Distribution of Perfluorooctane Sulfonate and Other Perfluorochemicals in the Ambient Environment around a Manufacturing Facility in China

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Perfluorinated compounds (PFCs) can be released to the surrounding environment during manufacturing and usage of PFC containing products, which are considered as main direct sources of PFCs in the environment. This study evaluates the release of perfluorooctane sulfonate (PFOS) and other PFCs to the ambient environment around a manufacturing plant. Among the nine PFCs analyzed, only PFOS, perfluorooctanoic acid (PFOA), and perfluorohexane sulfonate (PFHxS) were found in dust, water, soil, and chicken eggs. Very high concentrations of PFOS and PFOA were found in dust from the production storage, raw material stock room, and sulfonation workshop in the manufacturing facility, with the highest value at 4962 $\mu\text{g/g}$ (dry weight) for PFOS and 160 $\mu\text{g/g}$ for PFOA. A decreasing trend of the three PFCs concentrations in soils, water, and chicken eggs with increasing distance from the plant was found, indicating the production site to be the primary source of PFCs in this region. Risk quotients (RQs) assessment for surface water >500 m away from the plant were less than unity. Risk assessment of PFOS using predicted no-effect concentration (PNEC, 3.23 ng/g on a logarithmic scale) indicated no immediate ecological risk of a reduction in offspring survival. PFOS concentrations in most egg samples did not exceed the benchmark concentration derived in setting a reference dose for noncancer health effects (0.025 $\mu\text{g}/(\text{kg}\cdot\text{d})$).

Introduction

Perfluorinated compounds (PFCs) have been widely used in the industry as, for example, surfactants, lubricants, and pesticides due to their unique high surface activity, thermal and acid resistance, and hydro- and lipophobic properties (1). However, recent studies have proved that the continuous release of these substances from various applications and products has rendered them to become ubiquitous in the environment. PFCs have been found in biotic and abiotic

matrices including air (2), water (3), sediment (4), wildlife (5, 6), and in human biosamples such as breast milk (7) and blood (8–10). Related studies indicated that the most prevalent PFCs, perfluorooctane sulfonate (PFOS) is persistent (11), bioaccumulative (12), and toxic (13) in the environment. During the fourth Conference of the Parties of the Stockholm Convention (COP4), perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (POSF) were listed into Annex B to restrict/eliminate the production and usage of PFOS/PFOSF, albeit with some exemptions for minor specific usage due to the lack of environmentally safe alternatives (14).

Until 2002 when POSF production was ceased by the main producer 3M company, the total historical global production of POSF was about 96 000 tonnes while the estimated release into the environment was about 45 250 tonnes during 1970–2012. Thereinto, about 435–575 and 230–1450 tonnes were estimated to be released into air and water, respectively, during production (15). Correspondingly, another study on temporal trends of PFOS in biota showed doubling times of 5.8–10 years during the period of 1970–2000 (16).

After 2000, the worldwide productions dropped sharply and the predicted release into the environment reduced rapidly. Declining trends of PFOS have subsequently been reported in biota. Butt et al. reported a rapid response of declining PFCs levels in ringed seals which was thought to be due to the phase out of PFOS production (17). Similarly, declining concentrations of PFOS and several other PFCs was also found in adult blood donors in the US (18, 19). Olsen and co-workers found a downward trend for PFCs in American Red Cross blood donors and approximated that the 60% decline in PFOS concentrations from 2000–2001 to 2006 were consistent with the serum elimination half-lives in human body. However, other studies found increasing levels of PFOS in biota in some remote areas which was suspected to be due to continuous oceanic sources (20, 21).

China began to produce PFOS around the year of 2000, but before 2003 the production volume was relatively small (<50 tonnes). With the phase-out of PFOS in Europe and America, however, the production in China increased rapidly from 2005 and the produced volume intended for export increased to about 100 tonnes. After the European Union enacted a directive of PFOS in 2007, the export of PFOS products from China to Europe dropped off sharply.

Currently, due to important uses in specialized industrial processes and lack of feasible alternatives in certain applications, PFOS and related chemicals are still used in China. Previous investigations on PFCs levels in human blood in China showed differences in the concentrations profiles of various PFCs, indicating different exposure sources in various regions of China (8, 10). In this paper, we aimed to investigate the release, distribution and transport of PFCs to the ambient environment from a PFCs manufacturing facility in order to better understand the environmental fate, potential for long-range environmental transport, and risk assessment for the local inhabitants.

Experimental Section

Sampling. The manufacturing facility (Plant 1) is located in Wuhan, Hubei province, in central China. The main productions include perfluoroalkyl sulfonic acid, perfluoroalkyl carboxylic acid, perfluorotertiary amine and their derivatives using the electro-chemical fluorination (ECF) process. Most sampling sites are located around the plant. Dust sampling was mainly carried out inside the plant and next to roads near the facility. Sampling sites for soil and water and free

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TABLE 1. PFOS, PFOA, and PFHxS Concentrations in Dust Collected from Plant 1

sampling site	PFOS ($\mu\text{g/g}$)	PFOA ($\mu\text{g/g}$)	PFHxS ($\mu\text{g/g}$)
office 1	75.39	2.79	2.01
office 2	65.91	1.10	0.58
product storage 1	461.84	1.20	2.04
product storage 2	4305.68	1.09	25.82
raw material stock room 1	1046.07	2.78	4.34
raw material stock room 2	159.73	<LOD	0.59
electrolysis workshop 1	166.83	134.63	2.40
electrolysis workshop 2	141.26	105.69	1.46
electrolysis workshop 3	471.83	27.06	4.99
sulfonation workshop 1	3719.33	160.00	15.11
sulfonation workshop 2	4691.94	70.33	15.92
sulfonation workshop 3	2051.51	15.99	9.95
laboratory building	685.43	19.40	4.74
road 1	10.49	0.16	0.10
road 2	21.47	0.25	0.14
road 3	78.54	1.81	1.26

range chicken eggs were chosen around the plant at specific intervals. We also selected another plant, which used to produce PFCs but have ceased production in 2002, as a control site (Plant 2). In this sampling site, we also collected soil samples and free range chicken eggs. In total, 16 dust, 55 soil, 12 water, and 102 egg samples were collected. Furthermore, three soil samples were collected in another city in Hubei province with no known PFC industry as reference site. Detailed sampling sites of Plant 1 can be found in Supporting Information (SI) Figure S1.

Analytical Methodology and Data Analysis. In all, nine PFCs were analyzed, including perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTA), perfluoroundecanoic acid (PFUnDA), salts of perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS). Sample pretreatment, instrumental analysis, quality assurance, and quality control of the analytical method are described in detail in the SI. Statistical analyses were performed with SPSS 13.0 for Windows.

Result and Discussion

Dust. Very high levels of PFOS, PFOA, and PFHxS were found in dust in the facilities of Plant 1, whereas other PFCs were below detection limits (Table 1). Higher levels of the three PFCs in dust were found in the raw material stock room, sulfonation workshop, and product storage, indicating a higher emission potential to the indoor environment at these production sections. The concentrations of PFOS and PFOA in dust collected from the manufacturing sections in our present study were significantly higher whereas PFHxS concentrations were slight lower or at comparable levels than those in house dust collected from Ohio and North Carolina (maximal value of $12.1 \mu\text{g/g}$ for PFOS, $1.96 \mu\text{g/g}$ for PFOA, and $35.7 \mu\text{g/g}$ for PFHxS, respectively) (22), Stockholm City in Sweden (highest median concentration of 110 ng/g for PFOS and 93 ng/g for PFOA) (23) and several other developed countries (maximal concentration at $18.1 \mu\text{g/g}$ for PFOS, $9.82 \mu\text{g/g}$ for PFOA, and $43.8 \mu\text{g/g}$ for PFHxS, respectively) (24). Some studies have pointed out that house air and dust are important human exposure routes for PFCs, and dust exposure is the dominant source in some extreme exposure conditions whereas diet is the main exposure pathway of PFCs to the general population (23). Previous exposure studies have confirmed that occupational groups such as PFCs manufacturing works face risk of higher exposure levels than the general population (25, 26). It is therefore suspected that,

FIGURE 1. The concentrations of PFCs in soil surrounding the manufacturing facility (Plant 1). (Unit: ng/g, dry weight).

without proper protective measures, employees in the manufacturing sections could be exposed to elevated amounts of PFOS and PFOA.

Soil. In our present work, the two manufacturing plants were considered to be point emission sources of PFCs. Top soil samples (0–10 cm) at 30 different locations were collected around Plant 1 with increasing distance from the point source. Among these, three samples were collected inside the manufacturing facility and another 29 samples were taken outside the plant.

PFOS and PFHxS were detected in all soil samples whereas PFOA was present in 17 of 32 soils, with the highest concentrations found within Plant 1. The mean values ($n = 3$) reached 2583, 50.1, 35.3 ng/g dw for PFOS, PFOA, and PFHxS, respectively. Figure 1 shows the spatial distribution of soil concentrations of PFCs in and around Plant 1. Spatial concentrations of PFOS, PFOA, and PFHxS in soils were in the range of 0.68–189 (mean value, 22.6), <LOD–34.2 (mean value, 2.53), and 0.04–7.07 (mean value, 0.63) ng/g dw, respectively. The concentrations of these three chemicals in soils decreased in an exponential trend, with a 2–3 order of magnitudes higher concentrations in samples near the plant than those in distant sites. Soil samples were also collected from another city in Hubei Province (reference site) for comparison. The mean concentrations of PFOS and PFHxS were 0.65 and 0.01 ng/g dw, respectively, and the concentrations of PFOA were below LOD ($n = 3$). From Figure 1, it can be seen that the levels of PFOS and PFHxS in soils >2 km farther away from the plant have decreased to that of the reference site, whereas PFOA was not detected at that distance.

A former manufacturing facility was further used as a control area (Plant 2), which is located near the Yangtze River and has ceased production of PFCs since 2002. Twenty soil

samples were collected from 10 different locations near the plant and along the Yangtze River embankment. Each sampling site included two samples, one located at the outer river embankment and the other at the inner embankment from the plant.

Similar to the results above, PFOS and PFHxS were present in almost all the samples whereas PFOA was detected in more than half of the samples. Sample collected in close proximity to Plant 2 (<100 m) showed comparatively high concentration of PFOS (82.3 ng/g, dw) (SI Figure S2). The concentrations of PFOS, PFOA, and PFHxS in other samples ranged from 0.90–26.7 (mean value 7.06), <LOD–1.82 (mean value 0.79), and <LOD–0.54 (mean value 0.11) ng/g, dw, respectively. The concentration levels in this region were lower than those in the active manufacturing area and the samples from 0–0.5 km and comparable to the soils at 1–2 km from Plant 1 (Figure 1). In general, PFOS concentrations in soil samples from the west of Plant 2 (upstream of the Yangtze River) were higher than those from east of Plant 2 (downstream of the Yangtze River). A confounding finding was that soils from outer embankment had relative higher concentrations of PFOS than that from the inner embankment and the reason for this is yet to be known.

Water. Water samples were collected around the plant, including 1 groundwater sample, 1 tap water, 5 pond water, 2 river water, and 2 effluent samples from a wastewater treatment pond of the plant.

Very high concentrations of PFOS, PFOA, and PFHxS (sum concentrations of aqueous and particle phase) were found in the effluents from the wastewater treatment pond at Plant 1, with a mean value of 1021, 153, and 227 $\mu\text{g/L}$, respectively.

A pond water sample collected in close proximity to Plant 1 (less than 200 m) was found to have relative high concentration of PFOS (984 ng/L), PFOA (100 ng/L), and PFHxS (96.2 ng/L), respectively (SI Figure S3). The mean concentrations of these three chemicals in the other five pond water samples were 14.1 (PFOS), 9.99 (PFOA), and 7.80 (PFHxS) ng/L, respectively. These levels were lower than river water contaminated by semiconductor and electronics industries in Taiwan (maximum PFOS level at 5.4 $\mu\text{g/L}$) (27) and comparable to PFOS (0.4–123 ng/L) and PFOA (4.2–2600 ng/L) concentrations in surface water of the Yodo River basin in Japan (28).

Eggs. Seventy free-range chicken eggs were collected directly from homes of local residents around Plant 1 and separated into five groups: group 1 (<0.5 km), group 2 (0.5–1 km), group 3 (1–2 km), group 4 (2–3 km), and group 5 (>3 km). Seventeen eggs were collected from a chicken farm located in close proximity to Plant 1 (group 6) and 16 free-range chicken eggs were collected around Plant 2 as control samples (group 7). The concentrations of PFOS, PFOA, and PFHxS are shown in Figure 2 and Table 2, with all concentrations in eggs expressed on a wet weight basis.

For the free range chicken eggs, only PFOS was detected in all samples, whereas PFHxS and PFOA occurred in 91% and 52% of the samples. PFOS concentrations were several to hundreds of times higher than those of PFHxS and PFOA. Similar to the spatial distributions of soil and water samples, the concentrations of the three PFCs decreased rapidly with the increase of distance (from 0–3 km).

Around Plant 2, PFOS and PFHxS could be found in all free range chicken eggs (16 samples) and PFOA was present in 10 of 16 eggs. Relatively high concentrations of PFOS were present in eggs from this region with a range of 11.4–340 (mean value 85.2) ng/g although this manufacturing plant ceased production of PFCs in 2002. The results implied that once these PFCs are released, they can remain in the environment for a long period due to their high environmental persistence and can be further transferred to the local ecosystem.

FIGURE 2. Spatial distributions of PFCs in free range chicken eggs with increase of distance to Plant 1. (unit: ng/g). Thereinto, *farm* represents eggs collected from the chicken farm, *ref* is data collected from a related reference (28). Single values beyond the 150th percentiles of the difference between 25th and 75th percentiles are presented by “0”, while extreme values are presented by “*”, which are beyond the triplication of the difference between 25th and 75th percentiles.

An interesting observation is the low levels of PFCs in eggs collected from the chicken farm although it is located very near to Plant 1. The average value of PFOS in 17 chicken farm eggs was 0.19 ng/g, and PFOA and PFHxS were detected only in several samples at very low levels (24% and 41%, respectively). Similar to the possible exposure pathways to humans, sources of PFCs in chickens should usually be from drinking water, dietary intake and inhalation. The main drinking water for free range chicken is surface water and they scavenge their food directly from the ground. During feeding, the free range chickens usually deliberately ingest a certain amount of dust/soil to help with digestion. Therefore, a high relative amount of PFCs in the free range chickens are expected to be derived from digestion and inhalation of dust or soil, which are then transferred to their eggs. However, for farm chickens, the main source of food and drinking water is usually directly supplied by the farmers. The large differences of PFC concentrations between free range and farm chicken eggs implied that the dominant source of PFCs in chickens should be from diet since they are expected to be exposed to the same ambient air.

Studies of PFCs in chicken eggs are very scarce and only one paper regarding PFOS and related perfluorochemicals in chicken eggs in China was previously published (29). The concentrations of PFOS, PFOA, and PFHxS from other related studies are also summarized in Table 2. PFOS from group 1 were higher than those for chicken eggs and waterbird eggs from other parts of China but was lower than Guillemot eggs from the Baltic Sea (range 32–1023 ng/g, ww). Concentrations of PFOS in chicken eggs in group 2–6 were at the relative lower levels, which were only slightly higher than Laysan albatross and black-footed albatross eggs (North Pacific

TABLE 2. Concentrations of PFCs in Free-Range Chicken Eggs (ng/g) in This Study and Comparison to Other Reported Concentrations in Bird Eggs^a

location	distance	n		PFOS	PFOA	PFHxS	reference
manufacturing plant 1	<500 m	14	mean	109	0.90	0.52	this work
			range	6.67–283	0–1.91	0.07–2.13	this work
	500–100 m	13	mean	12.0	0.45	0.56	this work
			range	3.27–59.3	0–1.16	0–2.24	this work
	1000–2000 m	19	mean	8.59	0.17	0.15	this work
			range	0.80–75.9	0–0.97	0–0.54	this work
	2000–3000 m	17	mean	9.55	0.12	0.34	this work
			range	0.07–33.0	0–0.96	0–0.76	this work
	>3000 m	7	mean	9.79	0.15	0.78	this work
			range	2.70–18.1	0–0.53	0–3.18	this work
farm		17	mean	0.19	0.11	0.03	this work
			range	0–0.35	0–0.79	0–0.08	this work
manufacturing plant 2		16	mean	85.2	0.24	0.76	this work
			range	11.4–340	0–0.53	0.12–3.01	this work
South China (chicken egg)		24	range	34.7–87.6	<0.01–0.09	<0.01	29
South China (waterbird egg)		28	range	14.4–349	<0.01–1.39	<0.01–0.37	30
glaucous gulls eggs from Norwegian Arctic		10	range	51.7–196	<0.70	<0.27–1.23	31
Birds eggs around lake Shihwa, Korea		44	range	30.4–1206	<LOD–25.2	<LOD–9.5	32
guillemot egg from Baltic Sea (1968–2003)		146	range	32–1023	<LOD	NA	33

^a <LOD: below limit of detection. NA: not available.

FIGURE 3. Risk quotients of PFOS, PFOA, and PFHxS for water samples collected from around Plant 1. Sample identity: 1: Tap water in the plant; 2: pond water no. 1; 3: pond water no. 2; 4: pond water no. 3; 5: groundwater; 6: pond water no. 4; 7: pond water no. 5; 8: river water; 9: pond water no. 6; 10: effluent from wastewater treatment pond in the plant; 11: effluent from wastewater treatment pond of the plant; 12: upstream from the outfall of the plant. Provisional Health Advisory: PFOS: 200 ng/L, PFOA: 400 ng/L, and PFHxS: 600 ng/L. RQ is the value of PFCs concentrations in water divided by the value of Provisional Health Advisory.

Ocean) (2.48–3.17, ng/g, ww). The concentrations of PFOS in chicken eggs from Plant 2 were somewhat higher than the eggs of egret but lower than that of night heron from South China (30). The compositions profiles among the egg samples were also similar with PFOS as the dominant PFC. For PFOA and PFHxS, levels among these seven groups of chicken eggs from this study were higher than those among chicken and waterbird eggs from other areas, further implying that the release of PFCs during manufacture is the main source of PFCs in biota around the plant.

Risk Assessment. Risk quotients (RQs) associated with PFCs contaminated water samples around Plant 1 was calculated using the Provisional Health Advisory for PFCs (34). The RQs for PFOS, PFOA, and PFHxS from the surface water and groundwater >500 m away from the plant were less than unity (Figure 3), which suggests that the release of PFCs from the point source might not pose an immediate risk to the health of the local inhabitants. However, as the PFC concentrations in the wastewater of the plant were

FIGURE 4. Hazard ratio (HR) distributions of PFOS from chicken eggs consumptions by local inhabitants. Red circles, blue circles, and triangle represent HR of PFOS in eggs collected from near the Plant 1, Plant 2, and Chicken farm, respectively.

significantly higher than other water samples, the potential risk from the manufacturing should not be ignored.

Because of the lack of toxic reference values for evaluating the effect of PFOS to chickens, an avian toxicity reference value predicted no-effect concentration (PNEC) (3.23 ng/g, ww on a logarithmic scale) of PFOS was used to assess the ecological risk of PFOS (30). From Figure 4 (shown as cumulative accounts) it can be seen that all the concentrations measured in chicken eggs in this study were below the PNEC, which implied no immediate ecological risk of a reduction in offspring survival.

The health risk assessment of PFOS exposure from egg consumptions by local inhabitants were carried out by relevant hazard ratios (HR), which is calculated by the following formula: $HR = \text{average daily intake (ADI)} / \text{benchmark dose}$. Therein, PFOS ADI was calculated by $ADI = \text{egg consumption (g/kg body weight} \times \text{day)} \times \text{PFOS concentration}$. Benchmark dose of PFOS was derived in setting a reference dose for noncancer health effects (0.025 $\mu\text{g}/(\text{kg} \times \text{day})$) (35).

Using the reference value of average body weight for Asian people (60 kg) and the estimated daily egg consumption (g per person, wet weight) in China (7 g), the HR for PFOS due to egg consumption was estimated and shown in Figure 4. The results indicated that PFOS concentrations in only 4 of 71 eggs exposure level exceeded the benchmark concentration (HR > 1), which is consistent with results from different

regions in China (30). The results implied that consumption of most chicken eggs in our study pose low risks to the consumers. However, a more refined risk assessment should be carried out to better understanding the health risks of PFCs to the local inhabitants since PFOS concentrations in some egg samples were close to the benchmark concentration. Furthermore, other food sources and exposure pathways should also be taken into account in future studies as these could potentially be more significant than intake of eggs.

Perfluorosulfonates and perfluorocarboxylates are thought to be long-range transported via oceanic transport or indirectly from degradation of volatile precursors. Some studies suggested that PFOS and PFOA will reside in the aquatic compartment, to a greater extent than in the atmospheric medium (36). Gradual decreasing trends of PFCs in water and soils with the distance from the plant implied that the area directly influenced by the release of PFCs due to manufacturing are relatively small (<2 km in this work).

Dust is usually an important PFC exposure pathway to humans. Consequently, we calculated the estimated daily intake of PFOS and PFOA via ingestion ($EDI_{\text{ingestion}}$) and dermal absorption (EDI_{dermal}) of the worker by applying the exposure/ingestion factors recommended by Zhang et al. and U.S. Environmental Protection Agency (37, 38). We assumed that the workers only reside within the manufacturing compound and the exposure time is divided into two parts: during work time (supposed 8 h in the production section) and the remaining time is at off-work hours. Exposure levels in the production section was taken by the average value of the concentrations in dust from workshop and laboratory building, and the exposure concentrations of PFCs during the off-work hours was assumed to be the average value of concentrations in dust from the roads and office. Calculation details can be found in the SI. The average of $EDI_{\text{ingestion}}$ values of PFOS and PFOA was about 29.7 and 1.15 $\mu\text{g}/\text{day}$, respectively, and those of EDI_{dermal} values was about 7.42 and 0.30 $\mu\text{g}/\text{day}$, respectively, which implied that for the workers, dust ingestion is perhaps the most important exposure source of PFCs. These results suggest that PFCs exposure via dust ingestion in this occupational setting is much higher than those from other studies in China, the U.S., and other countries (2223, 34). However, these values are probably overestimated since the calculations do not consider protective measures such as gloves and face masks which would strongly reduce exposure. Furthermore, the exposure time is largely exaggerated as the workers would not be expected to reside within the manufacturing complex at all times.

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Supporting Information Available

Additional information regarding sampling information, pretreatment and instrument analysis, instrumental analysis, quality assurance and quality control, data calculations, Table S1, and Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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