New POPs in the water environment: distribution, bioaccumulation and treatment of perfluorinated compounds – a review paper

Shigeo Fujii, Chongrak Polprasert, Shuhei Tanaka, Nguyen Pham Hong Lien and Yong Qiu

ABSTRACT

Perfluorinated compounds such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are emerging environmental pollutants. From the available literature, tap and surface water samples in several countries were found to be contaminated with PFOS and PFOA. These compounds were detected globally in the tissues of fish, bird and marine mammals, but their concentrations in animals from relatively more industrialized areas were greater than those from the less populated and remote locations. The bioconcentration factors (BCFs) of PFOS in fish were in the range of 10,000 or above, while the BCF of PFOA in fish was below 200. Blood samples of occupationally exposed people and the general population in various countries were found to contain PFOS and PFOA which suggested a possibility of atmospheric transport of these compounds. There is still a dearth of information about the environmental pathways of PFOS and PFOA. Some advanced oxidation methods, photocatalysis, adsorption, and reverse osmosis membrane filtration were found effective in degrading or removing PFOS and PFOA from the water environment. The presence of these compounds in the tap water, surface water and animal and human tissues indicates their global contamination and bioaccumulative phenomena in the ecosystems.

Key words | bioaccumulation, perfluorinated compounds, perfluorooctane sulfonate, perfluorooctanoic acid, persistent organic pollutants, water environment

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ABBREVIATIONS

A_v	Specific surface area
BCF(s)	Bioconcentration factor(s)
BMF(s)	Biomagnification factor(s)
DCV	Direct current voltage
DDT	Dichloro-diphenyl-trichloroethane
I	Current
LOD	Limit of detection
LOQ	Limit of quantification
mM	Mili-mole
MPa	Mega Pascal
ND	Non-detectable
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PFCAs	Perfluorocaboxylates
PFCs	Perfluorinated organic compounds
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
POPs	Persistent organic pollutants

INTRODUCTION

Persistent organic pollutants (POPs) are organic compounds that remain intact in the environment for long periods, resist photolytic, chemical and biological degradation, become

widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. Some existing POPs are: aldrin, chlordane, DDT, dieldrin, heptachlor, hexachlorobenzene, mirex, PCBs, dioxins and furans. Over the past several years, due to the risks posed by POPs, there have been actions taken or proposed at the national and international levels to protect human health and the environment (www.chem.unep.ch).

Perfluorinated compounds (PFCs) have been synthesized and widely used in industrial and commercial applications since the 1960s. Two major processes to synthesize PFCs, in which hydrogen atoms in organics are substituted by fluorine atoms completely, include electrochemical fluorination which yields perfluoroalkyl sulfonates with branched isomers and shorter chained PFCs, and telomerization which generates even carbon chain perfluorocarboxylates. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are typical and predominant PFCs which have the following chemical formulas: $C_8F_{17}SO_3^-$ and $C_8F_{15}COO^-$, respectively. The chemical structures of these two compounds are shown in Figure 1.

Due to the combination of hydrophobicity from fluorinated structures and hydrophilicity from functional groups ($-SO_3^-$ and $-COO^-$), PFOS and PFOA possess excellent surface performance and have been widely used as surface treatment chemicals, polymerization aids and surfactants, etc. (OECD 2002; U.S. EPA 2002). Examples of PFOS application include: surface treatment (e.g. for carpet and fabric protection, wafer photolithography in semiconductor industry, etc.), paper protection (e.g. for coating of cups and plates, etc.) and performance chemicals (e.g. in aqueous fire fighting foam, hydraulic fluids, etc.); while PFOA is used as an emulsifier (such as Teflon used for coating of cooking pans) and surfactant (such as soap and shampoo, etc). Because both PFOS and PFOA are persistent in the environment, bioaccumulative and potentially toxic to humans and animals, they are being proposed as

candidates for a new class of POPs (http://www.oztoxics. org/cmwg/chemicals/new%20pop.html).

Recent concerns with the toxic effects of PFOS and PFOA began in the early 2000s when the 3M Company, U.S.A., the major PFCs manufacturer, decided to phase out the production of PFOS-related products. However, there are still a number of industries, such as the semiconductor etc., that still use PFOS in their production (Tang *et al.* 2006) and manufacturers that produce PFOA and its related products for consumer usage. From over 200 research articles published so far, most of them came out after the year 2000 and dealing mainly with the topics of PFOS and PFOA distribution and toxicity in biota samples in industrialized countries (Alexander *et al.* 2003; Austin *et al.* 2003; Hekster *et al.* 2003; Taniyasu *et al.* 2003; Saito *et al.* 2004; Lien *et al.* 2006; Sinclair *et al.* 2006). Probably due to their presence at trace (ng/L) levels, there are fewer articles dealing with the distribution of PFOS and PFOA in tap and surface water, much less about their treatment. Since PFOS has been applied in various products worldwide for the past 40 years and PFOA is still being manufactured and used, there are possibilities that these compounds are released into the water environment through both point-source (industrial and sewage treatment plant) and non-point-source (surface run-off and atmospheric) discharges, bioaccumulated in the food chains and thus become a potential health risk to humans and animals. The general objective of this review paper is to create more awareness among water-related professionals and researchers of this emerging environmental issue. Specifically, this paper aims to evaluate: (1) geographical distribution and contamination levels of PFOS and PFOA in the water environment, including their contamination sources, (2) extents of bioaccumulation and toxic effects of these compounds, and (3) methods of PFOS and PFOA degradation and removal from the water environment.

PFOS AND PFOA DISTRIBUTION IN THE WATER ENVIRONMENT

Prevedouros *et al.* (2006) estimated the global historical production of perfluorocarboxylates (PFCAs) up to 2006 to be 4,400–8,000 tones, while the total global (both direct
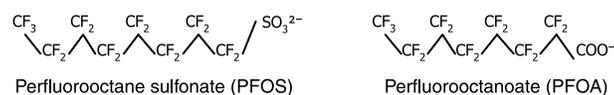
Figure 1 │ Chemical structures of PFOS and PFOA.

and indirect) emissions to the environment were 3,200–7,300 tones. The PFCAs emissions from consumer and industrial products were about 10% or 40–100 tones, of which the majority came from the fluoropolymer manufacturing and aqueous fire-fighting foam production. Among the various forms of PFCAs, PFOA is the most detected compound in the water environment and biota. The amount of PFOS and its related chemicals used in the U.S.A in 2000 was estimated at 3,000 tones (OECD 2005). The semiconductor industry in the European Union alone used an estimated 470 kg of PFOS annually (Brooke *et al.* 2004). The characteristics of PFOS and PFOA, shown in Table 1, indicate that they are rather low in vapor pressure, highly soluble in water, and persistent in the environment. Therefore, most of the PFOS and PFOA discharged into a water body would probably remain in the water medium, unless they are adsorbed onto particulate matter which would eventually settle down to the sediment. Some PFOS and PFOA can be assimilated by organisms and enter the ecosystems through bioaccumulation and biomagnification in the food chains. The persistence of PFOS and PFOA lies in the C–F bond which is the strongest among the carbon-halogen bonds (Marbury 2005) and the sheath effects of the fully substituted fluorine atoms (see Figure 1).

The first report on PFOS contamination of the water environment in Japan was made by Taniyasu *et al.* (see www.aist.go.jp/aist_e/latest_research/2002) who found

the Tokyo bay water to contain the highest PFOS concentration of 59 ng/L (mean value being 26 ng/L). Less mean PFOS concentrations were detected in the surface waters of Osaka bay (12 ng/L), Ariake bay (9 ng/L), Lake Biwa (7.4 ng/L), and Seto inland sea (4.3 ng/L). A later survey conducted by Saito *et al.* (2004) found the contamination of PFOS and PFOA in surface water at several locations in Japan to be in the ranges of 0.89–3.69 and 0.97–21.5 ng/L, respectively. The highest PFOA concentration of 21.5 ng/L was found in a surface water of Kinki area, western Japan, and the contamination source was a sewage treatment plant that was estimated to discharge about 18 kg of PFOA per day into a nearby Kanzaki river that eventually flows into the Osaka bay. From water quality surveys of the Yodo River basin (western Japan), Lien *et al.* (2006) found some sewage treatment plants discharged their treated effluents into the Yodo River which also flows into the Osaka bay. The PFOS and PFOA concentrations of these effluents were in the ranges of 3–76 ng/L and 25–922 ng/L, respectively, while the ranges of their mass loadings were negligible − 15 and 0.03–43 g/d, respectively (Figure 2). Accordingly, the amounts of PFOS and PFOA discharges into the Osaka bay through the Yodo River were estimated to be 64 and 375 g/d, respectively. Because there were no direct correlations between the numbers of population and the mass loadings of these compounds, it was hypothesized that industrial discharges into the sewage treatment plants could be a source

Table 1 | Physico-chemical properties of PFOS and PFOA (based on OECD 2002 & U.S. EPA 2002)

	PFOA	PFOS
Molecular weight	414	500 (for acid)
Melting point	45–50°C	$> = 400$°C
Boiling point	189–192°C (736 mmHg)	not calculable
Vapor pressure	10 mmHg (25°C)	3.31×10^{-4} Pa (20°C)
Solubility in pure water	3.4 g/L	570 mg/L (in pure water)
Air/water partition coefficient	not available	$< 2 \times 10^{-6}$
pKa	2.5	not available
pH	2.6 (at 1 g/L)	7–8 (for potassium salt of PFOS)
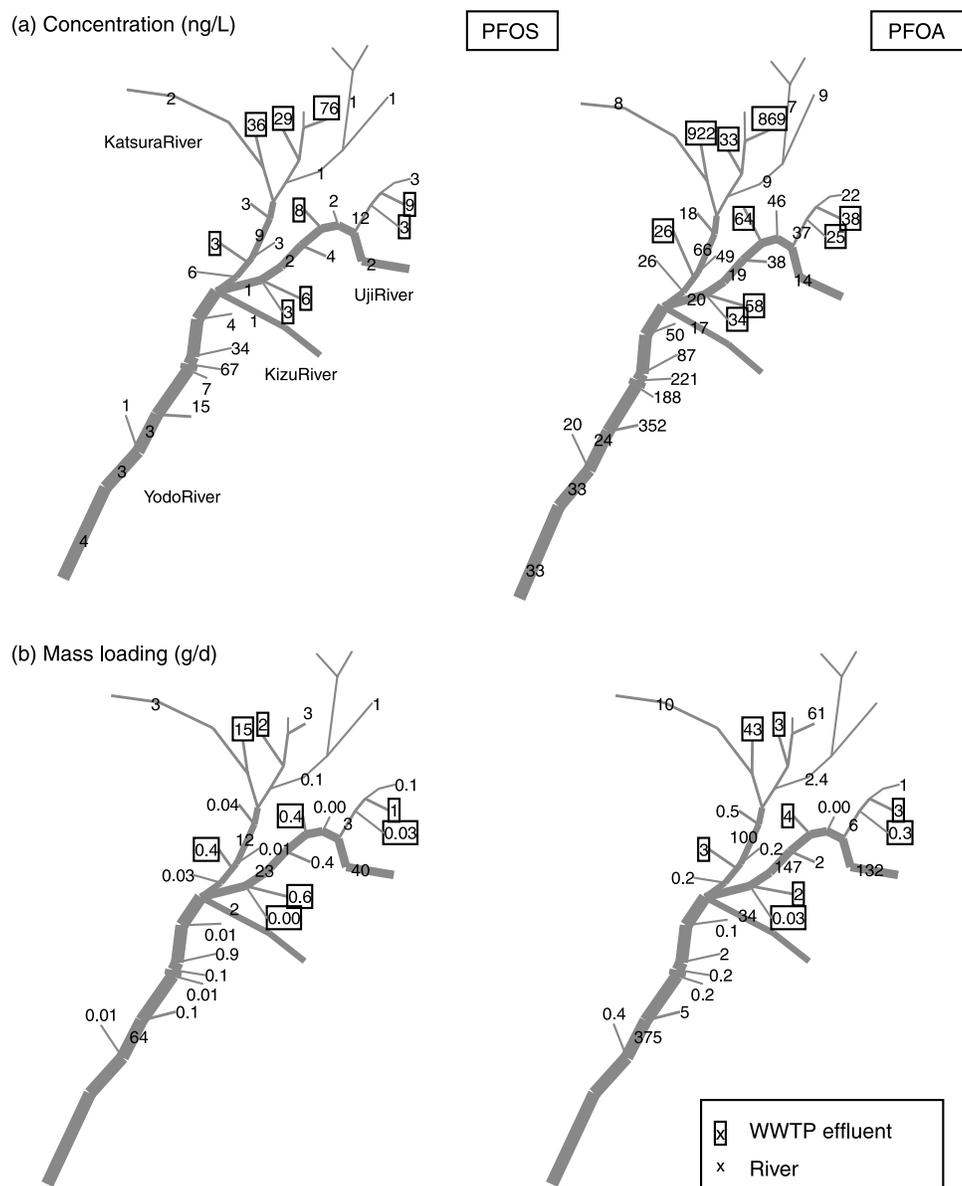
Figure 2 | Concentration and mass loading of PFOS and PFOA in Yodo River basin, Japan (Lien *et al.* 2006).

of PFOS and PFOA contamination, although domestic wastewaters and atmospheric transport could contribute to this contamination problem.

In Northeast U.S.A, Sinclair *et al.* (2006) found the PFOA concentrations in surface water of New York State to be 10–173 ng/L, consistently higher than those of the PFOS which were about 0.8–30 ng/L. Exceptionally high PFOS concentration of 198–1,090 ng/L were found in Lake Onondaga because of the high volume of industrial wastewater discharges into the Lake. Due to greater industrial uses of fluoropolymer and telomer-alcohols in New York State, Sinclair *et al.* (2006) speculated industrial discharges to be a major source of PFOS and PFOA contamination of the New York surface waters. Tang *et al.* (2006) reported the PFOS concentration of a semiconductor wastewater in U.S.A. to be 1,650 mg/L, much higher than its solubility in water (Table 1) because this wastewater contained about 5% isopropyl alcohol added to enhance

PFOS solubility. Because development of a PFOS substitute could be several years away, some industries will continue to use PFOS in their production processes and to seek permission for the critical uses of PFOS.

A comparison between tap and surface water contamination with PFOS and PFOA in Japan, North America and European Nordic countries is shown in Table 2. The PFOS and PFOA concentrations in tap water of some Japanese cities were in the range of non-detectable (ND) to 50 ng/L, less than those found in some river and lake water samples which were in the range of ND to 87,000 ng/L. The PFOS and PFOA concentrations in the surface water samples of U.S.A, and some European Nordic countries were ND-1,090 ng/L, the maximum values were less than those reported for the surface water in Japan. The PFOA concentrations of the surface waters in U.S.A. were comparable with those of PFOS, but in Japan and the European Nordic countries the PFOA concentrations were found to be higher than those of PFOS.

Another investigation conducted by Lien *et al.* (2006) found tap water of several Japanese cities to contain PFOS and PFOA concentrations in the ranges of ND-6.8 ng/L and 0.3–37.5 ng/L, respectively (Table 3) – the limits of quantification were 0.05 and 0.1 ng/L for PFOS and PFOA, respectively. The maximum PFOA value of 37.5 ng/L was similar to that found in tap water of Osaka city, Japan, by Saito *et al.* (2004). Tap water of some cities in Canada, China, Malaysia, Sweden, Thailand and Vietnam were also found to contain PFOS and PFOA in the ranges of ND-13.2 and ND-109 ng/L, respectively. The maximum PFOA concentrations were consistently higher than those of PFOS. The Minnesota Department of Health, U.S.A., recommended safe concentrations of PFOS and PFOA in drinking water to be 1 μg/L and 7 μg/L, respectively

Table 2 | PFOS and PFOA concentration (ng/L) in tap water and surface water samples from different countries

| | Country | Area | Mean/median or range of mean/median (range) | | Reference |
			PFOS	PFOA	
Tap water	Japan	Morioka, Miyako, Kyoto, Setagaya, Hyogo, Osaka, Iwate, Miyagi, Akita	(< LOD-50.9)	(0.7–40)	Saito *et al.* (2004), Harada *et al.* (2003)
Surface water	European Nordic Countries	Finland, Sweden, Norway, Denmark, Iceland, Faeroe Islands	<1	7.8	Berger *et al.* (2004)
	Japan	Country-wide: Hokkaido-Tohoku, Kanto, Chubu, Kinki, Chugoku, Kyushu-Shikoku	0.9–14.9 (0.2–157)	1.0–11,147 (0.2 – 87,000)	Harada *et al.* (2003), Saito *et al.* (2004), Morikawa *et al.* (2006)
	U.S.A.	Alabama State	(32–114)	(<25–394)	Hansen *et al.* (2002)
		Great Lake	40 (21–70)	43 (27–50)	Boulanger *et al.* (2004)
		Michigan State	1.8–17 (< LOQ-29)	4.4–22 (< LOQ-36)	Sinclair *et al.* (2004), Kannan *et al.* (2005)
		Minnesota State	(< LOD-47)	(0.14–19)	Simcik & Dorweiler (2005)
		New York State	1.6–64 (0.8–1,090)	14–49 (10–173)	Sinclair *et al.* (2006)

Table 3 | PFOS and PFOA concentration in tap water samples collected from different countries (Lien *et al.* 2006)

	Sample identification		PFOS (ng/L)	PFOA (ng/L)	Sampling date
Japan	Hokkaido	Sapporo	0.1	0.6	Aug-05
	Hyogo	Nishinomiya	–	0.3	Aug-05
	Kagawa	Kotohira	6.8	3.1	Oct-05
	Kyoto	Sakyo	0.9	6.7	Aug-05
		Yamashina	2.0	15.2	May-06
	Miyagi	Sendai	0.4	1.2	Mar-06
	Nara	Yamato-Koriyama	0.1	1.3	Aug-05
	Okayama	Kurashiki	0.6	4.2	Oct-05
		Okayama	0.1	7.5	Oct-05
	Osaka	Takatsuki	1.9	34.3	Aug-05
		Takatsuki	2.0	37.0	May-06
		Takatsuki	1.9	37.5	May-06
	Shiga	Otsu	1.5	8.3	Jul-05
		Otsu	–	9.5	Dec-05
		Otsu	2.5	13.9	May-06
	Tokyo	Tokyo	2.7	6.7	May-06
	Tottori	Tottori	0.1	0.7	Nov-05
	Yamagata	Yamagata	0.6	1.1	Mar-06
Canada	Alberta	Calgary	–	0.2	Sep-05
	BC	Vancouver	–	0.2	Sep-05
China	Shenzhen	Site 1	6.5	3.1	Oct-05
	(Guangdong)	Site 2	6.2	2.3	Oct-05
		Site 3	9.9	1.1	Jan-06
	Yunnan	Kunming	13.2	1.1	Oct-05
	Zhejiang	Hangzhou	1.5	109.0	May-06
Malaysia	Penang		–	–	Nov-05
	Kota Kinablu	Site 1	0.1	0.1	Aug-05

Table 3 | (continued)

	Sample identification		PFOS (ng/L)	PFOA (ng/L)	Sampling date
		Site 2	–	–	Sep-05
		Site 3	–	–	Sep-05
		Site 4	–	–	Nov-05
Sweden	Orebro	Site 1	0.3	1.3	Mar-06
		Site 2	0.8	–	Mar-06
Thailand	Bangkok	Site 1	1.9	4.6	Dec-05
	Khon Kean	Site 1	0.2	3.4	Jul-05
		Site 2	0.1	0.2	Jan-06
		Site 3	0.1	–	Jul-05
Vietnam	Hanoi	Site 1	–	–	Jan-06
		Site 2	–	–	Jan-06

Note: -:concentration less than LOQ.

(3M 2005). The concentrations of PFOS and PFOA found in tap water of several countries, as reported in Tables 2 and 3, are well below these recommended concentrations.

As shown in Figure 3, there appeared to be a direct correlation between the PFOS and PFOA concentrations in tap and surface water samples, although the source of some of the tap water was not always surface water. It is apparent from this result that the current treatment processes being employed at water purification plants cannot remove these compounds from the tap water.

EXTENTS OF BIOACCUMULATION AND TOXIC EFFECTS OF PFOS AND PFOA

The presence of PFOS and PFOA in surface and tap water obviously pose some environmental concerns because they could be taken up by animals that inhabit the surface water and bioaccumulated in the food chains. People who consume this contaminated tap water as well as the animals would also be subjected to some health risks. Since, as

stated in the previous section, the tap water samples of several countries are still well below the recommended safe limits, the risks to humans from drinking tap water of those cities listed in Tables 2 and 3 may be considered minimal.
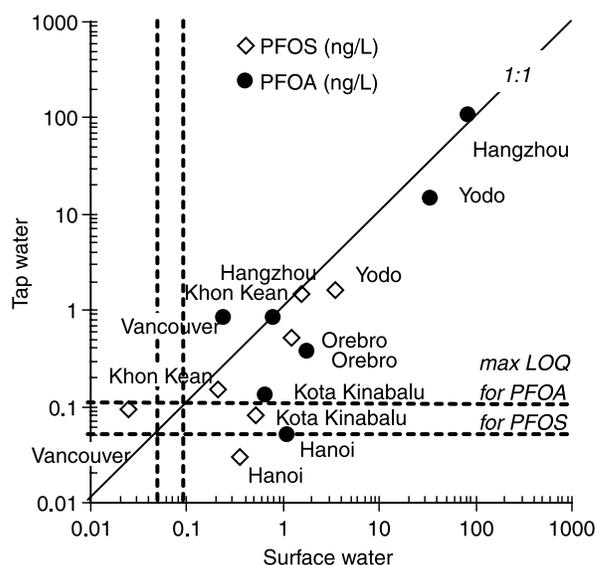

Figure 3 | Mean concentrations of PFOS and PFOA in tap water against those in surrounding surface water (Lien *et al.* 2006).

With respect to fish contamination, Taniyasu *et al.* (see www.aist.go.jp/aist_e/latest_research/2002) found the presence of PFOS in blood and liver samples of fish collected from several places in Japan at concentrations of 2–834 ng/ml. The highest mean PFOS concentration of 345 ng/ml was in the fish blood collected from Lake Biwa, followed by those collected from Tokyo bay (172 ng/ml), Osaka bay (100 ng/ml), Seto inland sea (29 ng/ml), Ariake bay (28 ng/ml) and Okinawa (10 ng/ml). Although the PFOS concentration in Lake Biwa (a fresh water lake) was about 4 times less than that of Tokyo bay, as reported in the previous section, the PFOS concentration in the fish blood collected from Lake Biwa was the highest. This phenomenon could be due to the lake hydrodynamics and biological effects of the freshwater ecosystem which, in combination with other factors, probably contributed to the high PFOS accumulation in the fish blood. These data suggest that the bioconcentration factors (BCFs) of PFOS in fish (ratio between concentrations in fish and in water) of Lake Biwa and Tokyo bay to be 46,620 and 6,615, respectively.

In U.S.A., PFOS was found in all liver samples of fish and birds collected from New York State at concentrations of 9–315 and 11–882 ng/g (wet weight), respectively (Sinclair *et al.* 2006). Comparing with the PFOS concentrations in the water bodies, a BCF of PFOS in fish in this area was suggested as 8850. Based on the ratio of PFOS concentrations in fish-eating birds and in fish, a biomagnification factor (BMF) of PFOS in birds was estimated to be 8.9. Giesy & Kannan (2002) estimated a BMF of PFOS in fish-eating minks to be 22. From the PFOA data, Sinclair *et al.* (2006) estimated a BCF of PFOA in fish of the New York State to be 184, much less than that of PFOS. Since PFOA was not detected in any samples of the bird livers, no BMF value was reported. The BCFs of other POPs such as PAHs, PCDDs, PCDFs, DDT, and PCBs were reported to be 44–10,000; 135–31,600; 360–10,700; 37,200–69,200; and 1,800–933,300, respectively (Lu *et al.* 2000), which are comparable with those of PFOS.

A survey conducted by Giesy & Kannan (2001) found PFOS to be distributed widely in animal tissues, even in such remote locations as the Arctic and North Pacific Oceans, although those from the industrialized areas had greater PFOS concentrations than those from the less populated regions. For example, the livers of some Alaskan polar bears were found to contain 180–680 ng/g PFOS, while the livers of some minks from the Midwestern U.S.A., a more contaminated location, contained 970–3,680 ng/g PFOS.

A summary of PFOS concentrations in human blood samples collected from different countries (Table 4) shows the levels of PFOS in whole blood to range from 1.7 to 20.2 ng/ml, while the concentrations in serum samples ranged from 3.6 to 1,656 ng/ml. The concentrations of PFOA in human blood samples were 2–7 folds lower than those of PFOS. There appeared to be no age and gender differences in the concentration of PFOS and PFOA in these blood samples (Kannan *et al.* 2004). According to Saito *et al.* (2004), tap water consumption was considered as a source of PFOA intake for people living in Osaka, Japan. In addition to consumption of tap water contaminated with PFOS and PFOA, consumption of fish contaminated with these compounds could be another source of PFOS and PFOA intake. Other sources of PFOS and PFOA intake by humans could be through consumption of contaminated foods and inhalation of air contaminated with other volatile PFCs that would be degraded to become PFOS and PFOA.

With respect to the effects of PFOS and PFOA on humans, not much information about acute and chronic effects are available. Alexander *et al.* (2003) suspected death of some workers exposed to PFOS to be caused by liver and bladder cancer. Gilliland & Mandel (1993) suggested a risk of mortality from prostate cancer in occupational workers exposed to PFOA. According to Austin *et al.* (2003), there was decreased food intake and body weight in a dose-dependent manner, including neuroendocrine effect, in rats exposed to PFOS. However, some epidemiological studies with occupationally exposed humans indicated no significant clinical hepato–toxicity at reported PFOA levels (Gilliland & Mandel 1996). The half lives of PFOS and PFOA in the human body were reported to be 8.67 and 1–3.5 years, respectively (Hekster *et al.* 2003). Based on toxicity studies with rats, a dietary concentration of approximately 15 μg/g of PFOS was considered a safe level (Giesy & Kannan 2002) – this concentration is much higher than those found in the tap water (Table 3) and animal tissues reported above and elsewhere (Giesy & Kannan 2001).

Table 4 | Concentration of PFOS (ng/ml) in human blood from different countries

Country	Number of sample	Mean	Range	Note	Reference
USA (Michigan, Kentucky and New York)	175	49.5	<1.3–164	Sera	Kannan *et al.* (2004)
Colombia	56	8.2	4.6–14		
Brazil	27	12.1	4.3–35		
Italy	50	4.3	<1–10.3		
Poland	25	44.3	16–116		
India	45	2.0	<1–10.3		
Malaysia	23	12.4	6.2–18.8		
Korea	50	21.1	3.0–92		
Japan	38	17.1	4.1–40.3		
USA, Atlanta	20	NA	3.6–164	Sera	Kuklenyik *et al.* (2004)
USA	645	34.9	<4.3–1,656	Sera	Olsen *et al.* (2003)
Japan	26	8.1	2.0–20.2	Whole blood	Masunaga *et al.* (2002)
Japan	10	9	2.4–14	Whole blood	Taniyasu *et al.* (2003)
Sweden	66	18.2	1.7–37	Whole blood	Kärrman *et al.* (2004)

DEGRADATION AND REMOVAL OF PFOS AND PFOA FROM THE WATER ENVIRONMENT

Due to the persistent characteristic of PFOS and PFOA, some potential methods that could effectively degrade or remove these compounds are, therefore: chemical methods, such as advanced oxidation and photocatalytic processes; and physical methods, such as adsorption and precipitation; or a combination of both. A summary of recent research on the degradation/removal of PFOS and PFOA (mostly at mg/L or µg/L concentrations) from water is shown in Table 5, while a brief description of these methods is given below.

Advanced oxidation methods

Previous work done by Schroder & Meesters (2005) found some oxidizing reagents such as O_3, O_3/ultraviolet (UV), O_3/H_2O_2 and Fenton to be ineffective in degrading PFOS and PFOA at the mg/L levels, but could break down some PFOS precursors and partly fluorinated molecules. Similar results were obtained by Qiu *et al.* (2006) when they employed these oxidizing reagents to treat water samples containing PFOS and PFOA at the µg/L levels.

A strong oxidant such as subcritical water (which is hot water at 350°C, but with sufficient pressure to maintain liquid phase) catalyzed with zero-valent metals, such as Fe, was found to be capable of degrading PFOS completely (Hori *et al.* 2006). The PFOS was observed to be strongly adsorbed onto the surface of the Fe_3O_4 compound generated by the reactions of iron and dissolved oxygen in liquid. Then the C–F bond was broken up completely due to oxidation by the oxygen molecules under high temperature and pressurized mixed liquid conditions. Moriwaki *et al.* (2005) found ultrasonic irradiation (20°C, 3 W/cm^2) to be able to pyrolyze both PFOS and PFOA on the surface of cavitation bubbles formed by the irradiation. Because of the ultrasonic irradiation effects, the PFOS was changed to PFOA by releasing the sulfonate group (see Figure 1), and the PFOA

Table 5 | Summary of studies on PFOS and PFOA degradation and removal

Process	Method	Target chemicals	Product chemical	Feed concentration (mg/L)	Volume (ml)	Removal rate (%)	Reaction time (hr)	Reference
Oxidation	Subcritical water, iron	PFOS	CO_2, HF	0.46 ~ 1.86	10	85 ~ 99.5	6	Hori *et al.* (2005)
	Ultrasonic irradiation	PFOS, PFOA	PFCA(C2 ~ C7)	10, 100	60	60 ~ 99	1	Moriwaki *et al.* (2005)
Photolysis	UV, oxygen	PFOA	PFCA(C2 ~ C7)	560	22	90	73	Hori *et al.* (2004)
	UV, catalyst	PFOA	CO_2, HF	140 ~ 1,400	22	100	24	Hori *et al.* (2004)
	UV, persulfate ion	PFOA	CO_2, HF	560	22	100	4	Hori *et al.* (2006)
	UV	PFOS, PFOA	PFCAs	0.02	250	60 ~ 80	24	Qiu *et al.* (2006)
Adsorption	GAC column	PFOA		2	pilot	>99		3M (2005)
	GAC 0.2 ~ 1g/L	PFOS, PFOA		0.1 ~ 100	50	>90	12	Qiu *et al.* (2005)

was consequently degraded to become other PFCAs which have shorter carbon chains and are less toxic to rats.

Photocatalysis

Direct photolysis employing UV (220 ~ 460 nm, 200 W) was found to be effective in degrading about 90% of 560 mg/L PFOA under 0.48 MPa oxygen, but the reaction time was as long as 3 days (Hori *et al.* 2004). Some synthetic catalysts such as heteropolyacid photocatalyst ($H_3PW_{12}O_{40}$), applied at 6.7 mM, was able to speed up the degradation of PFOA from 7.7% to 100% in 24 hours. Zhang *et al.* (2005) also found a 184 nm mercury lamp or 172 nm xenon quasi molecular laser light, both generating UV irradiation, to be able to degrade some PFCs completely. The degradation mechanisms were hypothesized to be stepwise break down of PFOA into shorter chain PFCAs and finally to CO_2 and HF. Another photocatalytic method employing persulfate ions irridated by UV could also degrade PFOA completely (Hori *et al.* 2005). The degradation mechanisms were hypothesized to be due to the sulfate radicals generated from UV irradiation of the persulfate ions which reacted with the PFOA and generated positively charged PFOA radicals which were eventually decomposed in water. A complete degradation of 560 mg/L PFOA to CO_2 and HF was achieved with 50 mM persulfate ions irradiated under 200 W UV lamps for 4 hours. A recent work conducted by Qiu *et al.* (2006) found PFOS and PFOA at 20 μg/L to be degraded about 80% and 60%, respectively, after being exposed to UV irradiation (254 nm, 10 W) for 24 hours. The degradation process and products were hypothesized to be similar to those reported by Hori *et al.* (2004).

Adsorption and membrane filtration

A pilot-scale granular activated carbon (GAC) column treating a wastewater containing 2 mg/L of PFOA from the 3M Cottage Grove facility, U.S.A., was able to remove more than 99% of the PFOA compound (3M 2005). Qiu *et al.* (2005) also found PFOS and PFOA to be removed more than 90% from a water sample treated by GAC adsorption. The range of PFOS and PFOA concentrations used in the adsorption experiments was 0.1–100 mg/L. Although

Fenton reagents cannot degrade PFOS and PFOA effectively as discussed above, the white granular sediment of $Fe(OH)_2^+$ formed in the reaction under pH 3 was found to be able to adsorb PFOS and PFOA. By applying excessive dosages of Fe_2^+ and H_2O_2 (4 mM and 40 mM, respectively) into a 20 μg/L PFOS and PFOA solution, more than 90% of the PFOS and PFOA were removed from the water samples after 4 days of contact time (Qiu *et al.* 2006).

Previous research by Pinitsakul *et al.* (2002) and Thaveemaitree *et al.* (2003) found the electrochemical process to be effective in removing some heavy metals from wastewaters through the adsorption and precipitation reactions. Some preliminary experiments (Qiu 2006) showed the electrochemical process to be able to remove about 90% of PFOS and 70% of PFOA from wastewater samples spiked with 103 and 53 μg/L of PFOS and PFOA, respectively (Figure 4) – the removal mechanisms were hypothesized to be due to adsorption of these compounds onto the surface of the electrochemical sludge which eventually settled down as sediment.

Tang *et al.* (2006) found 99% or more of PFOS could be removed by commercially available reverse osmosis membrane over a wide range of feed concentrations from 0.5 to 1,600 mg/L. The membrane flux decreased with increasing PFOS concentrations and was severely affected by isopropyl alcohol present in the semiconductor wastewater used in their experiments.
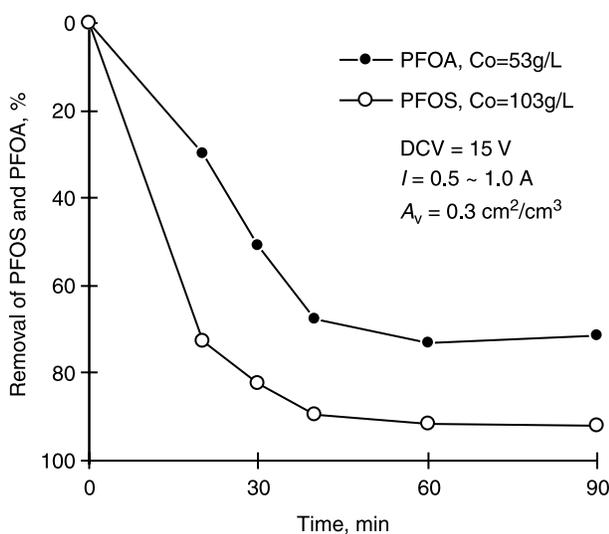

Figure 4 | PFOS and PFOA removal by electrochemical precipitation.

It should be noted that most of the treatment results mentioned above were obtained from laboratory- scale experiments conducted at PFOS or PFOA concentrations in the range of mg/L or μg/L, similar to those found in industrial wastewaters, but were much higher than the concentrations found in tap and surface water which are in the ng/L range. Nevertheless, at pilot- or full-scale operation, these treatment methods would usually generate sludge containing these compounds at concentrations normally higher than those in water. Sludge from some sewage treatment plants was found to contain PFOS and PFOA in the range of 200 ~ 500 ng/L (Nozoe *et al.* 2005). Therefore, methods to safely treat and dispose of contaminated sludge should be investigated. Some researchers, as reported in OECD (2002) and U.S. EPA (2002), expected PFOS and PFOA to be transformed into CO_2 and HF completely if incinerated in municipal solid waste incinerators at temperatures of 600°C or above. Yamada *et al.* (2005) found no PFOA emission during incineration of papers containing PFOA-related precursors and polymers at a temperature range of 600–1,000°C. This information suggests a possibility of also employing cement kilns which usually operate at temperatures above 1,000°C to degrade the PFOS- and PFOA-contaminated sludge.

SUMMARY AND CONCLUDING REMARKS

The global contamination of PFOS and PFOA in the water environment and in animal and human tissues is an emerging environmental concern. These compounds, which are persistent in the environment, bioaccumulative and can cause toxicity, have been found in the tap water of several cities at the ng/L levels. Both fresh and marine water samples collected from various places worldwide also contained PFOS and PFOA at concentrations generally higher than those of the tap water. Sewage treatment plants and industrial discharges have been identified as major point sources of PFOS and PFOA contamination, although non-point-source discharges, such as from agricultural run-offs and atmospheric transports, could contribute to the contamination problems.

Both PFOS and PFOA have been found in the tissues of fish, birds and marine mammals in the range of

100–1,000 ng/g, even in such remote locations as the Arctic and North Pacific oceans (which suggests atmospheric transport as a contamination route), but their concentrations in animals in industrialized areas were more than those from the less populated and remote regions. The BCF of PFOS in fish were estimated to be about 10,000 and above, while the BMF of PFOS in fish-eating birds and minks were in the range 10–20. The BCF of PFOA in fish was about 200 or less, much lower than those of PFOS. The PFOS and PFOA were also found in blood samples of occupationally exposed people and the general population in various countries at concentrations ranging from trace levels to more than 100 ng/ml. However, epidemiological studies of occupationally exposed people indicated no significant health problems at the exposed PFOA levels. Consumption of contaminated water and foods are obvious routes of PFOS and PFOA intakes, but other intake routes such as inhalation of contaminated air is a possibility. The half lives of PFOS and PFOA in human bodies were estimated to be 8.5 and 1–3.5 years, respectively. Based on toxicity studies with rats, a dietary concentration of approximately 15 μg/g was considered to be a safe level – this concentration is much higher than those found in the tap water and animal tissues reported in the literature. There is still a dearth of information about the environmental pathways of these compounds, their interactions in the ecosystems and toxicity to human and animals. More research to understand non-point source contamination of these compounds such as through surface run-offs, soil and groundwater pollution and atmospheric transport, is recommended.

Although there have not been epidemiological effects of PFOS and PFOA on animals and humans, the presence of these compounds in tap water, surface water and animal and human tissues indicates their global contamination and bioaccumulative phenomena in the ecosystems. It is thus important that appropriate measures be taken to control the point-source contamination such as at the factories that manufacture PFCs and related products and at sewage treatment plants that discharge PFCs-contaminated effluents into nearby water courses or on land. For the environmental engineering professionals, one of the immediate tasks would be to research into cost-effective methods to degrade or remove these compounds from tap water and wastewater streams. Previous lab-scale experiments showed some advanced oxidation, photocatalysis

and adsorption processes to be effective in treating water containing PFOS and PFOA. Other potential methods to remove PFOS and PFOA from contaminated water would be the membrane technology and electrochemical precipitation process. Methods to safely dispose of the contaminated sludge produced by the above treatment processes should be investigated. Regular monitoring of the contamination levels of PFOS and PFOA in the tap and surface water and in animals (especially fish because they have high BCF) and human tissues should be conducted.

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