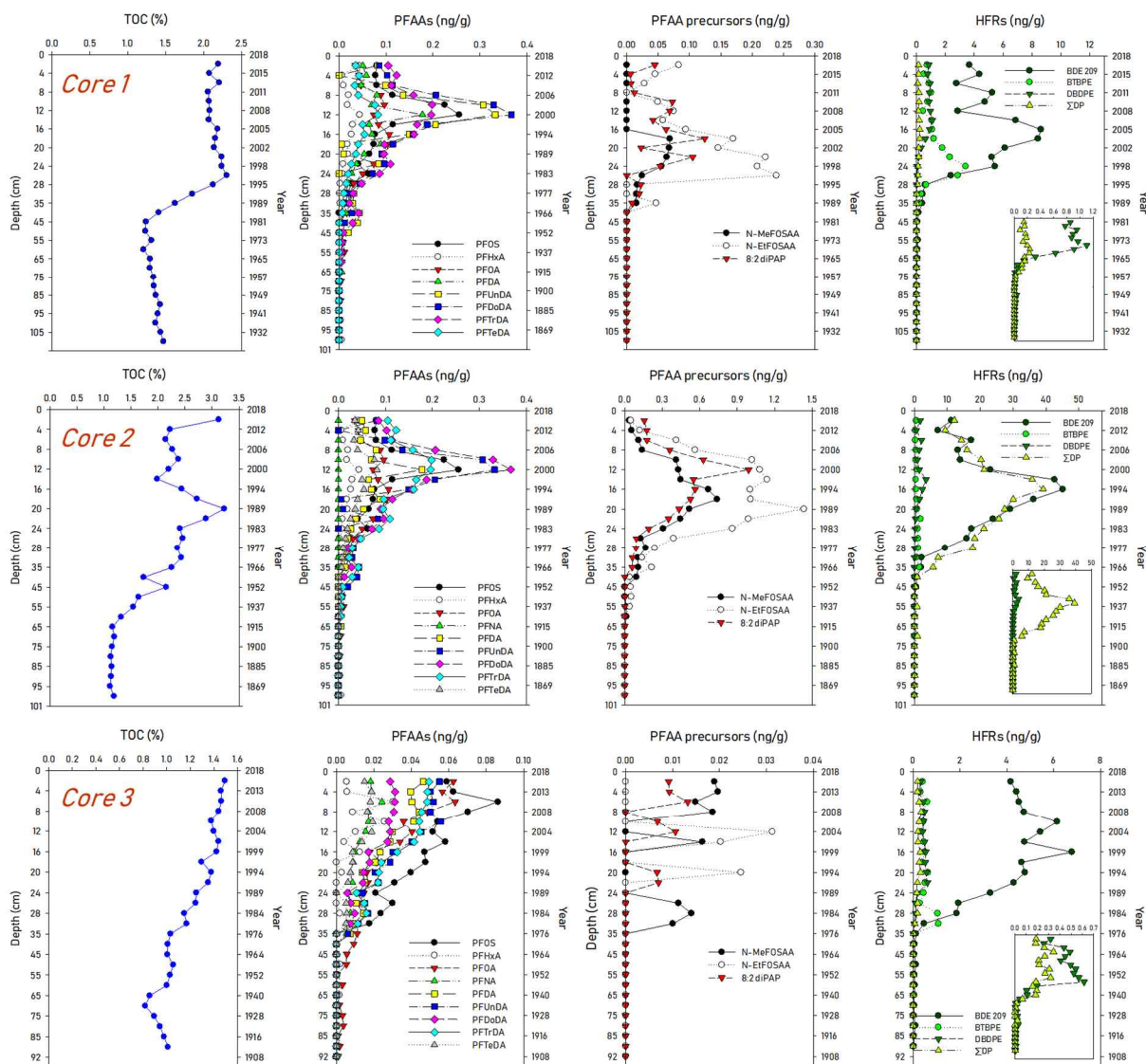


Figure 2. Comparison of TOC content and concentrations of PFAAs and their precursors in Core 1, 2 and 3 in Masan Bay.



**Figure 2.** Historical records of TOC (%), PFAAs, their precursors and HFRs in Core 1,2 and 3 of Masan Bay.

### Environmental burdens of PFASs

The average inventories of  $\Sigma$ PFAS were estimated to be 1515, 6030, and 754  $\text{pg}/\text{cm}^2$  for the Masan, Dukdong, and Haengam regions, respectively (Table 1). The average fluxes of  $\Sigma$ PFAS were estimated to be 217, 350, and 59  $\text{pg}/\text{cm}^2/\text{yr}$  for the Masan, Dukdong, and Haengam Bays, respectively (Table 1). PFOS, longer chain PFCAs including PFUnDA, PFDODA and N-EtFOSAA showed high inventories and fluxes. The inventories and fluxes of PFASs in Dukdong region were higher than those estimated for the other regions, indication a high contamination burden of PFASs from Dukdong WWTP. The inventories and flux of  $\Sigma$ PFAS calculated in Dukdong region were 4-8 times higher than those calculated for the other two regions. Considering the hydrophilic properties of PFASs, the water compartment also should be estimated for total environmental burden of PFASes in the Korean Coastal environment.

**Table 1.** Fluxes of PFOS, PFAAs and their precursors in Core 1, 2, and 3.

	PFOS	PFUnDA	PFDODA	N-MeFOSAA	N-EtFOSAA	$\Sigma$ PFAS
<b>Inventories (<math>\text{pg}/\text{cm}^2</math>)</b>						
Core 1	163±197	183±193	145±167	56±116	250±390	1515±1574

Core 2	242±351	331±478	378±519	902±1176	1981±2458	6030±6701
Core 3	132±146	99±109	57±66	23±39	14±43	754±815
<b>Flux (pg/cm<sup>2</sup>/yr)</b>						
Core 1	24±22	27±21	22±18	8±14	37±47	217±175
Core 2	15±22	18±29	23±32	55±72	121±151	350±418
Core 3	11±11	8±8	5±5	2±3	1±3	59±63

**Conclusion:** The concentrations of 25 PFASs were determined for sediment core from Masan Bay in Korea. The highest PFASs were found in mid 2000s–late 2000s and gradually decreased to the surface layer, suggesting global regulation effect on PFASs. Although alternatives of PFOS and PFOA were not detected in all of sediments, implying that use of alternatives is not reflecting in marine sediments yet (time-gap). Historical trends in PBDE, BTBPE and DP concentrations showed a clear increase since 1980s and the highest peak in 1990s, and then decreased with increasing time. However, the concentrations of DBDPE gradually increased since 2000s and then slightly decreased to the present. Historical trends in HFRs in dated sediments were well coincided with the consumption patterns and time-series of regulation in domestic and global scales.

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