

PERFLUOROALKYL COMPOUNDS (PFCs) IN MARINE ENVIRONMENT OF KOREA: COMPARISON WITH TOKYO BAY, JAPAN

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Introduction

Perfluorooctanesulfonate (PFOS) and related perfluoroalkyl compounds (PFCs) have been identified as ubiquitous contaminants in the global environment. PFCs have been reported to occur not only in wildlife from remote areas¹⁻³ but also in open ocean waters^{4,5} far from urbanized and industrialized areas. Although PFCs such as polyfluoroalkyl phosphonates⁶ were recently reported to occur in the environment, the most significant PFCs identified so far was PFOS, because of its ubiquitous occurrence, persistence and bioaccumulation potential. Three important risk profiles for PFOS, namely persistence, long range transportation and bioaccumulation allowed its inclusion in the Stockholm Convention on persistent organic pollutants (POPs) (August 2010) and listed as “Class I Specified Chemical Substances” under the Japanese Chemical Substances Control Law (April 2010). Some PFCs, *viz.* C₁₂ to C₁₆ perfluorocarboxylic acids (PFCAs) have been classified as “Monitoring Chemical Substances” in Japan. To date, very limited information about environmental pollution by PFCs in Korean coast is available. Previous studies have reported concentrations of PFCs in Korea to be relatively great, particularly among the Asian countries, and when compared to other regions around the globe. However, relatively little was known about sources, distribution and fate among matrices including sediment, soil, water, and biota. As part of an ongoing study to determine the current status and extent of PFC concentrations, as well as the potential for detrimental environmental effects, marine environmental samples were collected from Lake Shihwa and East/Japan Sea Korea during 2001-2012.

Lake Shihwa, an artificial saltwater lake, is located on west coast of Korea. There are large industrial complexes in the Lake Shihwa region thus has been regarded as highly contaminated area. Many studies continue to report substantial contamination of Lake Shihwa water, sediment and biota by POPs including PFCs^{7,8}. But there is no regulation about PFCs usage in Korea.

Our previous studies⁹ on sediment core collected from Tokyo Bay, Japan in May 2008, revealed vertical profile of PFCs and suggested the historical input seemed to be decreased after 2002, ban of use in Japan. However no such historical trend of environmental pollution in other Asian country was surveyed up to date even though the coastal environment of Japan, Korea and China are supposed to be most highly contaminated by PFCs in global scale¹⁰.

In this report, sediment samples collected in 2001 and 2011 in Lake Shihwa were analyzed for PFCs contamination using ISO25101 and most updated techniques developed in AIST Japan, and enabled complete analysis of PFSA and PFCA including shorter chains and longer chains. In combination with coastal seawater analysis, we updated situation of the environmental pollution by PFCs in Korean coast for the last 10 years.

Materials and methods

Surface sediments (0-4 cm depth) were collected from the artificial Lake Shihwa and its surrounding creeks, Korea in 2001 and 2011, using van Veen grab sampler (Figure 1). Sediment core samples were collected from Tokyo Bay, Japan in 2008, using acryl tube. Seawater samples were collected from Korean coasts during a research cruise by R/V Tamyang in 2012 (Figure 2). Sediment samples were freeze-dried and applied for residue analysis in AIST Japan. Analytical method based on literature⁹ and slightly modified by using EnviCarb clean up and accurate separation of serious of PFCs using solid phase extraction (SPE) cartridge. Pore water was extracted from wet sediment within 72 h by centrifugation at 10000 rpm for 10 min at a constant temperature of 10 °C (Avanti™ J-25 Centrifuge, Beckman, U.S.A.). The sediment was weighed before and after centrifugation to calculate the efficiency of the pore water extraction and then stored in a PP bottle. The pore water was then filtered through 0.45 µm nylon syringe filters (Iwaki, Fukushima, Japan) into a PP bottle. All of the bottles were

stored in a refrigerator at 4 °C until analysis. Solid phase extraction (SPE) with Oasis WAX cartridges was used for the pore water and sediment was extracted as described elsewhere^{11,12} with some modifications. 500 to 1000 ml of seawater and extracted solution of sediment samples were analyzed by following the modified International Standard Method (ISO25101:2009, published in March 1st) described elsewhere and the Japanese Industrial Standard Method (JIS K0450-70-10:2011, published in March 22nd). Briefly, water samples were extracted using Oasis® WAX cartridges following published methods. Separation and determination of target PFCs was performed using HPLC-MS/MS (electrospray ionization in negative mode). For highly accuracy, all extracted samples were injected both RSpak JJ-50 2D (2.0 mm i.d.× 150 mm length, 5 µm; Shodex, Showa Denko K.K., Kawasaki, Japan) , with 50 mM ammonium acetate and methanol as the mobile phase and Keystone Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 µm, 100 Å pore size, end-capped), with 2 mM ammonium acetate and methanol as the mobile phase. Seven PFASs (PFDS, PFOS, PFHpS, PFHxS, PFBS, PFPrS, PFEtS), fourteen PFCAs (PFOcDA, PFHxDA, PFTeDA, PFTrDA, PFDoDA, PFUnDA, There reported variability of efficiency of Oasis® WAX cartridge manufactured recent lot and accurate optimization using desalting procedure was applied in some samples. The recoveries for the seawater analysis ranged between 81% and 128% and for sediment analysis between 78% and 112%.

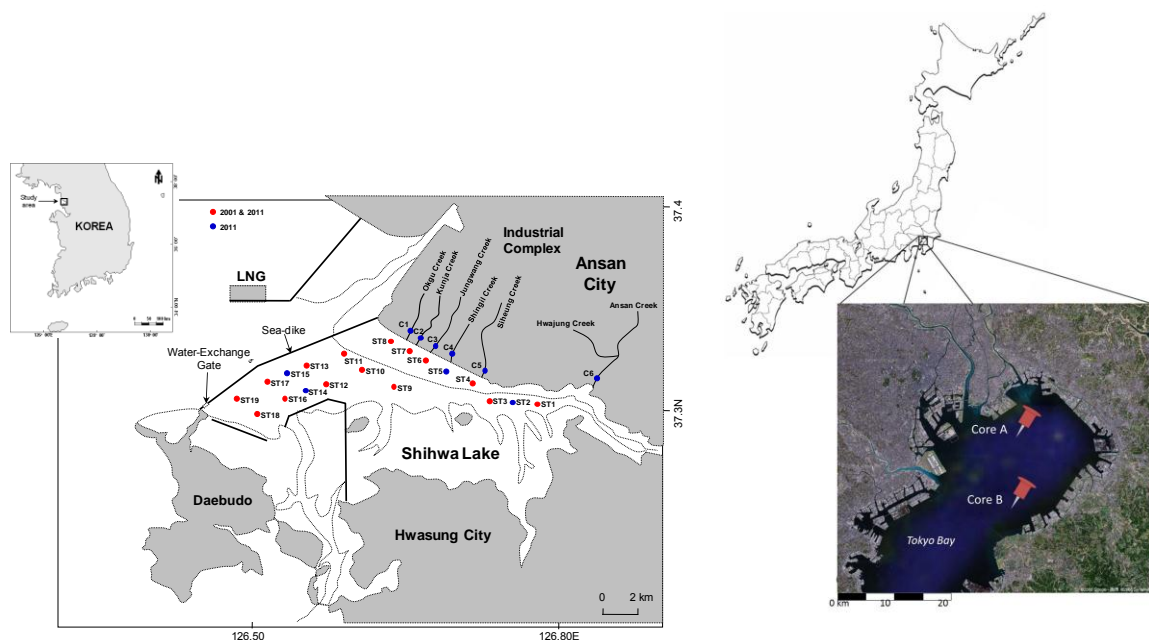


Figure 1. Sampling locations of surface sediments from Lake Shihwa, Korea in 2001 and 2011 and sediment cores from Tokyo Bay in 2008, Japan.

Results and discussions

Result of PFASs residue analysis in both sediment and seawaters were compared to Tokyo Bay survey carried out in 2008. In this survey, two sediment cores were collected from Tokyo Bay in May 2008 (core A, 79cm and core B, 70cm). The cores were sliced at 3 cm intervals for the first 6 to 9 cm and then at 2 cm intervals. The vertical profile of PFASs was shown in core A. In Figure 3, the maximum concentration of PFCs was found in layer of 9-11 cm, estimated dating was 2001 to 2002. Upper layer than 9 cm shown gradual decrease of PFCs up to surface layer can be representable to 2008. Surface sediment samples collected in 2001 and 2011 in Korea can be comparable to above sediment layers in Tokyo Bay core samples, marked in red squares respectively. Although similar trend of PFCs in sediment core collected from the Great Lakes in the North America were reported, there is no evidence of environmental remediation after ban of use of PFOS according to Stockholm convention in Korea. So, the international comparison using sediment samples assumed to be representative to 2001 and 2011 may provide useful information of change of industrial usage and discharge to the environment in Japan and Korea.

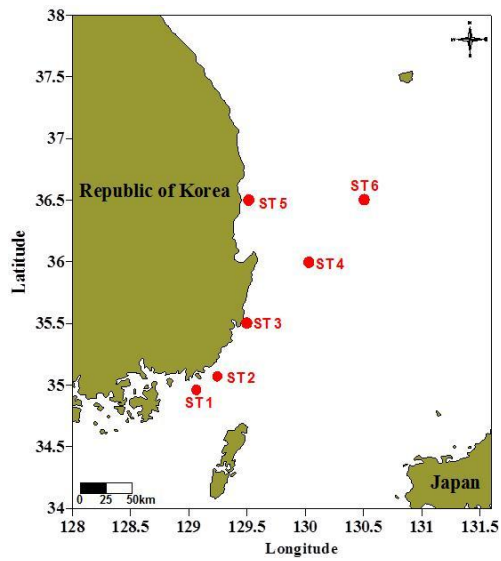


Figure 2. Sampling location of surface and deep seawaters from Korean coast in 2012.

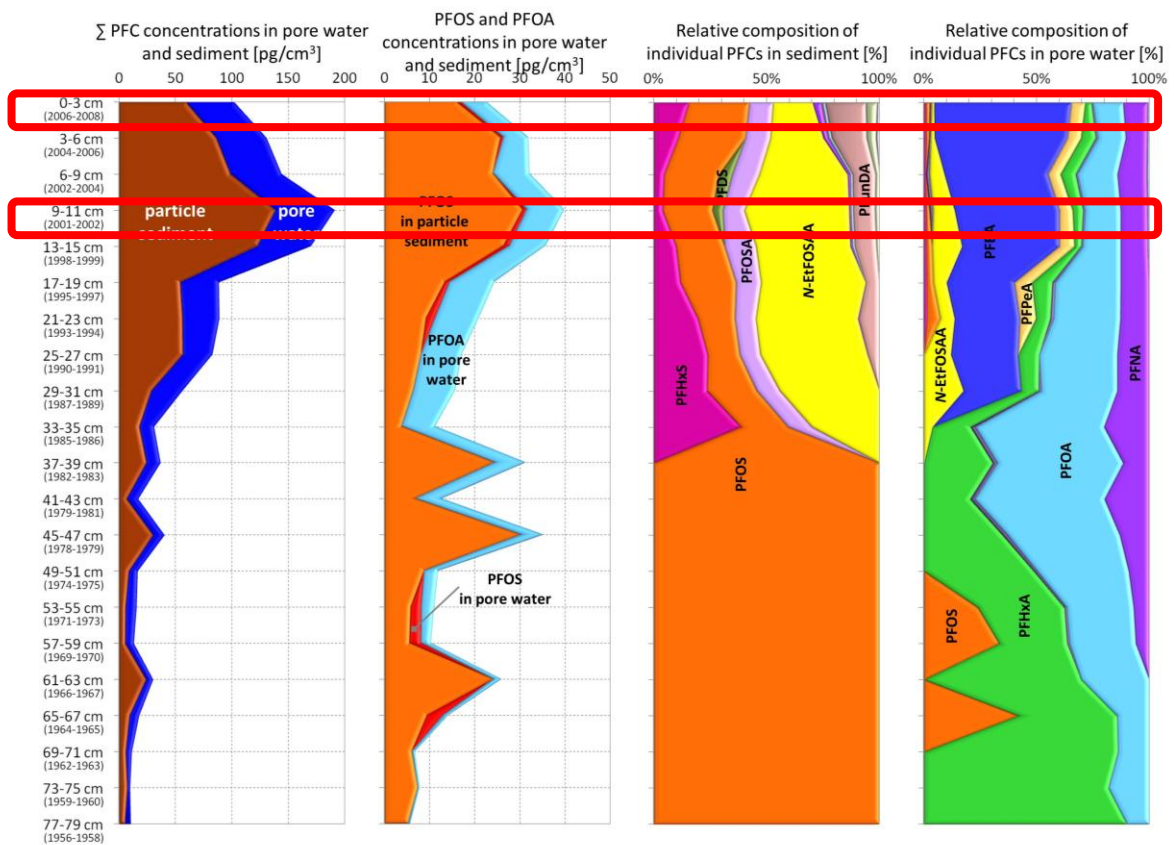


Figure 3. Vertical profiles of PFCs in sediment cores collected from Tokyo Bay in 2008.

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