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Distribution of Perfluoroalkyl Compounds in Osaka Bay and Coastal Waters of Western Japan

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Abstract

Perfluoroalkyl acids (PFAAs) including perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs) were analyzed in sediment samples taken from Ajifu Waterway in Osaka city, from Osaka Bay, and from Kagoshima Bay, as well as in fifteen seawater samples collected from Osaka Bay and coastal waters of Western Japan. In all sediment samples, only PFCAs were detected, and the highest concentration was determined in Ajifu Waterway, where ΣPFAA was 58990 ng kg^{-1} dry weight. The total concentrations of PFAAs in sea water samples ranged between the limit of quantification and 53.4 ng L^{-1}, and perfluorohexanoic acid was the most prevalent and had the highest concentration of 37 ng L^{-1}. The changes in the patterns and concentrations of PFAAs in Osaka Bay and coastal waters of Western Japan indicate that the PFAAs in surface waters are influenced by sources from Keihanshin Metropolitan Area, mainly the Yodo River basin, and the dilution effect which naturally occurs during their transport to the Pacific Ocean.

Keywords: Perfluorinated compounds, LC-MS/MS, Seawater, Osaka Bay, Western Japan

1. Introduction

The two most studied perfluoroalkyl acids (PFAAs) are perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$) and perfluorooctane sulfonic acid (PFOS, $C_8F_{17}SO_3H$) (Domingo 2012). PFOS, including its form as salts and its precursor, perfluorooctane sulfonyl fluoride, is classified as a persistent organic pollutant (POP, Stockholm Convention, 2012). A number of studies have reported their bioaccumulative and toxic properties, and the ubiquitous distribution of PFAAs in the environment, wildlife and humans because of their physico-chemical properties and their persistence (Haug et al.2011; Domingo 2012).

After Tokyo, the second largest urban region in Japan with nearly 19 million inhabitants is Keihanshin Metropolitan Area. This areaencompasses metropolitan areas of the cities of Osaka in Osaka Prefecture, Kobe in Hyogo Prefecture and Kyoto in Kyoto Prefecture. Keihanshin surrounds Osaka Bay, the semi-enclosed bay located in Western Japan (Fig. 1). The major river in this area is the Yodo River, which receives water from Lake Biwa, the largest lake in Japan, through the Uji River and water from two other upstream rivers, the Katsura River and the Kizu River. The Yodo River has 19 intakes for drinking water for various cities, along with 12 discharge sites from wastewater treatment plants, before finally, flowing into Osaka Bay. As a result of predominantly human activities, much nutrient is loaded out to Osaka Bay, organic matter is accumulated at the bottom, and nutrients are released from the bottom sediment. Because of the polar nature of PFAAs, the aquatic environment is a primary phase in the environment to harbor these chemicals (Ahrens et al. 2010). Many studies have confirmed that concentrations of PFAAs in the rivers of Keihanshin Metropolitan Area were higher than in other districts of Japan (Saito et al. 2004; Lein et al. 2008; Takagi et al. 2008). Although high PFOA concentrations have been detected in the river, information on levels of PFAAs in Osaka Bay is scarce (Takemine et al. 2014). The objective of our study was to investigate the occurrence, spatial distribution, and pattern of PFAAs in the aquatic environment i.e. in seawater samples (W1-W15) from Osaka Bay, Kii Channel, and coastal waters of Western Japan from Osaka to Kagoshima Bay as well as in sediment samples (S1-S4) from Osaka Bay and Kagoshima Bay. Although there are several recent studies on PFAA pollution in the rivers which discharge their waters to Osaka bay (Takemine et al., 2014; Niisoe et al., 2015), we wanted to confirm our hypothesis that Osaka bay is a source of pollution for the western part of the Pacific Ocean near Japan. Our study will contribute to further understanding of the distribution of PFAAs in these waters in Japan and in the Pacific Ocean, which is important for the protection of environment and human health as well as for future remediation measures for polluted sediment.

2. Materials and Methods

2.1. Chemicals

A standard solution PFAC-MXB of perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) and a standard solution MPFAC-MXA of mass-labeled PFCAs and PFSAs were purchased from Wellington Laboratories, Inc., Guelph, Canada and had individual chemical purities of >98%. All solvents used were HPLC grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan).

2.2. Sample collection

Fifteen seawater samples were collected from Osaka Bay, Kii Channel, the Pacific Ocean, and Kagoshima Bay (W1-W15) as well as sediment samples from the Osaka Bay mouth of the Yodo River (S1), south from Kansai International Airport (S2), from Kagoshima Bay (S3), and from Ajifu Waterway (S4) (Fig. 1). The water samples were collected from a depth of five meters using a peristaltic pump with a flow rate of about 1 L min^{-1} installed on board a ship. The water samples were collected in new 1L polypropylene containers with narrow mouths and screwtops. The sampling containers were rinsed with methanol, Milli-Q water and water from the individual sampling points prior to use. The use of Teflon bottles and Teflon-lined caps was avoided throughout the analysis, to avoid interference. Sediment samples (the top 15 cm) were collected using a standard Ekman sediment sampler from a water depth of 17 m in Osaka Bay and 11 m in Kagoshima Bay. The samples were collected from the ship during a sampling campaign from August 26-28, 2014.

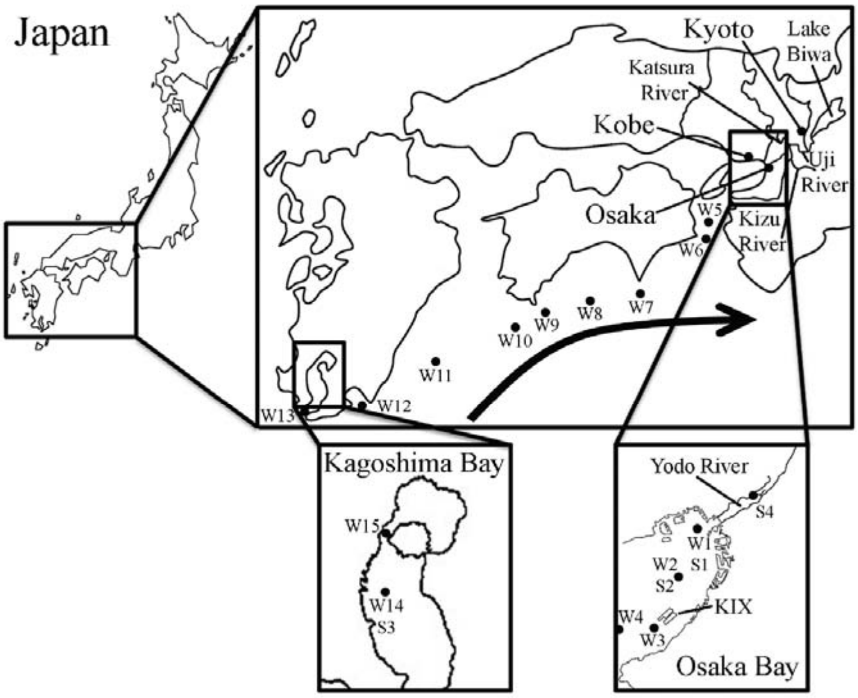

Fig. 1.

2.3. Sample extraction

Extraction of water samples was conducted on board the ship. Water samples were filtered with a glass filter (GC-50, Toyo Roshi Kaisha, Ltd., Tokyo, Japan). One liter of each sample was spiked with 20 μL MPFAC-MXA solution (each 100 pg μL^{-1} in methanol) as mass-labeled surrogates. The sample was then mixed with 60 μL formic acid and extracted with a solid-phase extraction (SPE) cartridge (Presep PFCII; Wako Pure Chemical Industries). SPE was preconditioned with 10 mL of 0.1% ammonium/methanol, then 10 mL of methanol, and finally 15 mL of Milli-Q water. The cartridges were washed with 10 mL Milli-Q water. The eluates were obtained using 5 mL 0.1% ammonium/methanol and concentrated to 1 mL by using a gentle nitrogen stream. Labeled 10 μL of $^{13}C_8$PFOA (100 pg μL^{-1} in methanol) was added as a syringe spike. Extraction of sediment samples was conducted in the laboratory as previously described (Beškoski et al. 2013). In brief, 5 g of homogenized sediments, previously dried to 105°C were extracted three times using 10 mL of methanol and ultrasonic extraction. MPFAC-MXA was spiked into each sediment sample before addition of methanol. After reducing the volume to 5 mL, 100 mL of Milli-Q water and 20 μL of formic acid were added, and the sample was extracted with preconditioned SPE. Further, the samples were extracted in the same manner as the water samples. All results of the sediment samples analyses were calculated according to dry matter. The seventeen perfluorinated compounds analyzed including perfluorinated carboxylates (C4-C14) and perfluorinated alkyl sulfonates (C4, C6, C8, and C10) are listed in Table S1.

2.4. PFAA analysis

Each final solution was analyzed by LC-MS/MS using a Xevo tandem quadrupole (TQ) MS (Nihon Waters K. K., Tokyo, Japan) coupled with an Acquity UPLC (Nihon Waters K. K.) equipped with a UPLC BEH C18 column (Nihon Waters K. K.) using negative electrospray ionization with multiple reaction monitoring as previously described by Takemine et al. (2014). Ammonium acetate (2 mM) and acetonitrile were used as a mobile phase under the gradient conditions: 1% to 95% of acetonitrile in 8 min, 95% of acetonitrile in 9 min, and 95% to 1% of acetonitrile in 9.1 min. The monitored transitions of analytes and surrogates used for quantification and confirmation are given in Table S2. Recovery rates (76-107%) were determined by spiking 200 mL Milli-Q water with 2 ng of all PFAA analytes using PFAC-MXB and conducting sample preparation and analysis in the same manner as for the samples ($n = 5$). By spiking 200 mL of seawater ($n = 1$) and 1 g of sediment ($n = 5$) with 5 ng of all PFAA analytes using PFAC-MXB a matrix spike recovery test was conducted. Recovery rates for seawater and sediment were 87-127% and 52-100%, respectively. PFAAs in the seawater and sediment samples were also analyzed without spiking and the recovery rates for the matrix spike test were calculated by subtracting the amount of PFAAs originally contained in the samples.

2.5. Quality control and quality assurance

The instrument limit of detection (LOD) was empirically defined as the injected amount producing a signal-to-noise ratio of 3, and the limit of quantification (LOQ) was defined as the injected amount producing a signal-to-noise ratio of 10. The method detection limit (MDL) and the method quantification limit (MQL) were determined by dividing the LOD and LOQ by the concentration factor. The MDLs for the PFCAs and PFSAs in seawater were 0.1 ng L^{-1} and 0.2 ng L^{-1}, respectively. The MQLs of PFCAs and PFSAs in the seawater were 0.3 ng L^{-1} and 0.6 ng L^{-1}, respectively. The MDLs for the PFCAs and PFSAs in sediment were 10 ng kg^{-1}-dry weight (dw) and 20 ng kg^{-1}-dw, respectively. The MQLs of PFCAs in sediment were 30 ng kg^{-1}-dw. All PFAA analytes in the laboratory blank ($n = 1$), confirmed conducting sample preparation and analysis in the same manner as for the water and sediment samples were less than the MDLs. A laboratory blank was included with each sample batch.

2.6. Other measurements

Sample pH, temperature, conductivity, salinity, chlorophyll concentrations, and ocean currents were determined during the sampling campaign.

2.7. Statistical analysis

The OriginPro 8.0 program was used for determination of Pearson's correlation coefficients.

3. Results and Discussion

3.1. PFAA distributions in Osaka Bay and coastal waters of Western Japan

Out of fifteen analyzed PFAAs, nine were detected in water samples at concentrations higher than the MDL (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, and PFOS). The total concentration of PFAAs (ΣPFAAs) in seawater samples ranged between the MDL and 53.4 ng L^{-1} (Fig. 2a, Table S5). Relatively higher levels occurred in Osaka Bay (W1-W4) as compared to Kii Channel (W5), the Pacific Ocean south from Shikoku Island (W6-W12), and Kagoshima Bay (W13-W15). The highest concentration of PFAAs was determined in sample W1, located at the mouth of the Yodo River, suggesting that the waters of the Yodo River are contributing to the pollution of Osaka Bay. Previous surveys showed that the concentrations in surface water of the Yodo River basin varied from 0.4 to 123 ng L^{-1} for PFOS and 4.2 to 2600 ng L^{-1} for PFOA (Lein et al. 2008). Lein et al. also showed the average concentrations in main stream sites of the Yodo River were 3 to 4 ng L^{-1} for PFOS and 23 to 33 ng L^{-1} for PFOA (Lein et al. 2008). Saito et al. found that the concentration of PFOS in the Yodo River ranged from 5.4 to 27.3 ng L^{-1}, and that the highest PFOA concentration of 141 ng L^{-1} was in surface water from the Yodo River (Saito et al. 2003; 2004). These studies showed that the main sources of PFOS and PFOA were effluents from three sewage treatment plants at Katsura River (upstream of the Yodo River). The amounts of PFOS and PFOA discharged into Osaka Bay through the Yodo River were estimated to be 64 and 375 g d^{-1}, respectively (Lein et al. 2006). In all collected samples in the current study which contained PFAAs, PFHxA was the most prevalent of the PFAAs, with the highest concentration of 37 ng L^{-1}. Relative amounts of PFHxA in ΣPFAAs ranged between 63% (W2) and 82% (W6). The second most abundant was PFOA, and the highest concentration was detected in sample W1 at a concentration of 6.2 ng L^{-1}.The other PFCAs, such as PFNA and PFBA, were detected at low concentrations only in W1 and W2, while long-chain PFCAs were not detected. The composition of PFAAs in the environment and their profile can be changed as a result of modifications in production and application patterns. Some companies have switched to shorter chain C6 PFAAs such as PFHxA to replace C8 chemicals such as PFOA (Daikin Industries Ltd., 2007). Wang et al. reported that shorter chain PFCAs have been emitted historically in large quantities (Wang et al. 2014). Water from Osaka Bay is carried via the Kii Channel to the Pacific Ocean, and it can be concluded that surface and ground waters of the Kansai area contribute to PFAA pollution of the Pacific off Western Japan. This is supported by the predominant PFAA, PFHxA, being detected in a seawater sample taken from W8, located in the open ocean, 50 km away from the nearest shore of Shikoku Island (Fig. 2a and Table S5). Whereas the north coast of Shikoku Island is an industrialized area, the south coast of Shikoku can be regarded as less industrialized. Because of that, the main source of pollution of these open ocean waters seems likely to be Osaka Bay. Concentrations of PFOA and PFOS were strongly positively correlated ($R^2 = 0.853$), and had similar profiles, even though the concentration of PFOA was 10 times higher than PFOS (Fig. S1a). The relationships of PFOA, PFOS, and PFHxA to ΣPFAAs were also examined (Fig. S1b-d). High linearity with determination coefficients of 0.902, 0.907 and 0.997 was observed for these three compounds, respectively. Since the spatial pattern of PFAAs did not vary in the water samples W1-W8, the high linearity suggested that PFAAs arrive from one source into Osaka Bay. If that is the case, the Yodo River basin must be considered the likely source, and PFAAs delivered by this water source could be uniformly spreading toward the Pacific Ocean. However, further research is needed to confirm the incidence and spread of PFAAs from Osaka Bay to the Pacific Ocean and to develop a model of contaminant spread.

The distribution between sediment and water is a key process which determines the fate of PFAAs, because sediment acts as a sink for PFAAs (Li et al. 2011). Since the layer of sediment in our samples encompassed only the top 15 cm, the PFAA concentrations in these sediments reflect recent contamination. Four sediment samples (S1-S4) were analyzed and the concentrations of PFHxA, PFHpA, and PFOA were the same in S1 and S2 which were located within 20 km of each other in Osaka Bay. However, the dominant PFAAs in S2 were those with longer perfluorinated alkyl chains such as PFNA, PFDA, and PFUnDA. This suggests that PFAAs in S2 had a different pollution source than PFAAs in S1.The highest concentration of PFAAs was determined in the sediment sample taken from Ajifu Waterway (S4) in Osaka (58990 ng kg^{-1} dw).

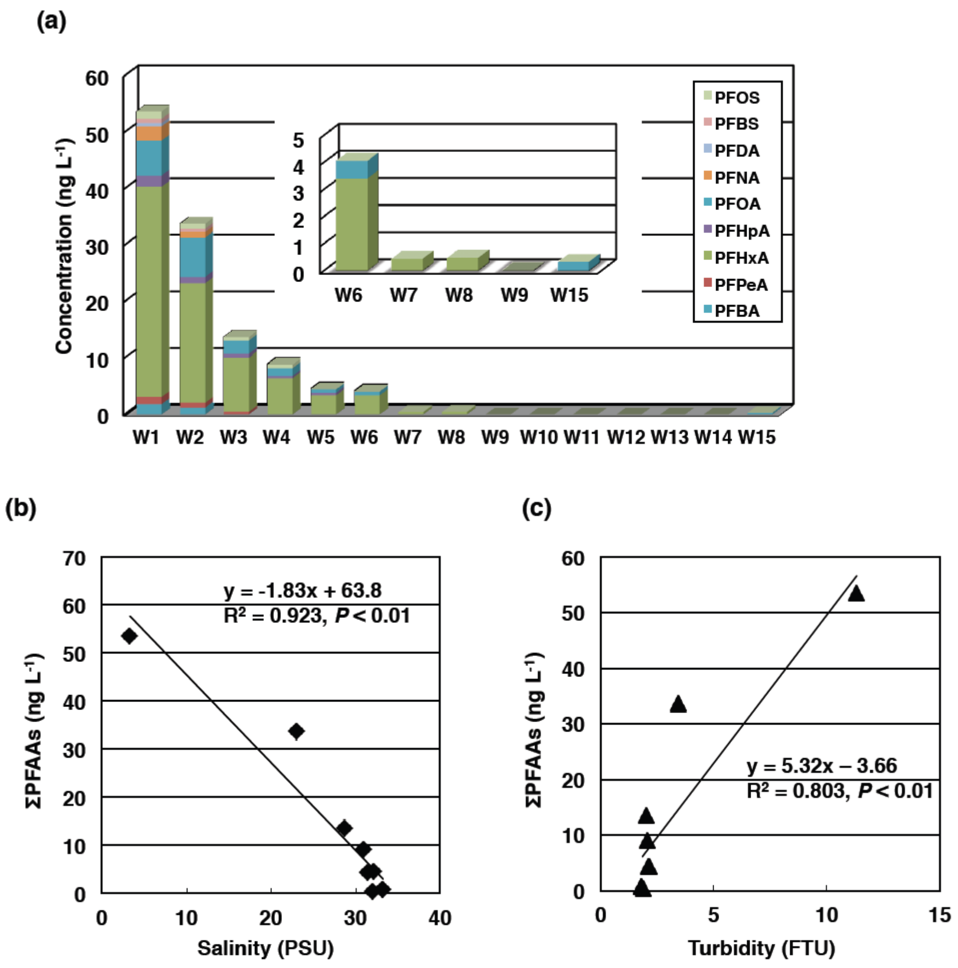

Fig. 2.

3.2. Basic parameters from sampling points

The average flow of the Yodo River is 267 $m^3 s^{-1}$, and the population of the Yodo River basin numbers more than ten million people. Inflow from the Yodo River caused low salinity and high chlorophyll concentration and turbidity in W1–3, which were located in Osaka Bay (Fig. 1 and Table S4). Kagoshima Bay is also a semi-enclosed bay, but the influence of river water on the bay water was not as strong as that of the Yoda River on Osaka Bay (Table S4). This was likely because the human population living on the river watershed which flows into Kagoshima Bay is approximately one-tenth of that of the Yodo River. The reduced pH in W15 was attributed to activity of the active volcano, Mt. Sakurajima (Table S4).

Determination of basic parameters has confirmed that fresh water carried by rivers has a strong influence on the chemistry of enclosed marine areas into which the watercourses drain. Furthermore, it would be expected that the distribution of several waterborne contaminants in Osaka Bay would be similar to each other and that correlation of PFAAs with salinity and turbidity may exist. Linearity with high determination coefficients between salinity and PFAAs (R^2>0.9) (Fig. 2b), and between turbidity and PFAAs (R^2>0.8) (Fig. 2c) confirmed that the distribution of PFAAs in Osaka Bay depends on fresh water distribution, ocean currents, and mixing.

3.3. Comparison of PFAA concentrations with those determined in previously published studies

The number of studies published on PFAAs has increased considerably during recent years. However, in most cases, only concentrations of PFOS and PFOA were reported. In Table S6, concentrations of PFAAs in sea and ocean water reported in the literature are given. The highest concentration was determined in the coastal sea area of Hyogo prefecture, Japan, suggesting significant contamination with PFHxA (Takemine et al. 2014). The PFHxA concentration we detected was 10 times lower than the concentration determined in the study by Takemine et al. (2014). However, sea water sampled at W1 had a PFHxA concentration three times higher than the German Bight maximum value (Ahrens et al. 2009). The concentration of PFOA in Osaka Bay determined in our study was two times lower than the concentration in the coastal sea area of Hyogo prefecture. The observed PFOA and PFOS concentrations in seawater of Osaka Bay were in the same range as the level of these pollutants in the coastal North Sea (Theobald et al. 2011). Interestingly, PFOA in the Pacific Ocean of Western Japan was in the same range as that determined in the open North Sea (Yamashita et al., 2005; Theobald et al. 2011). There are two main hypotheses for the global transport of PFAAs: direct transport of ionic PFAAs via sea and oceanic currents or long-range atmospheric transport of volatile precursor compounds. Our study supports the first hypothesis, and is in accordance with previous findings, that oceanic currents are the means for the spread of ionic PFAAs (Cai et al. 2012; Armitage et al. 2009; Prevedouros et al. 2006).

4. Conclusions

According to our study, the changes in PFAA patterns and concentrations in Osaka Bay and coastal waters of Western Japan indicate that the PFAAs in surface waters are influenced by sources from Keihanshin Metropolitan Area, mainly the Yodo River basin, and the dilution effect which naturally occurs during their transport to the Pacific Ocean. In the future, further study is needed to analyze the possible transfer of PFHxA and other shorter-chain PFAAs to biota in the enclosed aquatic environment of Osaka Bay.

Supplementary data

Fig. S1. Relationships between PFOA and PFOS (a); PFOA and ΣPFAAs (b); PFOS and ΣPFAAs (c); PFHxA and ΣPFAAs (d).

Pearson's correlation coefficients are shown in the graphs.

Table S1. The perfluoroalkyl acids (PFAAs) described in this study. Two types of functional groups with variable CF_2 chain length were included: perfluoroalkyl carboxylates and perfluoroalkyl sulfonates.

Table S2. Mass transitions for PFAAs and MPFAAs.

Table S3. Recovery of mass-labeled compounds in seawater and sediment samples.

Table S4. Sampling locations–coordinates and basic parameters.

Table S5. PFAA content in the seawater (ng L^{-1}) and sediment samples (ng kg^{-1}-dw).

Table S6. Concentrations of PFAAs in sea and ocean water (ng L^{-1}) reported in the literature.

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References

Ahrens, L., Felizeter, S., Ebinghaus, R.,2009. Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight. Chemosphere 76, 179–184.

Ahrens, L., Taniyasu, S., Yeung, L.W.Y., Yamashita, N., Lam, P.K.S., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 76, 266–272.

Armitage, J.M., Macleod, M., Cousins, I.T., 2009. Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxy acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources. Environ. Sci. Technol. 43, 5830−5836.

Benskin, J.P., Muir, D.C.G., Scott, B.F., Spencer, C., De Silva, A.O., Kylin, H., Martin, J.W., Morris, A., Lohmann, R., Tomy, G., Rosenberg, B., Taniyasu, S., Yamashita, N.,2012. Perfluoroalkyl acids in the Atlantic and Canadian arctic Oceans. Environ. Sci. Technol. 46, 5815−5823.

Beškoski, V.P., Takemine, S., Nakano, T., Slavković Beškoski L.,Gojgić-Cvijović, G., Ilić, M., Miletić, S., Vrvić, M.M., 2013. Perfluorinated compounds in sediment samples from the wastewatercanal of Pančevo (Serbia) industrial area. Chemosphere 91, 1408–1415.

Cai, M., Zhao, Z., Yin, Z., Ahrens, L., Huang, P., Cai, M., Yang, H., He, J., Sturm, R., Ebinghaus, R., Xie, Z.,2012 Occurrence of perfluoroalkyl compounds in surface waters from the North Pacific to the Arctic Ocean. Environ. Sci. Technol. 46, 661−668.

Daikin Industries, Ltd., 2007. Elimination of PFOA in Fluorochemical Products. http://www.daikin.com/press/2007/071221/. Accessed 10August 2016

Domingo, J.L., 2012. Health risks of dietary exposure to perfluorinated compounds. Environ. Int. 40, 187–195.

Filipovic, M., Berger, U., McLachlan, M.S., 2013. Mass balance of perfluoroalkyl acids in the Baltic Sea. Environ. Sci. Technol. 47, 4088–4095.

Haug, L.S., Huber, S., Becher, G., Thomsen, C., 2011. Characterisation of human exposure pathways to perfluorinated compounds–Comparing exposure estimates with biomarkers of exposure. Environ. Int. 37, 687–693.

Lein, N.P.H., Fujii, S., Takana, S., Nozoe, M., Wirojanagud, W., Anton, A., Lindstrom, G., 2006. Perfluorinated substances in tap water of Japan and several countries and their relationship to surface water contamination. Environ. Eng. Res. (Japanese Journal) 43, 611–618.

Lein, N.P.H., Fujii, S., Tanaka, S., Nozoe, M., Tanaka, H., 2008. Contamination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in surface water of the Yodo River basin (Japan). Desalination 226, 338–347.

Li, F., Sun, H., Hao, Z., He, N., Zhao, L., Zhang, T., Sun, T., 2011. Perfluorinated compounds in Haihe River and Dagu drainage canal in Tianjin, China.Chemosphere 84, 265–271.

Loos, R., Tavazzi, S., Paracchini, B., Canuti, E., Weissteiner, C., 2013. Analysis of polar organic contaminants in surface water of the northern Adriatic Sea by solid-phase extraction followed by ultrahigh-pressure liquid chromatography-QTRAP(R) MS using a hybrid triple-quadrupole linear ion trap instrument. Anal. Bioanal. Chem. 405, 5875–5885.

Moller, A., Ahrens, L., Surm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R.,de Voogt, P., 2010. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environ. Pollut. 158, 3243–3250.

Niisoe, T., Senevirathna, S.T.M.L.D., Harada, K.H., Fujii, Y., Hitomi, T., Kobayashi, H., Yan, J., Zhao, C., Oshima, M., Koizumi, A., 2015. Perfluorinated carboxylic acids discharged from the Yodo River Basin, Japan. Chemosphere 138, 81–88.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 40, 32−44.

Saito, N., Harada, K., Inoue, K., Sasaki, K., Yoshinaga, T., Koizumi, A., 2004. Perfluorooctanoate and perfluorooctane sulfonate concentrations in surface water in Japan. J. Occup. Health 46, 49−59.

Saito, N., Sasaki, K., Nakatome, K., Harada, K., Yoshinaga, T., Koizumi, A., 2003. Perfluorooctane sulfonate concentrations in surface water in Japan. Arch. Environ. Contam. Toxicol. 45, 149–158.

Sakurai, T., Serizawa, S., Isobe, T., Kobayashi, J., Kodama, K., Kume, G., Lee, J.H., Maki, H., Imaizumi, Y., Suzuki, N., Horiguchi, T., Morita, M., Shiraishi, H., 2010. Spatial, phase, and temporal distributions of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in Tokyo Bay, Japan. Environ. Sci. Technol. 44, 4110−4115.

So, M.K., Taniyasu, S., Yamashita, N., Giesy, J.P., Zheng, J., Fang, Z., Im, S.H., Lam, P.K., 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China and Korea. Environ. Sci. Technol. 38, 4056−4063.

Stockholm Convention, 2012. Guidelines on best available techniques and best environmental practices for the production and use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs (Draft). http://chm.pops.int/. Accessed 10August 2016

Takagi, S., Adachi, F., Miyano, K., Koizumi, Y., Tanaka, H., Mimura, M., Watanabe, I., Tanabe, S., Kannan, K., 2008. Perfluorooctane sulfonate and perfluorooctanoate in raw and treated tap water from Osaka, Japan. Chemosphere 72, 1409–1412.

Takemine, S., Matsumura, C., Yamamoto, K., Suzuki, M., Tsurukawa, M., Imaishi, H., Nakano, T., Kondo, A., 2014. Discharge of perfluorinated compounds from rivers and their influence on the coastal seas of Hyogo prefecture, Japan. Environ.Pollut. 184, 397–404.

Theobald, N., Caliebe, C., Gerwinski, W., Hühnerfuss, H., Lepom, P., 2011. Occurrence of perfluorinated organic acids in the Northand Baltic seas. Part 1: distribution in sea water. Environ. Sci. Pollut. Res. 18, 1057–1069.

Wang, Z.,Cousins, I.T., Scheringer, M., Buck, R.C.,Hungerbühler, K., 2014. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. Environ. Int. 70, 62–75.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Okazawa, T., Petrick, G., Gamo, T., 2004. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. Environ. Sci. Technol. 38, 5522–5528.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global survey of perfluorinated acids in oceans, Mar. Pollut. Bull. 51, 658–668.

Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P.P.K., Kannan, K., 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters.Chemosphere 70, 1247–1255.

Figure legends

Fig. 1. Sampling locations in the Osaka bay, Kagoshima bay, and coastal waters of Western Japan

The arrow represents ocean currents in the Pacific Ocean.

Fig. 2. Spatial distribution (a) of individual PFAAs in surface water samples obtained from Osaka Bay and coastal waters of Western Japan and relationship between salinity and PFAAs (b), and turbidity and PFAAs (c)

Pearson’s correlation coefficients were shown in the graphs.

Table S1. The perfluoroalkyl acids (PFAAs) described in this study. Two types of functional groups with variable CF_2 chain length were included: perfluoroalkyl carboxylates and perfluoroalkyl sulfonates.

Formula/Name/Acronym	No. of CF_2 groups	Acronym	Analyte
	$n = 2$	PFBA	Perfluorobutanoate
	$n = 3$	PFPeA	Perfluoropentanoate
	$n = 4$	PFHxA	Perfluorohexanoate
	$n = 5$	PFHpA	Perfluoroheptanoate
	$n = 6$	PFOA	Perfluorooctanoate
	$n = 7$	PFNA	Perfluorononanoate
	$n = 8$	PFDA	Perfluorodecanoate
	$n = 9$	PFUnDA	Perfluoroundecanoate
	$n = 10$	PFDoDA	Perfluorododecanoate
	$n = 11$	PFTrDA	Perfluorotridecanoate
	$n = 12$	PFTeDA	Perfluorotetradecanoate
	$n = 3$	PFBS	Perfluorobutanesulfonate
	$n = 5$	PFHxS	Perfluorohexanesulfonate
	$n = 7$	PFOS	Perfluorooctanesulfonate
	$n = 9$	PFDS	Perfluorodecanesulfonate

Table S2. Mass transitions for PFAAs and MPFAAs

Analyte	Parent ion	Product ion (Quantification/confirmation)	Surrogate
PFBA	213	169	MPFBA
PFPeA	263	219	MPFBA
PFHxA	313	269/119	MPFHxA
PFHpA	363	319/169	MPFHxA
PFOA	413	369/169	MPFOA
PFNA	463	419/169	MPFNA
PFDA	513	469/169	MPFDA
PFUnDA	563	519/169	MPFUnDA
PFDoDA	613	569/169	MPFDoDA
PFTrDA	663	619/169	MPFDoDA
PFTeDA	713	669/169	MPFDoDA
PFBS	299	80/99	MPFHxS
PFHxS	399	80/99	MPFHxS
PFOS	499	80/99	MPFOS
PFDS	599	80/99	MPFOS
MPFBA	217	172	-
MPFHxA	315	270	-
MPFOA	417	372	-
MPFNA	468	423	-
MPFDA	515	470	-
MPFUnDA	565	520	-
MPFDoDA	615	570	-
MPFHxS	403	84	-
MPFOS	503	80	-

Table S3. Recovery of mass-labeled compounds in seawater and sediment samples

Compound	Seawater (%)	Sediment (%)
MPFBA	82	84 ± 9
MPHxA	99	86 ± 6
MPFOA	91	93 ± 5
MPFNA	91	93 ± 3
MPFDA	87	98 ± 6
MPFUnDA	95	89 ± 5
MPFDoDA	92	69 ± 4
MPFHxS	103	93 ± 9
MPFOS	102	101 ± 15

Table S4. Sampling locations–coordinates and basic parameters

Sample no.	Location		Temp (°C)	pH	Conductivity (mS cm^{-1})	Salinity (PSU)	Chlorophyll (µg L^{-1})	Turbidity (FTU)	Sampling date	Sampling time (h)
	Latitude (N)	Longitude (E)								
W1	34°39.32'	135°21.71'	27.5	8.30	6.4	3.33	2.14	11.3		14:00
W2	34°31.34'	135°15.49'	28.3	8.80	38.9	23.01	9.54	3.5		15:00
W3	34°23.75'	135°10.71'	27.9	8.72	47.2	28.77	4.59	2.1		16:50
W4	34°21.06'	135°0.05'	27.1	8.33	49.6	31.03	1.44	2.1		0:50
W5	34°8.05'	134°56.18'	26.5	8.26	50.6	32.14	1.35	2.1		1:50
W6	33°47.77'	134°48.06'	27.5	8.35	50.5	31.37	1.12	2.2		3:30
W7	33°9.81'	134°8.93'	28.4	8.31	54.1	33.23	0.36	1.8		7:30
W8	33°3.72'	133°40.15'	28.2	8.31	53.9	33.27	0.34	1.8		10:00
W9	32°40.88'	133°5.61'	28.2	8.32	52.3	32.07	0.36	1.9		13:30
W10	32°23.68'	132°44.36'	29.3	8.32	56.4	34.11	0.30	1.8		16:00
W11	31°51.37'	132°3.52'	29.2	8.32	56.1	34.01	0.32	1.9		21:00
W12	31°14.77'	131°12.54'	27.8	8.33	54.6	33.98	0.54	1.9		2:50
W13	31°6.83'	130°39.74'	28.5	8.34	53.1	32.51	0.84	2.1		6:20
W14	31°33.36'	130°35.5'	26.5	8.40	50.3	31.86	1.32	2.3		8:50
W15	31°35.83'	130°34.04'	26.6	6.62	49.6	31.38	1.95	2.4		10:00
S1	34°39.32'	135°21.71'	/	/	/	/	/	/		14:20
S2	34°23.75'	135°10.71'	/	/	/	/	/	/		15:20
S3	31°33.36'	130°35.5'	/	/	/	/	/	/	August 28, 2014	9:00
S4	34°45.43'	135°33.51'	/	/	/	/	/	/	June 12, 2014	10:00

Table S5. PFAA content in the seawater (ng L^{-1}) and sediment samples (ng kg^{-1}-dw)

Sample	Concentration (ng L^{-1}) or (ng kg^{-1}-dw)															
	PFCA											PFSA				
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS	
W1	1.8	1.3	37	2	6.2	2.5	0.58	<MDL[1]	<MDL	<MDL	<MDL	0.76	<MDL[2]	1.3	<MDL	53.44
W2	1.2	0.85	21	1.1	7	0.95	<MDL	<MDL	<MDL	<MDL	<MDL	<MQL[3]	<MDL	0.89	<MDL	33.19
W3	<MDL	0.48	9.5	0.64	2.3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MQL	<MDL	13.12
W4	<MDL	<MQL[4]	6.4	0.38	1.4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MQL	<MDL	8.48
W5	<MDL	<MDL	3.4	0.43	0.6	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	4.43
W6	<MDL	<MDL	3.4	<MQL	0.65	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	4.15
W7	<MDL	<MDL	0.43	<MDL	<MQL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.53
W8	<MDL	<MDL	0.46	<MQL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.56
W9	<MDL	<MDL	<MDL	<MDL	<MQL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MQL
W10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
W11	<MDL	<MDL	<MDL	<MQL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MQL
W12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
W13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
W14	<MDL	<MDL	<MDL	<MDL	<MQL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MQL
W15	<MDL	<MDL	<MDL	<MDL	0.31	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.31
S1	<MDL[5]	46	130	62	88	<MQL[6]	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL[7]	<MDL	<MDL	<MDL	336
S2	<MDL	<MQL	110	65	94	110	220	430	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1039
S3	<MDL	<MQL	33	<MQL	77	50	31	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	211
S4	390	1100	2300	1100	9500	1900	2600	1500	16000	4600	18000	<MDL	<MDL	<MDL	<MDL	58990

The total concentration of PFAAs (ΣPFAAs) was calculated for the PFAAs detected by assigning the concentration to the MDL if the concentration ranged between MDL and MQL.

[1] MDL_{PFCAs} (0.1 ng L^{-1}) seawater

[2] MDL_{PFSAs} (0.2 ng L^{-1}) seawater

[3] MQL_{PFSAs} (0.6 ng L^{-1}) seawater

[4] MQL_{PFCAs} (0.3 ng L^{-1}) seawater

[5] MDL_{PFCAs} (10 ng kg^{-1}-d) sediment

[6] MQL_{PFCAs} (30 ng kg^{-1}-dw) sediment

[7] MDL_{PFSAs} (20 ng kg^{-1}-dw) sediment

Table S6. Concentrations of PFAAs in sea and ocean water (ng L^{-1}) reported in the literature

Location		Sample	PFHxA	PFOA	PFOS	Reference
	Adriatic sea	Sea	2.202	2.505	1.343	Loos et al. 2013
	Baltic sea	Sea	0.100-0.163	0.177-0.400	0.100-0.190	Filipovic et al. 2013
	Western Baltic Sea	Sea	0.096-0.188	0.47-1.05	0.33-0.9	Theobald et al. 2011
	German Bight, German	Sea	0.47-9.56	2.67-7.83	0.69-3.95	Ahrens et al. 2009
		Sea	<0.03-0.37	n.d.-0.59	0.26-1.40	Moller et al. 2010
		Sea	<0.024-1.722	0.54-5.9	0.28-3.1	Theobald et al. 2011
	Open North Sea	Sea	<0.024-1.722	0.084-0.77	0.048-0.43	Theobald et al. 2011
	North sea	Sea	0.170-0.180	0.140-0.146	0-0.0300	Filipovic et al. 2013
	Norwegian Sea	Sea	<MDL	0.045-0.060	0.025-0.08	Benskin et al. 2012
	Greenland Sea	Sea	<MDL	0.025-0.080	0.012-0.032	Benskin et al. 2012
	Eastern Atlantic	Ocean	0.047-0.110	0.096-0.259	0.061-0.192	Benskin et al. 2012
	Western Atlantic	Ocean	0.014-0.075	0.017-0.049	0.013-0.032	Benskin et al. 2012
		Ocean	-	0.100-0.439	0.037-0.073	Yamashita et al. 2005
		Ocean	-	0.067-0.439	0.013-0.073	Yamashita et al. 2008
	Mid to Eastern Atlantic	Ocean	<MDL*-0.051	0.023-0.089	0.030-0.078	Benskin et al. 2012
	Mid to southeastern Atlantic	Ocean	0.018-0.075	0.017-0.030	0.018-0.030	Benskin et al. 2012
		Ocean	-	0.160-0.338	0.0086-0.036	Yamashita et al. 2005
		Ocean	-	0.052-0.338	0.0086-0.036	Yamashita et al. 2008
Arctic Ocean	Arctic Ocean	Ocean	<0.027-0.028	<0.020-0.067	<0.021-0.053	Cai et al. 2012
	Southwest Atlantic	Ocean	0.003-0.017	0.003-0.026	0.018-0.045	Benskin et al., 2012
	East Coast U.S.	Ocean	0.053-0.150	0.080-0.252	0.046-0.191	Benskin et al. 2012
Eastern Pacific Ocean	Eastern Pacific Ocean	Ocean	-	0.136-0.142	0.054-0.078	Yamashita et al. 2004
	Central to Eastern Pacific Ocean	Ocean	-	0.015-0.062	0.0011-0.020	Yamashita et al. 2005
	Central to Western Pacific Ocean	Ocean	-	0.015-0.056	0.0011-0.0046	Yamashita et al. 2004
North Pacific Ocean	North Pacific Ocean and Bering Sea	Ocean	-	<0.020 - 0.100	<0.021-0.060	Cai et al. 2012
	Western Pacific Ocean	Ocean	-	0.136-0.142	0.054-0.078	Yamashita et al. 2005
		Sea	-	154.3-192.0	12.7-25.4	Yamashita et al. 2004
		Sea	-	1.8-192.0	0.338-57.7	Yamashita et al. 2005
		Sea	-	1.7-25	0.88-9.0	Sakurai et al. 2010
	Coastal sea area of Hyogo prefecture, Japan	Sea	8.7-510	<MDL-12	<MDL-<3.0	Takemine et al. 2014
	Japan Sea	Sea	<0.027	0.060-0.079	<0.021	Cai et al. 2012
		Sea	-	0.24-320	0.04-730	So et al. 2004
		Ocean	-	0.239-11.35	0.039-2.53	Yamashita et al. 2005
	Gyeonggi Bay, Korea	Sea	<0.50-0.60	0.94-3.29	2.24-8.26	Rostkowski et al. 2006
	Sulu Sea	Sea	-	0.088-0.510	<0.017-0.109	Yamashita et al. 2004
		Sea	-	0.73-5.5	0.09-3.1	So et al. 2004
		Ocean	-	0.673-5.45	0.070-2.6	Yamashita et al. 2005
	Coastal area of China	Ocean	-	0.243-15.3	0.023-9.68	Yamashita et al. 2005
	South China Sea	Sea	-	0.160-0.420	0.008-0.113	Yamashita et al. 2004
	Osaka Bay	Sea	6.4-37	1.4-7	<0.6-1.3	This study
	Kii Channel	Sea	3.4	0.6	<0.2	This study
	Kagoshima Bay	Sea	<0.1	<0.1-0.31	<0.2	This study
	Western Japan, Pacific Ocean	Ocean	<0.1-3.4	<0.1-0.65	<0.2	This study

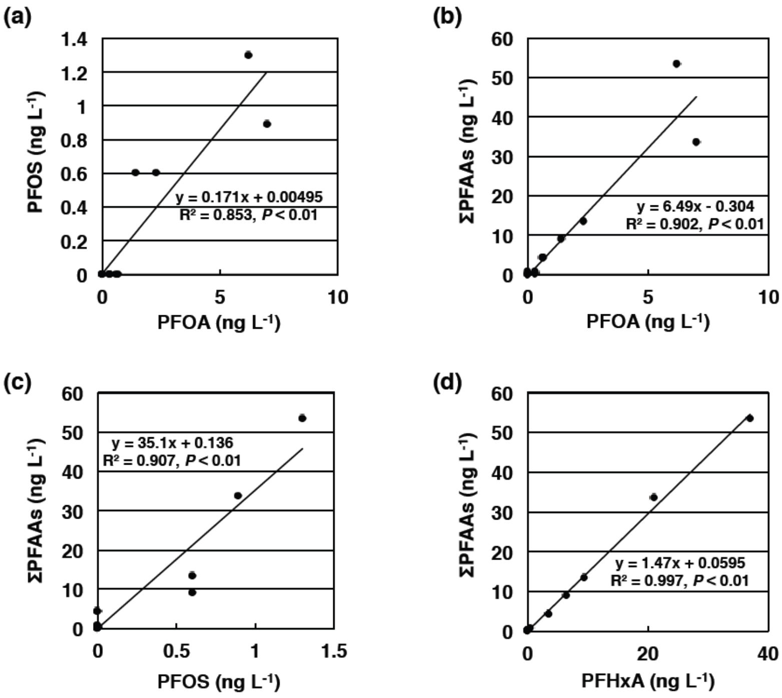

Fig. S1.

Fig. S1 Relationship between PFOA and PFOS (a); PFOA and ΣPFAAs (b); PFOS and ΣPFAAs (c); PFHxA and ΣPFAAs (d)
Pearson’s correlation coefficients were shown in the graphs.