



## Wastewater treatment plants (WWTPs)-derived national discharge loads of perfluorinated compounds (PFCs)

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### ABSTRACT

The discharge of perfluorinated compounds (PFCs) was investigated for 15 wastewater treatment plants (WWTPs), comprising 25% of total domestic wastewater and 23% of total industrial wastewater produced in Korea. PFCs concentrations in influent, effluent, and sludge were greater in industrial wastewater than in the majority of domestic wastewater. Individual PFCs were found to have differing industrial sources, with perfluorocarboxylates used in fabric/textiles, paper-mill, and dyeing industries, and perfluoroalkylsulfonates occurring in oil/chemical and metal-plating/processing industries. Total WWTP-derived national discharge loads were calculated based on the average concentrations in effluents and the total volume of wastewaters produced in Korea. The average WWTP-derived national discharge loads of individual PFCs were 0.04–0.61 ton/year, with 63% of perfluorooctanoate being from domestic wastewater, and 75% of perfluorooctanesulfonate being from industrial wastewater. These estimates accounted for the majority of national emissions, based on measurements in major river mouths, indicating the major contribution of WWTPs to PFC occurrence in Korean aquatic environments. Both the per capita emission factor ( $\mu\text{g}/\text{capita}/\text{day}$ ) for domestic discharge, and area-normalized national discharge loads ( $\text{g}/\text{capita}/\text{km}^2/\text{day}$ ) for all wastewaters were several factors lower in Korea than in Japan or Europe, which is consistent with the lower levels of human exposure to PFCs in Korea.

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### 1. Introduction

Perfluorinated compounds (PFCs) are fluorinated at all or a portion of the carbon atom of organic molecules with a terminal sulfonate or carboxylate group. These molecular structures exhibit unique properties, such as resistance to environmental degradation, high surface activity, and both hydro- and lipophobicity [1]. Since their first production in 1947, using an electrochemical fluorination process (ECF), PFCs have been used in a wide range of commercial and industrial applications such as polymers, metal plating and cleaning, surfactants, lubricants, pesticides, coating formulations, inks, varnishes, firefighting foam, and stain/water repellents for leather, paper, and textiles [2,3].

PFCs such as perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFASs) have emerged as global environmental pollutants, with persistent bioaccumulative and toxic properties [1]. These compounds also distribute worldwide in wildlife and humans, including those in Arctic region, by their long-range

transport potential (LRTP) via currents [4,5] and the atmosphere [6,7]. Due to the toxicity of these chemicals, voluntary commitments to reduce and/or restrict their manufacturing and use have been in place since 2000 [8,9]. Perfluorooctanesulfonate (PFOS) and related substances were also listed in Annex B of the Stockholm Convention on persistent organic pollutants (POPs) [10].

According to bottom-up estimates of PFCs, based on historical production of individual PFC-based articles, total global emissions could be 2600–5050 ton of ammonium perfluorooctanoate (APFO; a combined form of PFOA with  $\text{NH}_4^+$ ) over the period of 1950–2010 [4,11], and 450–2700 ton of PFOS during 1970–2002 [12]. The national emission of 0.1 ton of PFOA in 2004 was first reported in North America, with emissions occurring from the manufacture, use, and disposal of fluorotelomer-based products from all sources. These estimates assumed that emissions by DuPont represented 40% of total North American PFC emissions [13]. However, insufficient data are available to validate these estimates based on bottom-up approaches.

Most emissions of PFOA and PFOS in the environment are “direct” emissions, often released into the water environment during manufacturing and industrial/commercial uses [4,11,12,14]. Thus, top-down estimates calculated backwards from levels

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measured in water environment can be more favorable, not only in reflecting ongoing emissions but also in validating bottom-up estimates. For example, the total aqueous discharge loads of PFOA and PFOS, based on riverine PFC measurements, have been used to calculate total European emissions [15,16], as well as those of a river watershed in northern Italy [17]. Total aqueous loadings estimated in previous studies include both discharges from “point sources,” such as wastewater treatment plants (WWTPs), and releases from “non-point sources,” such as surface runoff.

WWTPs are considered a major point source of aqueous discharges [18–22]. However, recent studies have stressed the relative importance of non-point sources in aqueous loads [23–26]. Thus, determining which path is dominant contributor to total aqueous load is important for the efficient management policy. Nevertheless, most WWTPs studies to date have focused on the mass loading and/or mass balance of PFCs at individual WWTP facilities, which is insufficient to compute or validate WWTP-derived watershed and/or nationwide emissions [27–29], and subsequently to determine the relative contribution of WWTPs to total PFC discharge loads. Little is known of WWTP-derived total emissions at the national level. Only a few studies have reported the WWTP-associated national PFCs emission: per capita emission factors of municipal WWTPs in Switzerland [20] or municipal WWTP-derived annual PFC loading in Japan [21].

In the present study, the influent, effluent, and sludge data were presented for 15 WWTP facilities, which were selected to reflect a nationwide estimate and various influent activities: (1) the concentrations and discharge loads of individual PFCs were determined at 15 WWTPs, (2) the WWTPs that showed differing PFC discharge characteristics with application use were identified, and (3) annual loads of PFCs occurring from each type of domestic and industrial wastewater in Korea were estimated.

## 2. Materials and methods

### 2.1. Sample collection

To provide a national estimate of WWTP-derived PFC discharge loads, we had four selection criteria for WWTP facilities.

First, WWTPs in Korea were categorized into three typical groups with characteristic wastewater influents: domestic wastewater (D-WWTPs), industrial wastewater (I-WWTP), and a mixture of domestic and industrial wastewater (M-WWTPs) (Fig. S1 and Table 1). Second, the top 15 candidate WWTPs in each group were selected primarily in order of their daily treatment capacities. Third, five of the 15 candidates in each group were finally chosen and included a facility from each of five main Korean watersheds (Han, Nakdong, Keum, Yeongsan, and Seomjin Rivers) (Fig. S2). This watershed-based selection enabled discharge estimates to reflect PFC levels and patterns measured in ambient water in each watershed. Fourth, potential sources of PFCs were considered when selecting the targeted I-WWTPs from the 15 candidates. The final five I-WWTPs involved wastewater occurring in LCD manufacturing, semi-conductor manufacturing, chemical factories, steel mills, fabric/clothing manufacturing, and dyeing factories (Table 1). The five M-WWTPs include wastewater from paper manufacturing, metal plating, mechanical/electrical factories, and fabric/clothing manufacturers (Table 1). Thus, national discharge loads of industrial wastewater-derived PFCs extrapolated from targeted I- and M-WWTPs could be a conservative value.

The selected WWTPs represent typical D-WWTPs (i.e., domestic wastewater accounts for >90% of total influent), I-WWTPs (industrial wastewater >90%), and M-WWTPs (30–70% for each of domestic and industrial wastewaters). The population served by the five D-WWTPs and five M-WWTPs in this study comprises

20% of the total population of Korea. Furthermore, total wastewater treated by the 15 WWTPs accounts for 25% of total domestic wastewater and 23% of total industrial wastewater produced in Korea (Table 1).

In 2010, influent, effluent, and sludge (i.e., dried cake) samples were collected in spring, summer, and fall (i.e., April, July, and October) from each WWTP (Table 2). Flow-proportional 5-day composite samples of influent and effluent were collected in each season at each WWTP. A composite sample of sludge was also taken mass-proportionately, with the daily mass sampled adjusted according to the total production mass of 5 consecutive days. After collection at each WWTP, all samples were immediately frozen, transported, and kept below  $-20^{\circ}\text{C}$  until analysis to prevent microbial degradation.

### 2.2. Chemicals

An ionic PFC mixture (PFAC-MXB<sup>®</sup>; >98%) and individual intermediate PFC standards were purchased from the Wellington Laboratory Inc. (Ontario, Canada) to analyze eight PFCAs of C<sub>6</sub>–C<sub>13</sub> (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA, and PFTrDA), four PFASs (PFBS, PFHxS, PFOS, and PFDS), and three intermediates (FOUEA, EtFOSAA, and MeFOSAA; see full names in Table 3 and Table S1). Mass-labeled compounds were also purchased from Wellington Laboratory Inc. (>98% purity); <sup>13</sup>C-labeled ionic PFCs mixture (MPFAC-MXA<sup>®</sup> for MPFHxA, MPFOA, MPFNA, MPFDA, MPFUnDA, MPFDoDA, MPFHxS, and MPFOS), MFOUEA, d<sub>5</sub>-EtFOSAA, and d<sub>3</sub>-MeFOSAA (Table 3). These surrogate materials were spiked prior to sample extraction for recovery correction of individual native compounds (see details in Table 3 and Table S1).

### 2.3. Sample analysis

Influent ( $n=45$ ) and effluent ( $n=45$ ) were extracted using solid-phase extraction (SPE) with an Oasis HLB cartridge (6 cm<sup>3</sup>, 200 mg; Waters, Milford, MA). Liquid samples were centrifuged (10,000 rpm, 10 min) to settle the particles and remnants. The supernatant of 300 mL was spiked with 5 ng of mass-labeled compounds, and then the dissolved phase was loaded at 10 mL/min to the preconditioned SPE (Fig. S3). Target compounds were eluted with 10 mL of 0.1% NaOH in methanol from the SPE column, which was washed with 12 mL Milli-Q water and 6 mL 20% methanol and dried under vacuum.

The treatment of sludge samples ( $n=45$ ) was performed by a consecutive procedure of digestion, solvent extraction, and SPE cleanup as described elsewhere (Fig. S3) [30]; briefly, a subset of freeze-dried sludge sample was homogenized and ground. A 0.1-g solid, spiked with a mass-labeled compound, was digested in 0.1 mL 1 M NaOH, and then neutralized by the addition of 0.1 mL HCl. The digested solid sample was extracted for 1 h, with shaking in 7.5 mL acetonitrile:methanol mixture (50:50, v/v). After two more extractions, the total supernatants were combined and dried to 2 mL under a gentle stream of N<sub>2</sub>. After dilution with 98 mL Milli-Q water, the extracts were cleaned via SPE, following the same procedure as in the water sample extraction. Target analytes in extracts were identified and quantified using high-performance liquid chromatography (Agilent 1100 series) coupled with an API 4000 electrospray triple-quadrupole mass spectrometer (Applied Biosystems; Foster City, CA).

The solid-phase in water (influent or effluent) was not analyzed in this study because most solid-phase particles can be settled as sludge (dry-cake) where solid-associated PFCs exist.

**Table 1**  
Characteristics of wastewater treatment plant studies.

	Facility i.d.	Population ( $\times 1000$ , capita)	Wastewater daily flow ( $\times 1000$ , m <sup>3</sup> /day)		Daily dry-cake (ton/day)	Treatment process	Industry type
			Domestic	Industrial			
Domestic	D-WWTP-1	3,500	1,581	10	462	<b>Inf</b> → PC → CAS → SC → CI → <b>Eff</b> and <b>DC</b>	Medicals
	D-WWTP-2	1,868	829	–	286	<b>Inf</b> → PC → CAS → SC → CI → <b>Eff</b> and <b>DC</b>	Dyeing/fabric, chemicals, machine assembly
	D-WWTP-3	1,454	600	15	161	<b>Inf</b> → PC → CAS → SC → CI → <b>Eff</b> and <b>DC</b>	
	D-WWTP-4	1,350	540	60	167	<b>Inf</b> → PC → CAS → SC → CI → <b>Eff</b> and <b>DC</b>	
	D-WWTP-5	755	383	21	143	<b>Inf</b> → PC → A2O → SC → CI → <b>Eff</b> and <b>DC</b>	Fabric/textile, dyeing
Industrial	I-WWTP-1	–	1	69	86	<b>Inf</b> → PC → A2O → SC → UV → <b>Eff</b> and <b>DC</b>	LCD, audio equipment
	I-WWTP-2	–	4	40	107	<b>Inf</b> → PC → BF → SC → SF → CF → <b>Eff</b> and <b>DC</b>	Semiconductor, LED
	I-WWTP-3	–	1	47	32	<b>Inf</b> → PC → A2O → SC → UV → <b>Eff</b> and <b>DC</b>	Petrochemicals, fertilizer
	I-WWTP-4	–	0	3	2.8	<b>Inf</b> → PC → A2O → SC → O3 → TC → <b>Eff</b> and <b>DC</b>	Non-/metal processing, steel-mill
	I-WWTP-5	–	0	57	315	<b>Inf</b> → PC → CAS → SC → CI → <b>Eff</b> and <b>DC</b>	Textile-dyeing
Mixed (domestic + industrial)	M-WWTP-1	736	120	170	219	<b>Inf</b> → PC → CAS → SC → TC → <b>Eff</b> and <b>DC</b>	Metal plating and processing, textile-dyeing
	M-WWTP-2	14	35	85	199	<b>Inf</b> → PC → CAS → SC → FT → <b>Eff</b> and <b>DC</b>	LCD
	M-WWTP-3	68	28	23	21	<b>Inf</b> → PC → CAS → SC → <b>Eff</b> and <b>DC</b>	Paper-mill, dyeing, food
	M-WWTP-4	281	94	219	75	<b>Inf</b> → PC → A2O → SC → SF → UV → <b>Eff</b> and <b>DC</b>	LCD, electronic, dyeing, fabric, machinery
	M-WWTP-5	30	140	210	37	<b>Inf</b> → PC → CAS → SC → TC → → <b>Eff</b> and <b>DC</b>	Machine assembly, textile/fabric industries
	Sum	10,056	4,355	1,028	2,312		
	Total in Korea	49,552	17,113 <sup>a</sup>	4,557 <sup>b</sup>	7,719 <sup>c</sup>		

Treatment process: Inf: influent; PC: primary clarifier; SC: secondary clarifier; CI: chlorination; A2O: anaerobic-anoxic-oxic; CAS: conventional activated sludge; TC: third clarifier; BF: biofilter; FT: fenton treatment; SF: sand filter; CF: carbon filter; and Eff: effluent.

<sup>a</sup> Total production rate of domestic wastewater in 2008 in Korea, 92% of which is treated through WWTPs.

<sup>b</sup> Total production rate of industrial wastewater in 2008 in Korea, 66% of which is discharged after treatment in I-WWTPs.

<sup>c</sup> Total production rate of dry-cake from D-WWTPs in 2008 in Korea.

**Table 2**  
Sampling campaigns for influent, effluent, and sludge.

Wastewater type	Facility i.d.	Sampling duration of influent, effluent, and dry-cake <sup>a</sup>			
		Spring	Summer	Fall	n <sup>b</sup>
Domestic	D-WWTP-1	April/27–May/01	July/29–August/02	Oct./06–Oct./10	5/5/5
	D-WWTP-2	April/27–May/01	July/27–July/31	Oct./06–Oct./10	5/5/5
	D-WWTP-3	April/28–May/02	July/28–August/01	Oct./07–Oct./11	5/5/5
	D-WWTP-4	April/27–May/01	July/27–July/31	Oct./05–Oct./09	5/5/5
	D-WWTP-5	April/29–May/03	July/31–August/04	Oct./11–Oct./15	5/5/5
Industrial	I-WWTP-1	April/28–May/02	July/28–August/01	Oct./06–Oct./10	5/5/5
	I-WWTP-2	April/27–May/01	July/27–July/31	Oct./08–Oct./12	5/5/5
	I-WWTP-3	April/30–May/04 <sup>c</sup>	July/30–August/03 <sup>d</sup>	Oct./06–Oct./10	5/5/5
	I-WWTP-4	April/27–May/01 <sup>e</sup>	July/27–July/31 <sup>f</sup>	Oct./05–Oct./09 <sup>g</sup>	5/5/5
	I-WWTP-5	April/30–May/04	July/30–August/03	Oct./06–Oct./10	5/5/5
Mixed (domestic + industrial)	M-WWTP-1	April/28–May/02	July/28–August/01	Oct./04–Oct./08	5/5/5
	M-WWTP-2	April/25–August/29	July/27–July/31	Oct./06–Oct./10	5/5/5
	M-WWTP-3	April/28–May/02 <sup>h</sup>	July/28–August/01	Oct./04–Oct./08	5/5/5
	M-WWTP-4	April/27–May/01	August/02–August/06	Oct./06–Oct./10	5/5/5
	M-WWTP-5	April/30–May/04	July/29–August/02	Oct./05–Oct./09	5/5/5
Sum		n = 75	n = 75	n = 75	n = 225

<sup>a</sup>The sampling period for 5-day consecutive composite has a few days-gap among facilities in the same season with accessibility to the facility. Everyday, one sample was collected routinely.

<sup>b</sup>The number of samples collected at each season. 5-day consecutive samples (n = 5) were composited to make one representative. Thus, total number of samples were 45 for each of influent, effluent, and sludge.

The sampling period of sludge (dry-cake) varied for some facilities; <sup>c</sup>May/02–05; <sup>d</sup>July/30–August/01; <sup>e</sup>April/27 only; <sup>f</sup>July/27 only; <sup>g</sup>Oct./06–08; and <sup>h</sup>April/28–30.

#### 2.4. Quality assurance/quality control

Concentrations of PFCs in extracts were quantified using a 8-point external calibration curve (0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 25.0, and 50 ng/ml). The coefficient of determination ( $R^2$ ) for each constructed curve was greater than 0.99. Quality-control (QC) standards were analyzed every seven samples to check for shifts in instrument sensitivity. Acquired data were deemed acceptable if

the measured QC standard fell within 30% of the overall average. Otherwise, the analysis was stopped, and samples were reanalyzed with a new calibration curve. In every batch of 10 samples, procedural blanks and matrix-spiked samples were analyzed to ensure the quality of the analytical procedure and check the matrix effect. Field blanks, which were filled with SPE-cleaned Milli-Q waters and opened a few seconds on the site, were transported, stored, and analyzed following the same procedure with the sample

**Table 3**

Analysis results of matrix-spiked samples (n = 7) and the recovery of mass-labeled compounds spiked to individual samples prior to extraction.

Spiked samples	Accuracy (average ± stdev; %)		Samples	Recovery (average ± stdev; %)	
	Influent/effluent (n = 7)	Sludge (n = 7)		Influent/effluent (n = 90)	Sludge (n = 45)
Perfluorohexanoic acid (PFHxA)	112 ± 6	88 ± 4	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid (MPFHxA)	82 ± 21	– <sup>a</sup>
Perfluoroheptanoic acid (PFHpA)	88 ± 5	94 ± 7	– <sup>b</sup>	–	–
Perfluorooctanoic acid (PFOA)	84 ± 5	98 ± 5	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid (MPFOA)	93 ± 8	98 ± 21
Perfluorononanoic acid (PFNA)	81 ± 6	96 ± 5	Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid (MPFNA)	92 ± 9	97 ± 20
Perfluorodecanoic acid (PFDA)	89 ± 5	99 ± 5	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid (MPFDA)	81 ± 15	84 ± 19
Perfluoroundecanoic acid (PFUnDA)	101 ± 4	92 ± 5	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]undecanoic acid (MPFUnDA)	59 ± 15	77 ± 31
Perfluorododecanoic acid (PFDoDA)	90 ± 3	80 ± 7	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]dodecanoic acid (MPFDoDA)	45 ± 15	65 ± 24
Perfluorotetradecanoic acid (PFTrDA)	141 ± 9	74 ± 10	– <sup>b</sup>	–	–
Perfluorobutyl sulfonate (PFBS)	110 ± 7	136 ± 4	– <sup>b</sup>	–	–
Perfluorohexyl sulfonate (PFHxS)	92 ± 10	109 ± 5	Sodium perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate (MPFHxS)	97 ± 10	105 ± 29
Perfluorooctyl sulfonate (PFOS)	84 ± 2	107 ± 5	Sodium perfluoro-1,2,3,4-hexane[ <sup>13</sup> C <sub>4</sub> ]sulfonate (MPFOS)	100 ± 20	103 ± 23
Perfluorodecyl sulfonate (PFDS)	95 ± 3	90 ± 6	– <sup>b</sup>	–	–
2H-Perfluoro-2-decanoic acid (FOUEA)	96 ± 4	146 ± 6	2H-Perfluoro-[1,2- <sup>13</sup> C <sub>2</sub> ]-2-oceanoic acid (MFOUEA)	92 ± 11	89 ± 30
N-Ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA)	85 ± 6	99 ± 6	N-Deuterioethylperfluoro-1-octanesulfonamidoacetic acid (d5-EtFOSAA)	61 ± 15	72 ± 26
N-Methylperfluoro-1-octanesulfonamidoacetic acid (MeFOSAA)	97 ± 3	89 ± 6	N-Deuteriomethylperfluoro-1-octanesulfonamidoacetic acid (d3-MeFOSAA)	69 ± 13	80 ± 24

<sup>a</sup> Frequently detected at <40% and then excluded for quantification.

<sup>b</sup> Not available.

bottles every season. None of the target analytes were detected in the procedural and field blanks except for PFOA, which was detected at 0.25–0.75 ng/L in only the liquid blank samples. All reported concentrations were blank-subtracted.

Average recoveries of labeled compounds were within 45–100% for influents/effluent samples, and 65–105% for sludge samples (Table 3 and Table S3). For matrix-spiked samples, one composite sample for each of influent/effluent and sludge was made from the respective five samples collected in the spring season (v/v for influent/effluent and w/w for sludge). Thereafter, the composite samples were spiked by native compounds to be ~100 ng/L or ~100 ng/g. Seven spiked replicates for each of influent/effluent and sludge were analyzed. All target compounds were well-recovered in replicate matrix-spiked samples ( $n=7$  each); 81–141% of liquids and 74–146% of solid samples (Table 3). These results indicate that the potential matrix effect was efficiently removed during the analysis procedure as mentioned elsewhere [30]. However, all concentrations in the present study were normalized against recoveries of the labeled counterparts added prior to extraction to correct the loss of target compounds occurring in sample-to-sample or batch-to-batch. For PFHpA, PFTrDA, PFBS, and PFDS, for which there are no available counterparts, we used neighboring mass-labeled compounds (MPFOA, MPFDoDA, MPFHxA, and MPFOS, respectively) (Table 3). Perfluoro- $n$ -[1,2- $^{13}\text{C}_2$ ]hexanoic acid (MPFHxA), a mass-labeled counterpart of PFHxA, was largely lost in solid samples and thus PFHxA was not quantified in sludge samples.

The method detection limits (MDLs) were assigned as 3 standard deviations of concentrations determined in seven replicates which were prepared by spiking low concentrations (~1 ng/L or ~1 ng/g) to Milli-Q water (for influent and effluent) or sodium sulfate (for sludge). The MDL values for liquid and solid samples ranged from 0.2 to 1.6 ng/L and 0.5 to 1.5 ng/g, respectively (Table S2). Concentrations below the MDL were assigned half of the MDL value for statistical analyses.

### 3. Results and discussion

#### 3.1. Influent concentrations

Total PFCs (PFCAs, PFASs, intermediates) in influents were found in the following order: M-WWTs ( $1100 \pm 1500$  ng/L) > I-WWTs ( $610 \pm 420$  ng/L) > D-WWTs ( $110 \pm 130$  ng/L). Among 15 WWTs, the highest concentrations were observed in M-WWT-3 ( $1790 \pm 2100$  ng/L) and M-WWT-5 ( $2700 \pm 1600$  ng/L). In particular, M-WWT-5 influents contained total PFCs exceeding 1000 ng/L in all three seasons. Individual PFC concentrations varied seasonally, with a relative standard deviation <100% for most compounds. Seasonal trend was not observed in concentration levels and/or composition pattern.

Individual PFC concentrations detected in influents of individual WWTs are illustrated in Fig. 1. With the exception of D-WWT-5, the concentrations of individual PFCs distributed uniformly among the four other D-WWTs (RSD < 53% for  $n=12$  of total PFCs), where PFHxA and PFOA accounted for 55% of total PFCs (Fig. 1). This indicates a small difference of the PFC-associated domestic activities among cities. On the other hand, the concentrations and composition profiles varied much more among facilities treating industrial wastewater (I-WWTs or M-WWTs) (Fig. 1). The difference in the average concentrations of individual and total PFCs was less than a factor of 2 for D-WWTs (except D-WWT-5), whereas I-WWTs and M-WWTs showed 1–2 orders of magnitude between minimum and maximum values. PFHxA was predominant in I-WWT-1 and I-WWT-5 while PFBS in I-WWT-2 and PFOS in I-WWT-3 and I-WWT-4 (Fig. 1). These results indicate differing emission patterns of various industrial activities, consistent with those observed

in the wastewaters from several kinds of industrial point sources [19,29]. For example, PFOS and its various salts are manufactured for direct use as a mist suppressant in acids baths used in metal plating, photoresists, and anti-reflective coatings in semiconductor usage, photomasks in the semiconductor and liquid crystal industries, etching on circuit boards, photolithography, mining and oil well surfactants, and chemical intermediates [2]. Thus, relatively high PFOS at I-WWT-3 and I-WWT-4 ( $11\text{--}810$  ng/L;  $n=6$ ) can be plausible. However, at a plant servicing the semiconductor industry (I-WWT-2), wastewater PFOS was relatively low ( $7.1 \pm 6.5$  ng/L), compared with levels several orders of magnitude higher found in semiconductor industry wastewater in Taiwan [22]. Instead, the predominance of PFBS ( $340 \pm 130$  ng/L) at I-WWT-2 indicates that the shorter chain PFBS might substitute for PFOS substantially, in at least a semiconductor manufacturer served by I-WWT-2. One of the five M-WWTs (M-WWT-1), which primarily treats metal-plating industrial wastewater, was predominantly contaminated with PFOS (Fig. 1).

Generally, total PFCAs (PFCAs, FOUEA) were higher than total PFASs ( $\Sigma$ PFASs, EtFOSAA, MeFOSAA) for most D-WWTs, I-WWTs, and M-WWTs. High PFOA levels, >100 ng/L, were detected at D-WWT-5, M-WWT-3, and M-WWT-5, with PFOA being most abundant. In particular, influents at M-WWT-3 and -5 contained very high PFOA levels (several thousand ng/L). M-WWT-3 treats wastewater from paper-mill and textile-dyeing industries, and M-WWT-5 treats mostly fabric/textile industry wastewater. Despite its predominant treatment of domestic wastewater (95% of the total), D-WWT-5, which neighbors M-WWT-5 in the same city, also treats 21,000 ton of fabric/textile and dyeing industrial wastewater. Interestingly, PFOA concentrations at D-WWT-5 were 10-fold lower than those in M-WWT-5, which treats 210,000 ton of industrial wastewaters, but 20-fold higher than those at the four other D-WWTs (Fig. 1). This indicates that fabric/textile industrial wastewater can be a major discharge source of PFOA. Unlike readings at most WWTs, total PFCAs < total PFASs at I-WWT-3, I-WWT-4, and M-WWT-1 were found. In these three facilities, PFOS was a predominant compound and was frequently detected at >100 ng/L. Notably, these facilities treat pure or mixed industrial wastewater from oil/chemical industries, steel-mill, and/or metal plating/processing industries.

Shorter-chain  $\text{C}_6\text{--}\text{C}_{10}$  PFCAs and  $\text{C}_4$ ,  $\text{C}_6$ , and  $\text{C}_8$  PFASs were mostly detected at >MDL, whereas longer-chain PFCAs and PFDS were relatively rare ( $n=26$  out of 45 for PFUnDA;  $n=10$  for PFDoDA;  $n=4$  for PFTrDA; and  $n=0$  for PFDS at >MDL). EtFOSAA and MeFOSAA were detected at trace levels (1.5–2.7 ng/L) in only two and one samples, respectively. However, FOUEA, an intermediate compound of PFCAs, was detected more frequently (30/45 influents) at <0.5–5.7 (mean = 0.8) ng/L at D-WWTs, <0.5–120 (mean = 20) ng/L at I-WWTs, and <0.5–200 (mean = 33) ng/L at M-WWTs. Noticeably higher PFOA was detected in effluents than in influents at facilities (i.e., I-WWT-1 and -5, and M-WWT-5) where FOUEA was >10 ng/L. On the other hand, a decreasing FOUEA in effluent against influent was observed at 27 of total 30 pairs where FOUEA was detected at >MDL in influent. The presence of FOUEA indicates that PFCAs (particularly, PFOA) can also be produced by the degradation of precursor compounds during the treatment process within WWT facilities [28,31,32].

#### 3.2. Effluent concentrations

Generally, the concentrations of individual PFCs and their composition profiles were consistent between influent and effluent pairings at all facilities (Fig. 1). Similar to those in influents, long-chain PFCAs, PFDS, EtFOSAA, and MeFOSAA were rarely detected, although FOUEA was found more frequently than in influents ( $n=21$ , >MDL). This result implies that residuals of PFCs in

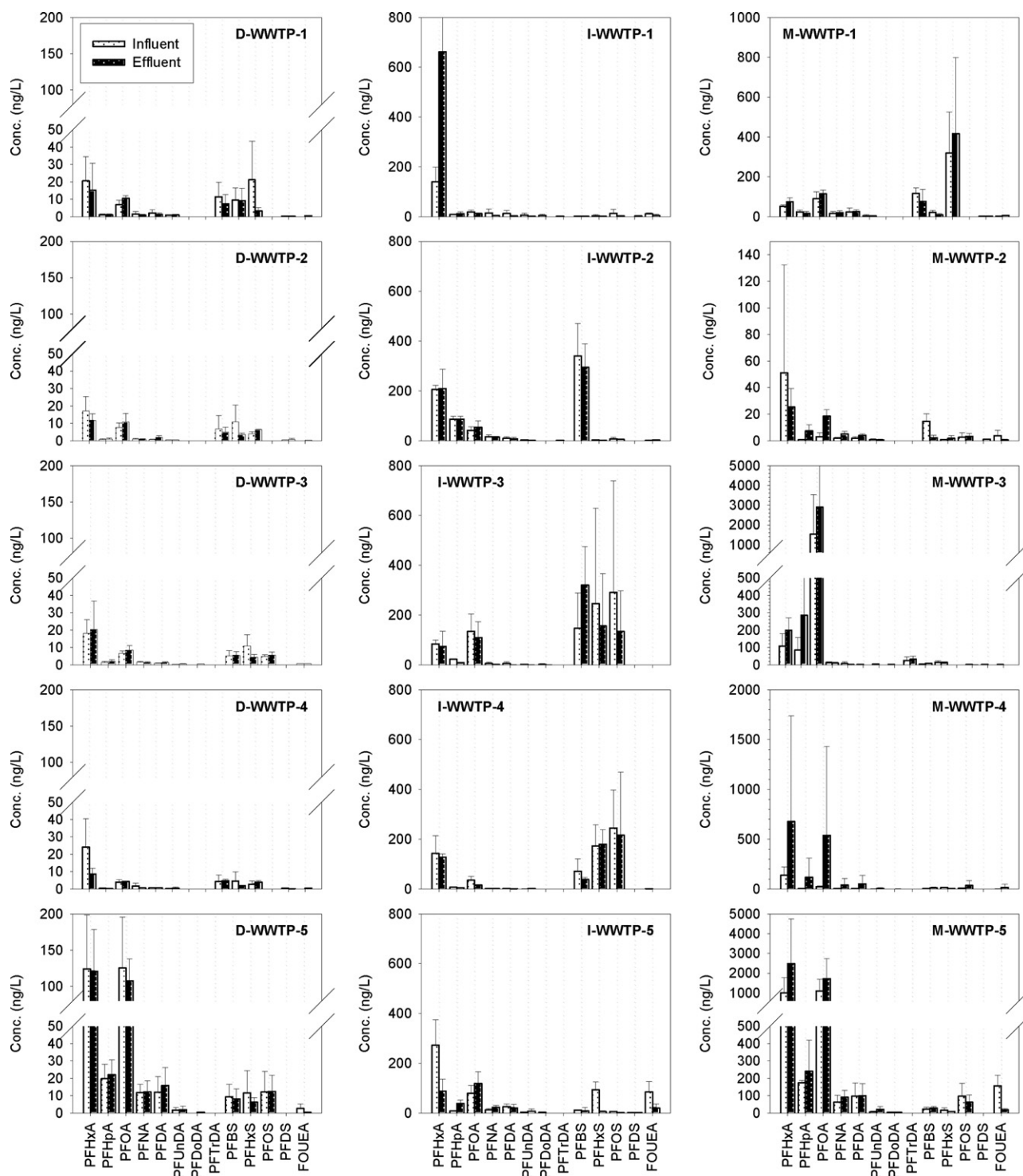


Fig. 1. Concentrations of individual PFCs in influent and effluent from D-WWTPs (a), I-WWTPs (b), and M-WWTPs (c).

effluent are determined primarily by their influent concentrations, not by chemical and/or physical treatment processes. Nevertheless, increased concentrations of individual PFCAs (particularly PFHxA and PFOA) in effluent were observed frequently, especially at M-WWTPs ( $n=12$  for PFHxA,  $n=13$  for PFOA, and  $n=10$  for total PFCAs), compared with D-WWTPs ( $n=2$ , 10, and 6, respectively) and I-WWTPs ( $n=6$ , 7, and 7, respectively) (Fig. 1). In particular, PFOA was enriched by more than 10-fold at M-WWTP-2, -3, and -4. The enrichment of PFCAs observed in effluents of M-WWTPs may be from their additional production via precursor degradation,

which makes PFC discharge at this type of facility more complex [28,31,32]. In contrast, the relative enrichment of PFASs was less clear at all D-WWTPs, I-WWTPs, and M-WWTPs (i.e., enriched or depleted in effluent).

In this study, we observed the use of different PFCs in industrial applications: relatively high PFOS occurred at oil/chemical (I-WWTP-3), steel-mill and metal plating (I-WWTP-4), and metal plating/processing (M-WWTP-1) industries, whereas relatively high PFOA and PFHxA at fabric/textile (M-WWTP-5) and papermill (M-WWTP-3) industries. This is consistent with other studies

showing relatively high PFOS concentrations in industrial effluents from metal-plating facilities (44–8410 ng/L) [19] and high PFCAs levels in textile and/or dyeing industry effluents (64–590 ng/L) [19,33].

The concentrations of PFOA and PFOS in domestic wastewater effluents were on average 2- to 20-fold lower in Korea than in Japan or the United States, but were similar to other countries for industrial wastewaters (Fig. S4). The concentration and composition pattern of PFCs observed from the WWTPs in this study were directly reflected in the ambient running waters of their corresponding watersheds. For example, the highest PFOA concentrations in Korean running waters were observed in Keumho/Nakdong River waters that received wastewater from D-WWTP-5, I-WWTP-5, and M-WWTP-5, and the highest PFOS was found in Shihwa/Ansan stream waters receiving effluent from M-WWTP-1 [34]. This indicates a substantial contribution of these WWTPs to aquatic PFC contamination in their watersheds. Among total 45 effluents, three I-WWTP effluents and five M-WWTP effluents contained PFOS exceeding the suggested avian protective value of 50 ng/L [35]. The concentrations of PFOA and PFOS in domestic wastewater effluents were on average 2- to 20-fold lower in Korea than in Japan or the United States, but were similar to other countries for industrial wastewaters (Fig. S4).

### 3.3. Concentration in sludge (dried cake)

Total PFCs in sludge were highest at M-WWTPs, followed by I-WWTPs and D-WWTPs, consistent with influent and effluent levels (Table S4). PFOA and PFOS in sludge ranged from <0.6 to 1400 (mean = 71; median = 8.6) ng/g d.w. and <0.8 to 1200 (mean = 110; median = 19) ng/g d.w., respectively. The relatively higher amounts of PFOA and PFOS in sludge were found at the same facilities with high levels in influent and effluent; M-WWTP-3 (760 ± 700 ng/g) and M-WWTP-5 (150 ± 100 ng/g) for PFOA and I-WWTP-3 (220 ± 130 ng/g) and I-WWTP-4 (1000 ± 200 ng/g) for PFOS. This indicates that PFC residuals in sludge can be determined primarily by PFC levels in influent.

However, the composition pattern of PFCs in sludge was totally different from those in influent and effluent. Long-chain C<sub>11</sub>–C<sub>13</sub> PFCAs were detected in the majority of sludge samples at >MDL values. Furthermore, they accounted for 44 ± 18% of total PFCAs, compared with 1.5 ± 2.3% in influent and 1.0 ± 1.2% in effluent. Similarly, the frequency of EtFOSAA and MeFOSAA, which were rarely detected at >MDL in influent (*n* = 2) or effluent (*n* = 4), increased greatly in sludge samples (*n* = 37 and 33, respectively). These two compounds accounted for 29 ± 26% of the total PFASs concentration measured in sludge. In two C<sub>8</sub> PFCs, PFOS was more frequently higher than PFOA in sludge samples (31 out of 45 samples) than in influent (*n* = 11) or effluent (*n* = 8). We observed PFOA concentrations greater than PFOS only in the sludge from facilities containing more than 10-fold PFOA than PFOS in their influent (e.g., D-WWTP-5, M-WWTP-3, and M-WWTP-5). *K*<sub>ow</sub> values generally increase with the molecular size of PFC (log *K*<sub>ow</sub> = 3.26 for PFHxA to 5.76 for PFUnDA) [36]. Three- to ten-fold higher *K*<sub>oc</sub> and *K*<sub>ow</sub> values were reported for PFOS relative to PFOA; log *K*<sub>oc</sub> = 2.57 versus 2.06 [37] and log *K*<sub>ow</sub> = 5.25 versus 4.30 [36]. Thus, the relative abundance of longer-chain PFCs and PFOS in sludge could be due to its higher sorption capacities to the sludge. Similarly, the previous studies [38,39] also found that PFOS and longer-chain PFCs relative to shorter-chain PFCs were much enriched in sludge, compared with a little or no detection of longer-chain PFCs in influent and effluent. Another possibility for PFOS in sludge is the prevalent presence of its intermediates. Concentrations of EtFOSAA and MeFOSAA in sludge ranged from <MDL to 34.4 ng/g (mean = 8.0) and from <MDL to 24.7 ng/g (mean = 3.4), respectively, in contrast to being little detected in influents and effluents. Thus, sludge appears

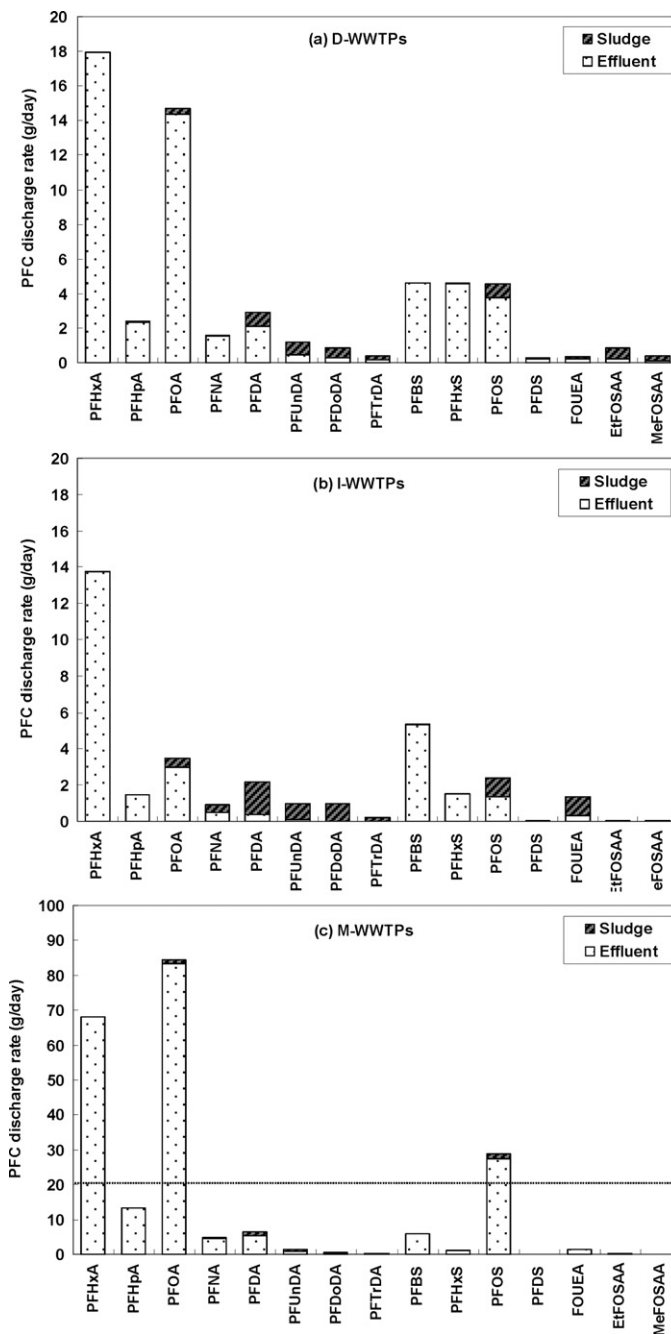


Fig. 2. Average daily discharge rate of individual PFCs via effluent and sludge from D-WWTPs (a), I-WWTPs (b), and M-WWTPs (c).

to be a more important medium for the longer-chain PFCs or PFOS in the mass balance within and in discharge out of WWTPs (see more in next section).

### 3.4. Discharge loads of PFCs from WWTPs

The daily load of PFCs discharged out of a facility (g PFCs/day) was calculated from the PFC concentration multiplied by the daily production (kiloton/day) of wastewater and/or sludge. The inflow rate of influent to D-WWTPs (190–1800 kiloton/day) was 10–1000 times greater than that to I-WWTPs (2–93 kiloton/day), and 10–100 times greater than that to M-WWTPs (20–360 kiloton/day). At all facilities, the effluent discharge rate was 95% of the inflow rate.

**Table 4**  
Annual emission rate (ton/year) of PFCs estimated for Korea and other countries.

Countries	Source	PFHxA	PFHpA	PFOA	PFNA	PFOS	Total PFCs	References
Korea	Domestic-1 <sup>a</sup>	0.29	0.05	0.24	0.03	0.05	0.78	This study
	Domestic-2 <sup>b</sup>	0.22	0.03	0.18	0.02	0.04	0.59	This study
	Industrial <sup>c</sup>	0.39	0.05	0.10	0.02	0.12	1.03	This study
	Sum of wastewater <sup>d</sup>	0.61	0.08	0.28	0.04	0.16	1.63	This study
	River mouth <sup>e</sup>	–	–	0.27	0.06	0.31	–	CNU [43]
Japan	Domestic	–	2.6	5.6	2.6	3.6	–	Murakami et al. [21]
Europe-1	River mouth <sup>e</sup>	2.8	0.86	14.3	0.26	–	–	McLachlan et al. [15]
Europe-2	River <sup>f</sup>	–	–	31.3	–	21.3	–	Pistocchi and Loos et al. [16]
Global	Inventory	–	1 <sup>g</sup>	200 <sup>g</sup>	25 <sup>g</sup>	14–84 <sup>h,i</sup>	–	<sup>g</sup> Prevedouros et al. [4]; <sup>h</sup> Paul et al. [12]

<sup>a</sup> Emission from domestic wastewater (ton/year) = capita-based emission factor ( $\mu\text{g}/\text{capita}/\text{day}$ )  $\times$  Korean total population (49,552,000).

<sup>b</sup> Emission from domestic wastewater (ton/year) = average PFC concentration in domestic wastewater ( $\text{ng}/\text{L}$ )  $\times$  total production of domestic wastewater in Korea (17,113 kiloton in 2008).

<sup>c</sup> Emission from industrial wastewater (ton/year) = average PFC concentration in industrial wastewater ( $\text{ng}/\text{L}$ )  $\times$  total production of industrial wastewater in Korea (4557 kiloton in 2008).

<sup>d</sup> Sum of emissions from domestic and industrial wastewater (ton/year) = domestic-2 + industrial.

<sup>e</sup> Estimated from a production of PFC concentration and water discharge rate measured in river mouths.

<sup>f</sup> Estimated from capita-based emission factor calculated from concentration and population in each watershed.

<sup>g</sup> From Prevedouros et al. [4].

<sup>h</sup> Paul et al. [12].

<sup>i</sup> Estimated from annually normalizing total global historical PFOS emission (450–2700 ton) during 1970–2002.

Daily production of sludge (dried cake) was relatively uniform among the three types of facilities (Table 1).

PFCs concentrations in influent and effluent were lower in D-WWTs than I-WWTs but the difference was less than one order of magnitude, as discussed earlier (Table S4). As a result, PFC discharge loads via influents or effluents were rather higher at D-WWTs than at I-WWTs, due to the vast difference in wastewater production (Fig. 2 and Fig. S5). Total PFCs discharge loads of individual WWTs, derived from the sums of effluent- and sludge-derived discharge loads, were 9.1–180 (mean = 56) g/day at D-WWTs, 0.92–77 (mean = 34) g/day at I-WWTs, and 3.6–1300 (mean = 220) g/day at M-WWTs, respectively. The sludge-derived discharge loads accounted for a relatively small portion of total discharge loads of total PFCs: 12% ( $\pm 6.3\%$ ) at D-WWTs, 27% ( $\pm 24\%$ ) at I-WWTs, and 8.6% ( $\pm 9.6\%$ ) at M-WWTs (Fig. 2). However, the contribution of sludge was greater, as the chain length of compounds was longer, with >50% of C<sub>11</sub>–C<sub>13</sub> PFCAs, EtFOSAA, and MeFOSAA, but <10% of most shorter-chain PFCs contributed by sludge (Fig. 2 and Fig. S6). Of total sludge (dried cake: 2800 kiloton/year in 2008) produced from Korean domestic WWTs, 61% is dumped into the ocean, and 3.7% is buried in landfills [40]. Thus, sludge can be an important medium for transport of these longer-chain PFCs to other environments.

The per capita discharge load (hereafter, emission factor) of PFCs derived from domestic activities was calculated from normalizing effluent-derived daily PFCs loads of each D-WWT by the population served by each D-WWT. We obtained an emission factor ( $\mu\text{g}/\text{day}/\text{capita}$ ) of 1.5–89 (mean = 16; median = 4.2) of PFHxA, 0.8–76 (13; 4.2) of PFOA, 0.5–13 (2.6; 2.1) of PFOS, 2.9–210 (36; 10) of total PFCAs, 1.6–23 (6.9; 5.5) of total PFASs, and 4.9–230 (mean = 44; 18) of total PFCs (Fig. S7). These values were several factors lower than those from domestic WWTs of other countries; reported PFOA and PFOS were 12 and 57 in Switzerland [20], 11 and 42 in the U.S. [27], 30 and 40 in Germany [41], 18 and 24 in Singapore [42], and 25 and 140 in Japan [24,25], respectively. Domestic WWTs-derived emission factors in Korea were also lower than European river water-derived values (19.2  $\mu\text{g}/\text{day}/\text{capita}$  for PFOA; 27.4  $\mu\text{g}/\text{day}/\text{capita}$  for PFOS) [16]. This result implies that PFCs from domestic activities are emitted at a much lower rate per capita in Korea. For example, carpeting is much less popular in Korea.

To produce the wastewater-derived national discharge loads, we multiplied the effluent concentration of D-WWTs and

I-WWTs by the total volume of domestic ( $4557 \times 10^3 \text{ m}^3/\text{year}$ ) and industrial ( $17,113 \times 10^3 \text{ m}^3/\text{year}$ ) wastewaters produced in Korea (Table 1). We also estimated domestic wastewater origin based on the production of a per-capita-based emission factor from D-WWTs and the total national population (49,552,000).

The domestic wastewater estimates of the two methodologies were largely consistent with each other (Table 4). For individual PFCs, the average values of the total WWT-derived national discharge loads (sum of national PFCs discharge loads via domestic and industrial WWTs) were 0.04–0.61 ton/year. Industrial wastewater accounted for 64% of PFHxA and 75% of PFOS national loads, and domestic wastewater consisted of 63% of PFOA and 57% of PFNA, indicating the different uses of individual PFCs in Korea. Notably, most PFOS in Korea are likely used in industrial applications, whereas PFOA seems to be derived mainly from domestic and commercial uses. This result is different from findings in Europe and Japan, where the occurrence of PFOS, rather than PFOA, was more correlated with domestic and commercial activities related to ubiquitous sources (or population size in a watershed) [16,21]. Carboxylic-based PFCs are manufactured in Europe and Japan, where 40% and 10% of the total historical global emission of APFO are estimated to occur in Europe and Japan, respectively, particularly from industrial manufacturing and/or use [11,21]. Korea has not produced carboxylic-based PFCs. However, the further study to determine total riverine aqueous loads is necessary to be carried out with WWT-based discharge study to confirm the relative contribution of point source (such as industrial activities).

In a previous study, national PFCs emissions were calculated from the PFC concentrations measured in each river mouth of the five main watersheds in Korea [43]. The total WWTs-derived national discharge loads were fairly consistent with previous river-mouth-derived estimates (Table 4). Thus, the majority of PFCs occurring in Korean ambient waters mostly originate from point sources (mainly, WWTs). In comparison to estimates of national PFC emissions of other countries, Korean emissions were 10-fold lower than those in Japan and 100-fold lower than those of Europe (Table 4).

### 3.5. Implications and uncertainties

The annual emissions of PFOA and PFOS shown in Table 4 were again normalized by each territory area. The area-normalized annual emissions ( $\text{g}/\text{year}/\text{km}^2$ ) of PFOA and PFOS in Korea were



much lower than those in Japan and Europe (2.8 for PFOA and 2.6 for PFOS in Korea, 14.8 for PFOA and 9.5 for PFOS in Japan, and 6.4 for PFOA and 4.3 for PFOS in Europe). These per-capita and area-normalized values reflect the strength of exposure in a given territory. The recent compilation of Korean serum PFOA and PFOS ( $n = 1379$ ) showed a median concentration of  $\sim 1.5$  ng/mL of PFOA and  $\sim 5.0$  ng/mL of PFOS [44], which are also several factors lower than the 4.4 and 11.7 ng/mL, respectively, in Japan [45] and 4.13 and 13.2 ng/mL, respectively, in the United States. [46]. The greatly lower per-capita- and area-normalized national discharge loads values in Korea are consistent with the lower levels of human exposure reported.

It is unclear why relatively higher PFC concentrations were detected in facilities treating mixtures of domestic and industrial wastewater, because we expected PFCs in mixed wastewaters to be diluted relative to those in pure industrial wastewater. One possible explanation could be that the discharge of PFCs-application sources such as metal plating, textile/fabric, and paper-mill industries is concentrated near M-WWTPs. Of total production of industrial wastewater in Korea, 36.5% is treated together with domestic wastewaters at M-WWTPs, and only 11.6% to I-WWTPs [47]. If relatively high PFCs residual is present in uninvestigated M-WWTPs as well, the estimates of PFCs national discharge loads could be greater than those presented here. On the other hand, the wastewaters of industries with PFCs application uses were included when selecting I-WWTPs. This can cause overestimation of PFCs discharge loads via industrial activities. Thus, further study involving various types of industrial wastewaters will reduce the uncertainty of estimation with sources.

In 2008, a total dried cake of 2817 kiloton was produced in Korea, of which 61% was dumped into the ocean. The ocean dumping of sludge will be banned in Korea, starting in 2012, by an international convention on the prevention of marine pollution by dumping of wastes and other matter. Thus, recycling is expected to be greater than the 19% recorded in 2008. Land application of sludge, such as use as a soil conditioner, can contaminate drinking water via leaching from contaminated soil. Thus, the treatment and disposal of PFC-containing sludge will be a challenging problem in the future.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.11.036.

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