

# Perfluorinated Compounds in Coastal Waters of Hong Kong, South China, and Korea

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Perfluorinated compounds (PFCs), such as perfluorooctanesulfonate (PFOS) and related compounds, have recently been identified in the environment. PFOS, the terminal degradation product of many of the PFCs, has been found globally in many wildlife species, as well as open ocean waters, even in remote regions far from sources. In this study, a solid-phase extraction procedure coupled with high-performance liquid chromatography interfaced to high-resolution mass spectrometry was used to isolate, identify, and quantify small concentrations of PFCs in seawater. These techniques were applied to investigate the local sources of PFCs in several industrialized areas of Asia and provide information on how the PFCs are circulated by coastal currents. Ranges of concentrations of PFOS in coastal seawaters of Hong Kong, the Pearl River Delta, including the South China Sea, and Korea were 0.09–3.1, 0.02–12, and 0.04–730 pg/mL, respectively, while those of perfluorooctanoic acid (PFOA) were 0.73–5.5, 0.24–16, and 0.24–320 pg/mL, respectively. Potential sources of PFCs include major industrialized areas along the Pearl River Delta of southern China and major cities of Korea, which are several of the fastest growing industrial and economic regions in the world. Detectable concentrations of PFOS and PFOA in waters of southern China were similar to those in the coastal marine environment of Japan and certain regions in Korea. Concentrations of PFCs in several locations in Korean waters were 10–100-fold greater than those in the other locations on which we report here. The spatial and seasonal variations in PFC concentrations in surface seawaters in the Pearl River Delta and South China Sea indicate the strong influence of the Pearl

River discharge on the magnitude and extent of PFC contamination in southern China. All of the concentrations of PFOS were less than those that would be expected to cause adverse effects to aquatic organisms or their predators except for one location in Korea adjacent to an industrialized area. Hazard quotients were from <0.001 to 0.002 for aquatic animals and ranged from <0.001 to 17 for predatory birds.

## Introduction

Perfluorinated compounds (PFCs) have been manufactured for over 50 years and, due to their unique properties of repelling both water and oil, have been used as surfactants and surface protectors in carpets, leather, paper, food containers, fabric, and upholstery and as performance chemicals in products such as fire-fighting foams, floor polishes, and shampoos (1). Certain PFCs, e.g., perfluorooctanesulfonyl compounds, have been manufactured through electrochemical fluorination with anhydrous hydrofluoric acid as the fluorine source (1, 2). Telomerization has recently become more widely used in the production of many PFCs. Perfluorooctanesulfonyl fluoride (POSF) is the basic building block of many PFCs, whereas PFOS is considered to be the terminal degradation product of many of the commercially used PFCs and is the predominant perfluorinated acid (PA) found in most environments that have been studied. However, there are a number of other PFCs used commercially that can occur in the environment, including perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA), perfluorohexanesulfonate (PFHS), perfluorobutanesulfonate (PFBS), and perfluorononanoic acid (PFNA) (2).

Specific properties of fluorinated compounds arise from the characteristic nature of the elemental fluorine atom (2). Fluorine, possessing the greatest electronegativity (4.0) relative to the other halogens, has the strongest inductive electron withdrawal ability and forms a strong carbon–fluorine (C–F) covalent bond (3). The C–F bond is very strong (110 kcal/mol), which gives the thermal and chemical stability to many PFCs. Indeed, many PAs are resistant to hydrolysis, photolysis, biodegradation, and metabolism. These properties account for the environmental persistence and bioaccumulative potential of PFCs and their derivatives, including PAs (4). PFOS is now known to be a ubiquitous contaminant and is found globally in many environmental media even in remote regions far from sources. PFOS has been found in fish-eating birds such as cormorant and herring gulls in the Laurentian Great Lakes (5), dolphins from Florida (6), polar bear and ringed seal from the Canadian Arctic (7), fish, shrimps, and crabs from the Western Scheldt estuary and the southern North Sea (8, 9), and human serum (10). Even though the environmental fate of PFOS is not fully understood, volatile precursors, containing a PFOS moiety, reaching remote locations and finally being metabolized to PFOS is the accepted mechanism accounting for the occurrence of PFOS in these areas (11). Due to the widespread occurrence and potential toxicities of many PFCs, the 3M Co., one of the largest producers of PFCs, ceased most production of PFOS in 2000.

Various studies have demonstrated toxicity of certain PFCs, including PFOS toxicity to rats and monkeys, and the toxic effects include mortality, carcinogenicity, and adverse

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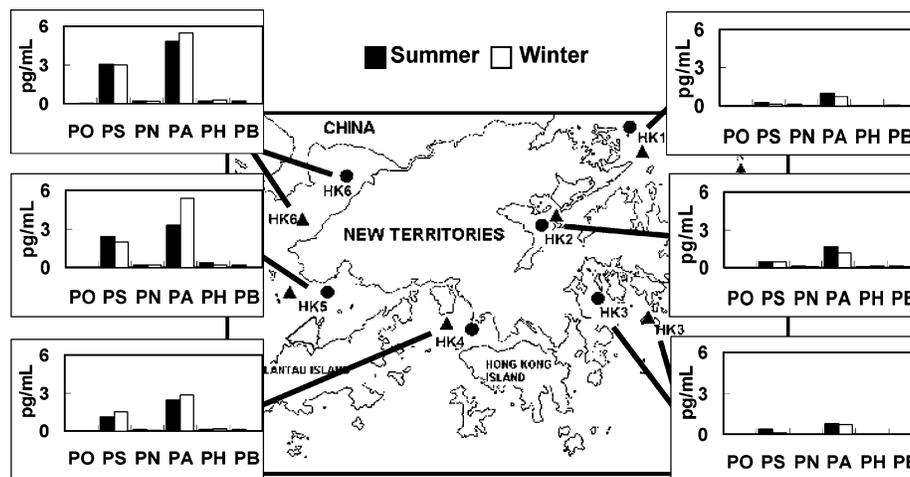


FIGURE 1. Concentrations of PFCs in coastal waters collected from Hong Kong in the summer and winter (PO, PFOSA; PS, PFOS; PN, PFNA; PA, PFOA; PH, PFHS; PB, PFBS).

effects on development, thyroid functions, pancreatic functions, and reproduction (1, 12). Furthermore, Hu et al. (13) demonstrated the ability of PFOS to affect gap junctional intercellular communication (GJIC). GJIC plays a vital role in maintaining the homeostasis of tissues by an exchange of chemical signals among adjacent cells without passing through the extracellular space.

The Pearl River Delta (PRD) in South China, with a population of 42 million people and a land area of approximately 41000 km<sup>2</sup>, has experienced an extremely rapid rate of development in the past decade. In 2001, the gross industrial output (GIO) of the industry in the PRD region was approximately \$145 billion, accounting for 13% of the total GIO of China exclusive of Hong Kong. Production of electronic and telecommunication equipment and electric equipment and machinery accounts for more than a third of the GIO in the PRD. These industries, together with a large number of small- and medium-sized private manufacturing operations, have transformed the PRD into one of the "world's factories". The manufacturing processes of electronic/electric and plastic goods and textiles are expected to be potential sources of PFCs, such as PFOS and PFOA.

Hong Kong, situated at the southeastern corner of the PRD, is strongly influenced by the Pearl River, which has an annual discharge of 340 billion m<sup>3</sup>. The Pearl River, with its increased flow volume in the summer (about 80% of the annual discharge), has been considered the major source of environmental contaminants in Hong Kong coastal waters. Consequently, the western waters of Hong Kong tend to have greater concentrations of environmental contaminants than the eastern coastal waters (14).

As part of an ongoing study to determine the current status and trends as well as the magnitude and extent of contamination of the marine environment with PFCs, an international joint survey of concentrations of PFCs in coastal seawaters of Asia was conducted in 2003–2004. Concentrations of various PFCs, including PFOS, PFOA, PFOSA, PFHS, PFBS, and PFNA, were measured in coastal seawaters in the PRD, including Hong Kong, surface waters from the South China Sea, and Korea. These results, combined with the hydrological information of PRD and open ocean currents in different seasons, help to make clear the sources and transport pathways of PFCs in the PRD region and its nearby South China Sea. In addition, a preliminary hazard assessment was also undertaken to determine the potential risk to aquatic animals and predatory birds associated with exposure to PFOS in Asian coastal waters.

## Materials and Methods

**Chemicals and Standards.** 1H,1H,2H,2H-perfluorooctanesulfonate (THPFOS) (100 ng/mL) and the external standards, a mixture of perfluorinated compounds (PFCmix) containing PFOS, PFOSA, PFOA, PFHS, PFBS and PFNA at 100 ng/mL, were supplied by the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan. All distilled water and methanol used in this study were of HPLC grade, and were purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan).

**Water Sample Collection.** Seawater samples were collected from six locations in Hong Kong in July 2003 and again in January 2004, and eight and six locations along the PRD and South China Sea in September 2003 and January 2004, respectively (Figures 1–3). Samples collected in July and September represented summer conditions, while those collected in January represented winter conditions. In addition, water samples were also collected from 11 locations along the west and south coasts of South Korea (Figure 4).

Six liters of surface water was collected from each sampling station by using a stainless steel bucket. Water samples were stored in six 1 L polypropylene (PP) containers with narrow mouths and screw tops. All the equipment including the stainless steel bucket and PP bottles was precleaned by rinsing with methanol, distilled water, and then water from the specific location before sample collection. Residual chlorine in each water sample was reduced by adding 200  $\mu$ L of 250 mg/mL sodium thiosulfate solution using a disposable PP syringe. Addition of sodium thiosulfate had no significant effect on recoveries (data not shown). Disposable PP laboratory ware, instead of glassware, was used to prevent binding of the analyte to the glass surfaces. Most samples were extracted within 24 h of collection. However, when this was not possible, samples were refrigerated at 4  $\pm$  2  $^{\circ}$ C in darkness before extraction. Teflon-containing materials and laboratory ware as well as the analytical instrumentation were minimized to avoid contamination of the samples, which allowed the development of a method with sufficient detection limits to quantify the majority of PFCs in most seawater samples.

**Sample Extraction.** Seawater samples were extracted using Oasis HLB extraction cartridges (0.2 g, 6 cm<sup>3</sup>) (Waters Corp., Milford, MA). Prior to the Oasis cartridge being loaded with the water sample, the cartridge was preconditioned by eluting with 5 mL of methanol followed by 5 mL of distilled water at a rate of 2 drops/s. An aliquot of water (200–500 mL) was spiked with 10  $\mu$ L of 100 ng/mL THPFOS, and then loaded onto the cartridge, eluting at a rate of 1 drop/s, and

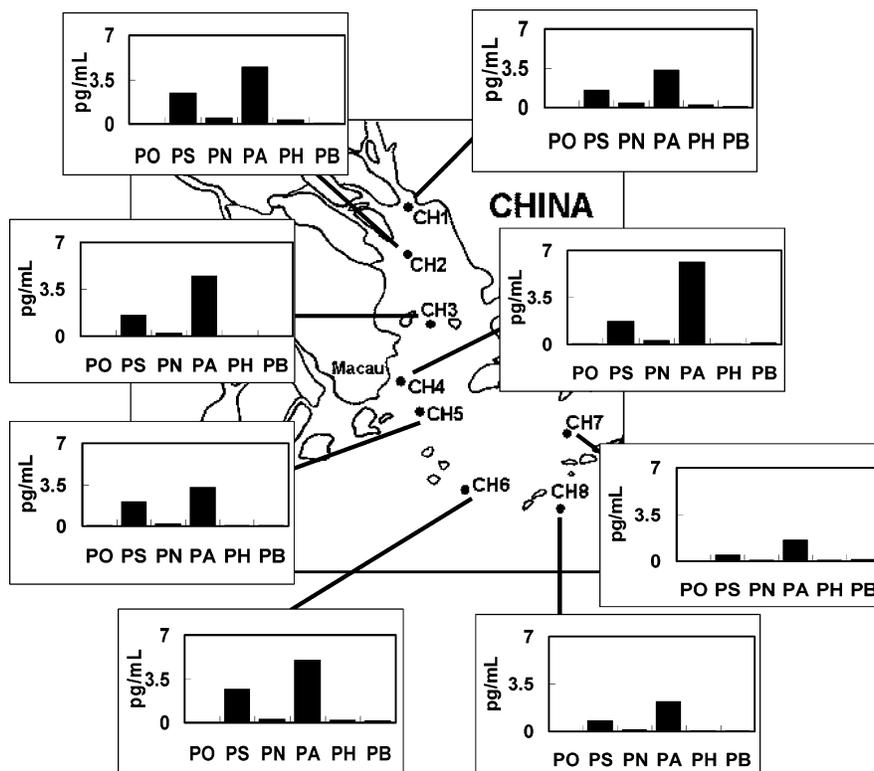


FIGURE 2. Concentrations of PFCs in coastal waters collected from the Pearl River Delta and South China Sea in the summer (PO, PFOSA; PS, PFOS; PN, PFNA; PA, PFOA; PH, PFHS; PB, PFBS).

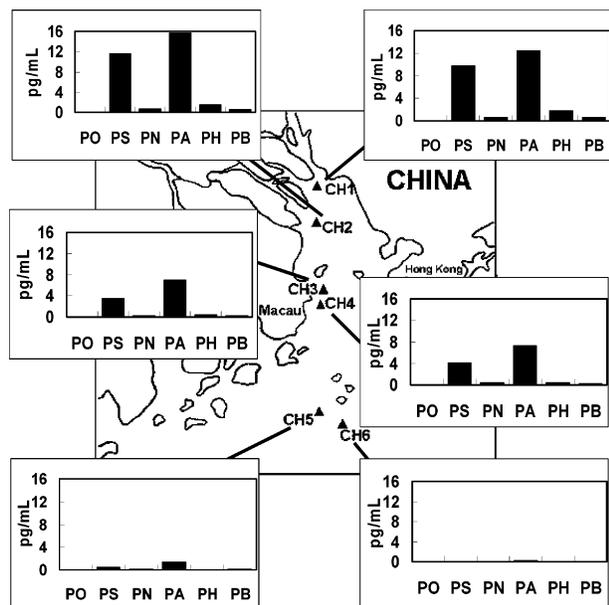


FIGURE 3. Concentrations of PFCs in coastal waters collected from the Pearl River Delta and South China Sea in the winter (PO, PFOSA; PS, PFOS; PN, PFNA; PA, PFOA; PH, PFHS; PB, PFBS).

the eluate was discarded. The cartridge was prevented from becoming dry at all times during loading of the water sample. The cartridge was then washed with 5 mL of 40% methanol in water at a rate of 1 drop/s, and the eluate was again discarded. During this step, the cartridge was allowed to run dry. Finally, the target fraction was eluted with 10 mL of methanol at a rate of 1 drop/s. The eluate was reduced to a known volume of 0.2–0.5 mL under a gentle stream of high-purity nitrogen gas, depending on the loading volume of the sample, and then transferred into a polypropylene vial for chemical analysis.



FIGURE 4. Sampling locations along the west and south coasts of South Korea.

**Instrumental Analysis.** Concentrations of PFCs in water samples were analyzed using high-performance liquid chromatography with high-resolution, electrospray tandem mass spectrometry (HPLC–MS/MS). Separation of analytes was performed by an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) interfaced with a Micromass Quattro II mass spectrometer (Waters) operated in the electrospray negative mode. A 10  $\mu$ L aliquot of extract was injected onto a Keystone Betasil C<sub>18</sub> column (2.1 mm i.d.  $\times$  50 mm length, 5  $\mu$ m) with 2 mM ammonium acetate/methanol as the mobile phase starting at 10% methanol at a flow rate of 300  $\mu$ L/min. The gradient increased to 100% methanol at 10 min before

TABLE 1. Recoveries (%) and Level of Blank (pg/mL) for Individual PFCs

target analyte	recovery (%)				blank (pg/mL)			
	range	mean	SD	no. of samples	range	mean	SD	no. of samples
PFOSA	76–98	86	9.1	4	<0.005	<0.005		12
PFOS	84–120	98	17	4	<0.005	<0.005		12
PFNA	92–110	100.5	6.9	4	<0.02–0.086	0.04	0.02	12
THPFOS	120–150	140	14	4	<0.02–0.024	0.02	0.001	12
PFOA	160–190	170	13	4	0.032–0.72	0.24	0.21	12
PFHS	80–140	110	29	4	<0.005	<0.005		12
PFBS	73–130	91	24	4	<0.005	<0.005		12

reverting to the original conditions at 12 min. The desolvation gas flow and temperature were kept at 750 L/h and 400 °C. The collision energies for PFOSA, PFOS, PFNA, THPFOS, PFOA, PFHS, and PFBS were 25, 35, 10, 22, 10, 30, and 25 eV, respectively. The cone voltages, in the same order, were 55, 90, 35, 55, 35, 70, and 50 V, respectively. The MS/MS parameters were optimized to transmit the  $[M - K]^-$  ion. Primary and transition ions monitored for quantification were 497.6 > 77.7 for PFOSA, 498.6 > 98.6 for PFOS, 462.7 > 418.8 for PFNA, 426.6 > 406.7 for THPFOS, 412.9 > 368.7 for PFOA, 398.6 > 79.7 for PFHS, and 298.6 > 79.7 for PFBS.

**Statistical Analysis.** A Spearman rank correlation analysis was used to assess the correlations among PFCs in water samples collected from Hong Kong, the Pearl River Delta, and the South China Sea during the summer and winter months.

## Results and Discussion

**Accuracy and Precision.** Currently, there are a number of limitations to instrumental analyses of PFCs, but the two most severe limitations are high levels of background and a lack of authentic standards. The background comes from the fact that PFCs are in a number of laboratory appliances and results in contamination of not only samples, but also laboratory reagents (15). This contamination can come from everything from the septa used in autosampler vials to internal parts of the HPLC instrument. It was found that, to conduct analyses of PFCs with sufficiently small concentrations of the analytes of interest in blanks to allow for reasonable limits of quantification (LOQs), a number of internal parts on a standard LC/MS instrument must be replaced. The instrument in which the necessary changes are easiest is the 1100 series from Agilent Technologies. The necessary alterations are to substitute stainless steel or peek tubing for Teflon in all parts of the instrument including the inlet filter. In addition, the instrument should be operated without the degasser and inlet valves made of Teflon in the original configuration. Septa that contain Teflon or Viton contribute PFCs, including PFOA, PFOS, PFHS, and PFOSA, to the samples. Polyethylene was found to be the best material for septa.

Standards exist for only a few PFCs, and these are often technical mixtures of varying isomer distributions. The PFOS standard, which has often been used as an external standard for quantification and as a matrix spike, is available from Fluka (Milwaukee, WI). The internal standard that has been used in most studies is THPFOS, which can be purchased from ICN (Costa Mesa, CA). The only commercially available, authentic, isotopically labeled standard is for PFOA, which has just become available from the Perkin-Elmer Co. (Boston, MA).

The accuracies of the instrumental analyses were determined by use of a matrix spike and matrix spike duplicates. The recovery of THPFOS was used to monitor instrumental conditions. Recoveries of PFOS and other PFCs and laboratory blank tests were performed to determine the precision and accuracy of the extraction and analytical procedures. To

determine the recovery of PFOS and other PFCs, 10  $\mu$ L of PFCmix was spiked into distilled water samples and then extracted following the same procedures used for the seawater samples. The recoveries for PFOSA, PFOS, PFNA, PFOA, PFHS, and PFBS are summarized in Table 1. Concentrations of all target analytes were quantified by using calibration curves constructed using external standards. Concentrations of target analytes, in procedural blanks analyzed with each set of water samples, were in the range from <0.005 to 0.72 pg/mL (Table 1). The LOQ for each target analyte was determined as the lowest standard injected which could meet the acceptance criteria for a particular run. The LOQs were 0.005 pg/mL for PFOSA, PFOS, PFHS, and PFBS and 0.02 pg/mL for PFNA, THPFOS, and PFOA.

**Concentrations of PFOS and Other PFCs in Coastal Waters of China and Hong Kong.** Concentrations of PFCs in waters of Hong Kong and China during the summer and winter are summarized (Figures 1–3). All of the water samples contained detectable concentrations of PFOS and PFOA. Concentrations of PFOS and PFOA ranged from 0.02 to 12 pg/mL and from 0.24 to 16 pg/mL, respectively. PFOSA, PFNA, PFHS, and PFBS were detected in approximately 90% of the samples at concentrations greater than the LOQ, but the concentrations of these PFCs were less than those of PFOS and PFOA. Concentrations of other PFCs ranged from <0.005 to 0.07 pg of PFOSA/mL, from <0.02 to 0.69 pg of PFNA/mL, from <0.005 to 1.8 pg of PFHS/mL, and from <0.005 to 0.62 pg of PFBS/mL. Although PFOS and PFOA were the dominant PFCs found in the water samples in the present study, Martin et al. (7) have found higher concentrations of PFNA (16 ng/g) than PFOS (8.7 ng/g) in the liver samples of minks. This indicates that PFNA and other PFCs should also be considered in future risk assessment. Notwithstanding, PFOS and PFOA were the primary PFCs released from local sources in Hong Kong and the PRD, and thus subsequent discussion will concentrate on PFOS and PFOA.

The greatest concentrations of PFOS (3.1 and 3.0 pg/mL) and PFOA (4.9 and 5.5 pg/mL) in Hong Kong coastal waters were observed at location HK6. The next greatest concentrations were observed at locations HK5 (2.4 and 2.0 pg of PFOS/mL, 3.3 and 5.4 pg of PFOA/mL) and HK4 (1.1 and 1.5 pg of PFOS/mL, 2.4 and 2.8 pg of PFOA/mL). Concentrations of PFOS and PFOA were generally small at station HK1 (0.27 and 0.11 pg of PFOS/mL, 1.0 and 0.75 pg of PFOA/mL). These concentrations were comparable to those measured at HK3 (Figure 1). Concentrations of PFOS and PFOA were greater in coastal waters along the west coast than they were along the east coast of Hong Kong. The Pearl River discharge has a major influence on the quality of Hong Kong's western waters (CH5 and CH6), although other sources of PFCs, such as waste discharges from the Shenzhen River and local streams, should also be considered. The influence of the Pearl River discharge is progressively less from the western to the eastern side of Hong Kong (16). Station HK4, situated within Victoria Harbor and less influenced by the Pearl River discharge, is influenced primarily by domestic sewage and industrial effluent from the nearby highly urbanized and

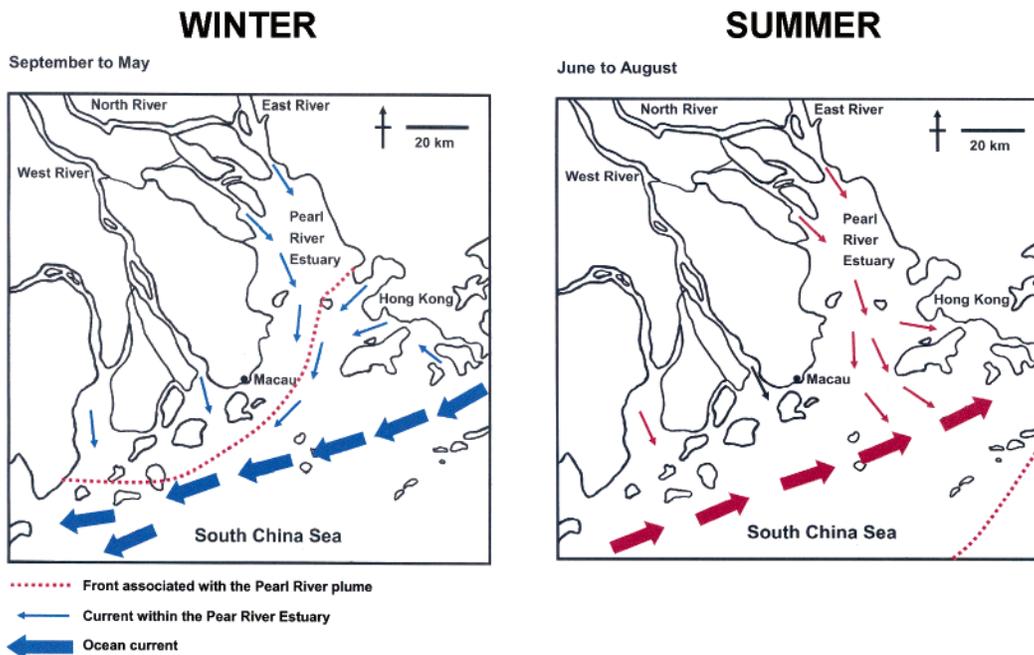


FIGURE 5. Simplified schematic diagram showing the seasonal variations in ocean and estuarine currents in the Pearl River Delta and South China Sea (data from ref 17).

industrialized areas of Hong Kong Island and Kowloon. Stations (HK1, HK2, and HK3) situated on the east coast of Hong Kong are largely oceanic, but may be influenced by coastal discharges, albeit to a smaller extent.

Waters within the PRD region contained greater concentrations of PFCs than those of other locations in the South China Sea (CH7 and CH8 in the summer) (Figures 2 and 3). In the winter, the greatest concentrations of PFOS (12 pg/mL) and PFOA (16 pg/mL) were observed at station CH2, which were greater than those measured in water from HK6, the site that had the greatest concentrations of PFCs in Hong Kong. Concentrations of PFOS and PFOA measured in water from CH1 were slightly less than, but comparable to, those found in water from CH2. Lower concentrations of PFCs were found in samples from CH3 (3.4 pg of PFOS/mL and 7.0 pg of PFOA/mL) and CH4 (4.1 pg of PFOS/mL and 7.3 pg of PFOA/mL) where the sampling stations were farther away from the land-based industrial areas in the PRD. Concentrations of PFOS and PFOA were even less in samples from CH5 and CH6, stations that were close to the open ocean of the South China Sea, and thus were more remote from the perceived pollution sources (Figure 3). In the summer, the differences in concentrations of PFOS and PFOA among locations were less. Lower concentrations of PFCs were observed at stations CH1 to CH6. Comparatively lower concentrations of PFCs were measured in the two open ocean stations (CH7 and CH8) (Figure 2).

Correlations among PFCs at different sampling locations were determined. For Chinese water samples collected in the winter, the concentration of PFOS was positively correlated with those of PFNA, PFOA, PFHS, and PFBS ( $r_s > 0.91$ ,  $P < 0.01$ ) and PFOSA ( $r_s > 0.58$ ,  $P < 0.05$ ). Similar correlation patterns were found between the concentrations of PFOA and PFOS, PFNA, PFHS, and PFBS ( $r_s > 0.92$ ,  $P < 0.01$ ). For Chinese water samples collected in the summer, positive correlations were found between PFOS and PFOSA ( $r_s > 0.57$ ,  $P < 0.05$ ) and PFNA, PFOA, and PFHS ( $r_s > 0.63$ ,  $P < 0.01$ ). PFOA was found to be positively correlated with PFOSA and PFNA ( $r_s > 0.56$ ,  $P < 0.05$ ) and PFOS ( $r_s > 0.63$ ,  $P < 0.01$ ). For Hong Kong water samples collected in the winter, significant positive correlations were found between the concentrations of PFOS and PFOSA, PFNA, PFOA, and

PFHS ( $r_s > 0.92$ ,  $P < 0.01$ ). Similar correlation patterns were also observed between PFOA and other PFCs ( $r_s > 0.93$ ,  $P < 0.01$ ). In the summer, positive correlations were found between PFOS and PFOSA, PFOA, PFHS, and PFBS ( $r_s > 0.79$ ,  $P < 0.01$ ) and PFNA ( $r_s > 0.70$ ,  $P < 0.05$ ). PFOA was found to be positively correlated with PFOSA ( $r_s > 0.65$ ,  $P < 0.05$ ) and PFOS, PFNA, PFHS, and PFBS ( $r_s > 0.84$ ,  $P < 0.01$ ). The reasons for such correlations were not known, but could be related to the production/usage of PFCs, and the subsequent release of PFCs as byproducts in Hong Kong and Chinese waters. The absence of correlations between PFOS and PFBS and between PFOA and PFHS and PFBS in water samples collected in China during the summer could probably be attributed to the overwhelming effects of dilution and/or dispersion due to the large spate of freshwater discharged from the PRD.

**Seasonal Variations in the Concentrations of PFOS and PFOA in Coastal Waters in Hong Kong and China.** Seasonal differences in the distribution patterns of PFOS and PFOA in the PRD are observed (Figures 2 and 3). Concentrations were greater in coastal water in the winter than in the summer. Appreciable concentrations of PFOS and PFOA were only recorded inside the PRD area in the winter. There was a trend of decreasing concentrations from CH1 (9.7 pg of PFOS/mL, 12 pg of PFOA/mL) to CH6 (0.02 pg of PFOS/mL, 0.24 pg of PFOA/mL). In the summer, concentrations of PFOS and PFOA were relatively similar at CH1 and CH6, and small but measurable concentrations were measured at stations CH7 and CH8, which were away from the coastal area out in the South China Sea. During the winter, which is the dry season, the ocean currents, driven by the prevailing northeasterly winds, move along the shore from northeast to southwest. This causes runoff from the Pearl River to move westward toward the southwest shoreline (Figure 5). During the summer, which is the wet season, the prevailing winds are generally southerly and may reverse the direction of the surface water currents to the northeast. The above seasonal variations in current flow have an important implication for the movement of water-borne contaminants in the PRD and, to a lesser extent, Hong Kong. During the winter months, most Pearl River water generally does not enter Hong Kong waters. However, during the summer, part of the Pearl River

TABLE 2. Concentrations (Mean ± Standard Deviation) of PFCs in Waters in South Korea

sampling location	concentration of PFCs (pg/mL)					
	PFOSA	PFOS	PFNA	PFOA	PFHS	PFBS
K1	<0.005	0.19 ± 0.05	0.12 ± 0.01	11 ± 1.6	<0.005	0.05 ± 0.01
K2	<0.005	0.04 ± 0.005	<0.02	0.24 ± 0.02	<0.005	<0.005
K3	<0.005	0.09 ± 0.003	0.04 ± 0.006	1.5 ± 0.05	0.03 ± 0.001	0.06 ± 0.002
K4	0.02 ± 0.001	2.3 ± 0.33	0.59 ± 0.02	8.4 ± 0.74	0.46 ± 0.008	0.07 ± 0.001
K5	0.01 ± 0.003	1.7 ± 0.11	0.41 ± 0.05	5.7 ± 0.21	0.40 ± 0.004	0.12 ± 0.004
K6	<0.005	0.17 ± 0.03	0.05 ± 0.004	2.2 ± 0.22	0.07 ± 0.002	0.14 ± 0.02
K7	0.01 ± 0.006	0.62 ± 0.005	0.08 ± 0.006	1.6 ± 0.25	0.16 ± 0.02	0.10 ± 0.001
K8	0.33 ± 0.007	730 ± 22	13 ± 0.43	320 ± 25	52 ± 1.4	5.0 ± 0.28
K9	0.01 ± 0.001	0.71 ± 0.05	0.06 ± 0.006	1.4 ± 0.02	0.30 ± 0.002	0.06 ± 0.005
K10	0.02 ± 0.003	0.71 ± 0.06	0.06 ± 0.001	1.3 ± 0.23	0.33 ± 0.02	0.07 ± 0.006
K11	0.12 ± 0.007	3.1 ± 0.03	0.14 ± 0.02	4.1 ± 0.14	1.7 ± 0.07	0.31 ± 0.005

water flows eastward, and may enter into Hong Kong waters. Furthermore, the greater river discharge during the wet summer months pushes a large amount of freshwater out to the South China Sea, while the spatial influence of the Pearl River discharge is much more restricted in the winter (Figure 5). Thus, in the summer, the greater pollution loads carried by the Pearl River can, in theory, have an influence on the water quality of Hong Kong, particularly in the western waters. Indeed, the spatial occurrences of PFOS and PFOA in the PRD in the summer and winter were consistent with the fronts of the Pearl River plume in the two seasons (17; summarized in Figure 5). The generally lower concentrations of PFOS and PFOA observed in the western coastal waters of Hong Kong during the summer were likely caused by the diluting effects from the greater discharge of the Pearl River. In contrast to those of the PRD, concentrations of the PFOS and PFOA measured in coastal waters of Hong Kong did not exhibit large seasonal differences. This, together with the occurrence of detectable concentrations of PFCs in Hong Kong's eastern oceanic waters, indicates (i) the possible existence of local sources of PFCs, (ii) transboundary input of PFCs from mainland China into the eastern waters of Hong Kong, and/or (iii) atmospheric inputs from other sources. The above observations, taken together, suggest that the PRD is an important source of PFCs in southern China.

**Pearl River Delta as a Source of PFCs.** Comparatively greater concentrations of PFCs within the PRD may have originated from various tributaries, of which the Zhujiang River and Dongjiang River (East River) are two of the major rivers. The watershed of the Dongjiang River, the major source of potable water supply to Hong Kong, is the base of a wide variety of industries including chemical and biochemical products manufacturing, petrochemicals, printed circuit boards, bleaching, dyeing, pulp and paper, pharmaceuticals, electroplating, and food processing. Of the industrial wastewater treatment plants in the area, only 56.7% meet the environmental standards stipulated by the local authority (18). The Zhujiang River receives its industrial and domestic contaminants mainly from Guangzhou, the capital city of Guangdong Province, which is a highly urbanized city with increasing industrial and commercial activities (19). Discharges from these rivers enter the PRD and may thus account for the high concentrations of PFOS and PFOA at stations CH1 and CH2, with progressively lower concentrations in the outer stations (CH3 and CH4, followed by CH5 and CH6) due to dilution and dispersion.

**Comparison of PFC Concentrations in Waters among Hong Kong, China, and South Korea.** The greatest PFC concentrations were observed in water samples from K8, which is located on the west coast of Korea (Table 2). Concentrations of PFCs were 0.33 pg of PFOSA/mL, 730 pg of PFOS/mL, 13 pg of PFNA/mL, 320 pg of PFOA/mL, 52 pg of PFHS/mL, and 5.0 pg of PFBS/mL. These concentrations were, respectively, 5-, 63-, 19-, 20-, 29-, and 8-fold greater

TABLE 3. PFOS to PFOA Ratios in Coastal Waters in Hong Kong, China, and South Korea

Korea					
sampling location	PFOS/PFOA ratio	sampling location	PFOS/PFOA ratio	sampling location	PFOS/PFOA ratio
K1	0.02	K5	0.30	K9	0.51
K2	0.17	K6	0.08	K10	0.56
K3	0.06	K7	0.40	K11	0.77
K4	0.27	K8	2.3		

Hong Kong and China					
sampling location	PFOS/PFOA ratio		sampling location	PFOS/PFOA ratio	
	summer	winter		summer	winter
Hong Kong					
HK1	0.27	0.15	HK4	0.45	0.54
HK2	0.27	0.38	HK5	0.74	0.36
HK3	0.49	0.12	HK6	0.63	0.55
China					
CH1	0.48	0.78	CH5	0.64	0.33
CH2	0.55	0.73	CH6	0.54	0.08
CH3	0.35	0.49	CH7	0.29	
CH4	0.28	0.56	CH8	0.35	

than the maximum concentrations of corresponding PFCs measured in the coastal waters of Hong Kong or China. Station K8, situated within Kyeonngi Bay, is heavily influenced by the effluents of a number of local industries, such as steel manufacturers, machine and pulp factories, dye houses, and sewage treatment plants (20). Apart from this "hotspot", concentrations of PFCs at other sampling stations were comparable to those detected in coastal waters of Hong Kong and China. The relatively greater concentrations of PFOA at locations K4 and K5 are attributed to local, but as yet unidentified, sources (Table 2). The PFOS to PFOA ratios were also compared between locations (Table 3). PFOS/PFOA ratios at all of the sampling locations, except for K8, were less than 1.0 (0.02–0.78), indicating that PFOA was the dominant PFC in water samples collected from these areas. The great PFOS/PFOA ratio in water samples from K8 could indicate an independent source of PFOS in the nearby area. In addition, the concentrations of PFHS observed in water samples from this location (52 pg of PFHS/mL) also suggest a local source of this PFC, which generally occurs at much smaller concentrations. This observation suggests that PFHS may be one of the major PFCs used and/or produced by industries in this part of South Korea.

**Comparison of PFC concentrations in Hong Kong and China to Those in Other Areas.** Concentrations of PFOS and PFOA in coastal waters of Hong Kong, the Pearl River Delta, and the South China Sea were generally less than those observed in freshwaters of North America and other coastal marine environments. For instance, concentrations of PFOS

in the Tennessee River ranged from 28 pg of PFOS/mL at an upstream site to 120 pg of PFOS/mL downstream (21). The greatest concentration of PFOS recorded in the Tennessee River (140 pg of PFOS/mL) was 34-fold and 12-fold greater than the greatest concentrations of PFOS recorded in Hong Kong and Chinese waters, respectively. These high PFOS concentrations are likely to be associated with the presence of a fluorochemical plant near the Tennessee River. PFOS concentrations measured in this study were less than the mean concentration (26 pg/mL) detected in the surface waters around Tokyo Bay (22), the Jinzu River (135 pg/mL), and the Tama River (157 pg/mL) (23) and were far much smaller than the greatest concentration (2.2 µg of PFOS/mL) detected in surface water samples from the Etobicoke Creek following an accidental release of fire-retardant foam (24). The greatest PFOS/PFOA ratio (195.6) observed in the Etobicoke Creek was greater than the greatest values from Hong Kong, Chinese, and Korean waters. Such a high PFOS/PFOA value was probably attributed to the released fire-retardant foam, which contained a large proportion of PFOS (24). Future studies may examine the concentrations of PFCs in the source rivers in the PRD to further elucidate the sources of these compounds.

#### Hazard Assessment of PFOS Exposure to Aquatic Species.

An evaluation of the ecological risk to aquatic animals associated with exposure to PFOS was performed by comparing the measured concentrations of PFOS in water with water quality (guideline) values that are protective of aquatic organisms. Currently, there are no guidelines specifically derived for saltwater. These guideline values were derived following the procedures outlined in U.S. EPA's Great Lakes Initiative and were based on the results of toxicity testing with freshwater organisms (25). The final plant value (FPV), for the protection of aquatic plants, was determined to be 8.2 mg of PFOS/L. The water quality criteria for aquatic animals are represented by the secondary maximum concentration (SMC) and secondary continuous concentration (SCC). The values for SMC and SCC were 0.78 and 0.46 mg of PFOS/L, respectively. These values mean that aquatic organisms would not be unacceptably affected if the four day average and 1 h average concentrations did not exceed 0.78 or 0.46 mg of PFOS/L more than once every three years on the average. The greater value for FPV indicates that criteria which are protective of aquatic animals should also be protective of aquatic plants. The safe water concentration that is protective of avian wildlife was determined to be 0.043 µg of PFOS/L (26). This value is based on the geometric mean of values calculated for the bald eagle, kingfisher, and herring gull, which were 0.026, 0.038, and 0.079 µg of PFOS/L, respectively. Furthermore, because there was limited information available, particularly for chronic effects, uncertainty factors and a conservative acute-to-chronic ratio (ACR) were used to derive the threshold levels for the protection of aquatic life. For this reason, these values are probably overly conservative, possibly by as much as 50–100-fold, depending on the true distribution of sensitivities among organisms and differences in sensitivities between freshwater and saltwater organisms. A preliminary estimate of risk was determined by comparing the concentrations of PFOS to these protective values. In this study, the concentrations of PFOS were less than the threshold for effects (hazard quotient (HQ) < 1) at all of the locations studied regardless of which guideline values were used, except at location K8, where the PFOS concentration was higher than the guideline value that is protective of avian wildlife (HQ > 1) (Table 4). This suggests that current concentrations of PFOS in all sampling locations, except K8, are unlikely to cause harm to aquatic animals and avian wildlife. The comparatively high HQ value obtained at location K8 (HQ = 17) indicates that a more refined risk assessment is needed, and that some appropriate control or

TABLE 4. Preliminary Estimation of Risk Due to Exposure to PFOS in Coastal Waters in Hong Kong, Pearl River Delta, South China Sea, and Korea Using an HQ Analysis

location	concn of PFOS (pg/mL)		HQ WQC for protection of aquatic life		HQ WQC for protection of predatory birds	
	summer	winter	summer	winter	summer	winter
HK1	0.27	0.11	<0.001	<0.001	0.006	0.003
HK2	0.45	0.45	<0.001	<0.001	0.01	0.01
HK3	0.38	0.09	<0.001	<0.001	0.009	0.002
HK4	1.1	1.5	<0.001	<0.001	0.03	0.03
HK5	2.4	2.0	<0.001	<0.001	0.06	0.05
HK6	3.1	3.0	<0.001	<0.001	0.07	0.07
CH1	1.6	9.7	<0.001	<0.001	0.04	0.23
CH2	2.5	12	<0.001	<0.001	0.06	0.28
CH3	1.6	3.4	<0.001	<0.001	0.04	0.08
CH4	1.7	4.1	<0.001	<0.001	0.04	0.10
CH5	2.1	0.45	<0.001	<0.001	0.05	0.01
CH6	2.7	0.02	<0.001	<0.001	0.06	<0.001
CH7	0.46		<0.001		0.01	
CH8	0.77		<0.001		0.02	
K1	0.19		<0.001		0.004	
K2	0.04		<0.001		<0.001	
K3	0.09		<0.001		0.002	
K4	2.3		<0.001		0.05	
K5	1.7		<0.001		0.04	
K6	0.17		<0.001		0.004	
K7	0.62		<0.001		0.01	
K8	730		0.002		17	
K9	0.71		<0.001		0.02	
K10	0.71		<0.001		0.02	
K11	3.1		<0.001		0.07	

management measures may be required at this location. However, it should be noted that more toxicological data will be needed to undertake a more comprehensive risk assessment. Specifically, estimation of concentrations of PFCs in biota samples will further allow an assessment of risks to ecological systems due to exposure to these compounds.

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