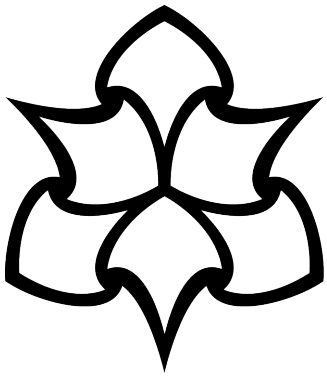

Environmental and dietary exposure of perfluorooctanoic acid and perfluorooctanesulfonic acid in the Nakdong-river, Korea

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Abstract

This study performed the first environmental and dietary exposure assessment to explore plant uptake of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) from agricultural soil and irrigation water in the Nakdong River delta, South Korea. Annual average concentrations of total PFOA and PFOS ranged from 0.026 to 0.112 μg L^{-1} (irrigation water), and from 0.818 to 1.364 μg kg^{-1} (soil), respectively. PFOA and PFOS hotspots were identified downstream of the Nakdong River, and were influenced by seasonal climatic variations. The observed average biennial concentration of the sum of PFOA and PFOS decreased in irrigation water, from 0.112 μg L^{-1} in 2013 to 0.026 μg L^{-1} in 2015, suggests that the 2013 Persistent Organic Pollutants Control Act may have helped to reduce levels of PFAS at this location. This study calculated some of the highest plant uptake factors reported to date, with values ranging from 0.962 in green onions to < 0.004 in plums. Leafy vegetables and rice are important components of the Korean diet; these groups had the largest contribution to the estimated dietary intake of PFOA and PFOS, which was calculated at 0.449 and 0.140 ng kg_{bw}^{-1} day^{-1}, respectively. This corresponded to 66.4% for PFOA and 7.9% for PFOS of the EFSA reference dose (RfD). The dietary intake of PFOA and PFOS from crops alone did not exceed the RfD. However, when the estimated daily intake (EDI) from other sources such as tap water, meat, fish, dairy and beverages were included in the exposure risk assessment, both of the EDIs to PFOA and PFOS exceeded the RfDs, indicating there may be a risk to human health. This study concludes that consumption of crops might, therefore, be a significant and underappreciated pathway for human exposure to PFAS.

Key words: PFAS, PFOA, PFOS, estimated daily intakes, agricultural environment, crop uptake

Introduction

Per- and polyfluoroalkyl substances (PFAS) have been widely used in the fabric, paper, metal, surfactant, and electronic industries since the 1950s (Wang et al. 2014; Filipovic et al. 2015, Seong et al. 2019). Two of the most widely used PFAS include the long-chain perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). These have high detection frequencies, bioaccumulate in crops, the environment, and humans, and are highly toxic. Both of these substances have been classified as persistent organic pollutants (POPs) by the Stockholm Convention (Kim et al. 2015a; Xiang et al. 2020).

A wide number of reports have detected PFOA and PFOS in soil, water, biota, and food all over the globe. These studies identified contamination from historic and recent PFAS usage, as well as identifying direct and/or indirect human exposure in Europe (Kowalczyk et al. 2012; Toft et al. 2012; Flores et al. 2013; Filipovic et al. 2015; Lindim et al. 2016), the Americas (Olsen et al. 2012; Geiger et al. 2014; Rankin et al. 2016; Harris et al. 2017; Olsen et al. 2017), Australia (Baduel et al. 2014; Toms et al. 2014; Gomis et al. 2017; Gallen et al. 2018; O'Connor et al. 2018), Antarctica (Bengtson et al. 2010; Cai et al. 2012; Llorca et al. 2012), Africa (Hanssen et al. 2010; Essumang et al. 2017; Verhaert et al. 2017; Groffen et al. 2018), and Asia (Fujii et al. 2012; Lee et al. 2013b; Choi et al. 2017; Kim and Kim 2018; Kim et al. 2019; Li et al. 2020).

The major exposure pathway for humans is through the ingestion of PFOA and PFOS accumulated in food and water (Vestergren and Cousins 2009; Heo et al. 2014; Ghisi et al. 2019; Luo et al. 2019). The respective guideline values of PFOA and PFOS for reference doses (RfD) were updated by the European Food Safety Authority (EFSA) and were changed from 1500 and 150 ng kg^{-1} day^{-1} in 2008 to 0.8 and 1.8 ng kg^{-1} day^{-1} in 2018, respectively (Xiang et al. 2020). The International Agency for Research on Cancer classified PFOA and PFOS as "possibly carcinogenic to human" (IARC 2020). The major sources of PFAS in human diets are from dairy, fish, and meat products. Little is known about exposure from plant based products, although exposure from these sources is believed to

represent a minor source due to their relatively low bioaccumulation factors (< 0.01 – 4.7) (Lechner and Knapp 2011; Blaine et al. 2013; Garcia-Valcarcel et al. 2014; Choi et al. 2018; Ghisi et al. 2019). Despite the relatively low bioaccumulation factors reported to date, it is still crucial to monitor the residue of PFOA and PFOS in agricultural environments and products, to improve exposure assessment and establish environmental guidelines.

South Korea, a developed and industrialized country, previously used PFAS in the textile and electronic industries. In 2012, South Korea listed PFOA and PFOS as POPs, in recognition of the hazard that these pollutants pose to human and the environment. The POPs Control Act was enforced for PFAS in 2013. The Act initially focused on the production and use of the C_8-PFAS, as stipulated in Article 13 (1) – (4) (Jeong and Ma 2016). Nationwide, baseline environmental surveys (2011–2013) on PFOA and PFOS concentrations were conducted in agricultural and coastal environments. Several studies have identified elevated concentrations of PFAS above EFSA's annual average environmental quality standard for surface water (0.65 ng L^{-1} PFOS) and the United States Environmental Protection Agency's (USEPA) health advisory value for drinking water (70 ng L^{-1} for the sum of PFOA and PFOS; Gobelius et al. 2018). The source of these exceedances was stipulated to be from factors such as the potential use of biosolids from wastewater treatment plants, irrigation water, and illegal or accidental discharges. Maximum concentrations of ∑(PFOS & PFOA) downstream of the Nakdong River were recorded as 0.183 μg L^{-1} and 1.12 μg kg^{-1} for water and soil respectively (Lam et al. 2016; Choi et al. 2017; Kim and Kim 2018).

Six years after the first baseline survey, most studies have focused on correlations between potential dietary sources of PFAS and impacts on human health as well as dietary exposure and impacts on sex and age (Ji et al. 2012a, 2012b; Lee et al. 2017). However, the scarcity of PFOA and PFOS data within the South Korean agricultural sector coupled with the limited number of studies that have reported dietary exposure assessments in some agricultural products have necessitated a need for further studies. To address this knowledge gap, this manuscript provides an evaluation of the following:

(1) seasonal variation in PFOS and PFOA concentrations (2013–2017) in agricultural soil and irrigation water that might impact plant uptake, and (2) an assessment of dietary exposure to PFOS/PFOA from agricultural crops based on the revised 2018 EFSA RfDs.

This assessment uses the Nakdong River as a test site as it is one of the largest rivers in South Korea and passes through a wide range of land uses. Previous studies on sediments and surface water from the Nakdong River basin (influents, effluents, tributaries, and estuaries) identified mean sediment concentrations of PFOA (< 0.05 - 0.929 ng g^{-1}) and PFOS (< 0.01 – 2.682 ng g^{-1}), and mean surface water concentrations of PFOA (0.002–1.450 μg L^{-1}) and PFOS (0.001–0.626 μg L^{-1}) (Cho et al. 2010; Kim et al. 2012; Hong et al. 2013; Lam et al. 2014). The relatively high PFOA and PFOS concentrations in surface water of the Nakdong River, which may have resulted from illegal and/or accidental discharges from industrial activities, have raised concerns about the possibility of uptake by crops cultivated in the environment of the Nakdong delta. These studies were used data collected prior to the enforcement of the POPs Control Act, 2013; thus, an updated assessment is needed to establish risks. This study is the first to determine human dietary exposure to PFOA and PFOS from locally cultivated crops as well as identify seasonal changes in PFOA and PFOS concentrations in soil and surface water of the Nakdong delta.

Materials and method

Study site and sampling

The Nakdong-river, one of South Korea's largest and longest (length = 506.17 km, total watershed = 23,384.21 km^2), passes through Daegu and Busan (two major industrialized cities) with eight main tributaries. The total annual precipitation of the basin is approximately 1,200 mm, 60 % of which falls from June to September, the monsoon climate and typhoons in the Korean Peninsula substantially affect the precipitation pattern (Kim et al. 2015b). As a major drinking source to over ten million people, past emissions and chemical spillages in the Nakdong River present potential risks upon

consumption (Lee et al. 2013a). The choice of sampling months was influenced by climatic conditions that characterize periods before the agricultural season (March - May: spring, cool milder temperatures interspersed with mild rainfall), start of crop growth (June - August: summer, abundant rain), period prior to harvesting (September - November: autumn, hot climate with mild rain), and periods of no agricultural activity (December - February: cold air Asian monsoon in winter, snowy, little to no rain). The choice of sampling sites was chosen based on a previous study performed by Choi et al. (2017); six sampling sites (A-F) were selected (Fig. 1). Detailed information on the site locations is shown in Table S1. Selection of sites A - D were along the longest waterway in the area, and sites E and F were located near site A, but isolated from sites A - D.

The water and soil were sampled with the reported method by Choi et al. (2017). 2 L of irrigation water was sampled in 2 L polypropylene containers on a three-month interval in 2013 and 2015. Grab surface water samples were collected approximately 0.1 m under the surface with pre-cleaned polypropylene container which had been rinsed with methanol. Soil was sampled 50 m from the irrigation water sampling site once a year in March from 2013 to 2017. 3 kg of surface soil were collected to a depth of 0.15 m, and placed in polypropylene bags. Soil samples was collected in triplicates in each farmland, and a composite representative for each site was obtained by mixing equal weights. Sampled soil was dried in a fume hood for five days at the room temperature and stored at -20°C. The soil for calculation of plant uptake factor (PUF) was collected near the root of crops, after crop sampling. As the Korean diet is predominantly vegetarian and includes rice on a daily basis, the choice of vegetables selected in this study was aligned with those grown in the Nakdong region. These included: Chinese chive, green onion, lettuce, onion, parsley, spinach, tomato, and white cabbage. Other food crops sampled included apricot, plum, raspberry, and rice (grain). The each crop samples were collected 3 kg with three replications on the farm. Each bulk crop sample was finely chopped and ground with dry ice and stored at -20°C.

145 **Chemicals and reagents**

146 Two natives, PFOA and PFOS and isotope labeled standard solutions: $^{13}C_4$- and $^{13}C_8$-PFOA and PFOS
147 were purchased from Wellington Laboratories Inc. (ON, Canada). ENVI-Carb^{TM} (Supelco, PA, USA),
148 hydrophilic lipophilic balance (HLB) solid phase extraction (SPE) cartridge (0.5 g, 6 mL) were
149 purchased from Waters Co. Inc. (Ireland) and nylon membrane filter (0.23 μm) were from Silicycle
150 Inc. (Quebec, Canada) Distilled water (DW) was freshly prepared, and all solvents (acetic acid, acetone,
151 acetonitrile and methanol) used were HPLC grade from Merck KGaA (Darmstadt, Germany).
152

153 **Analytical sample preparation of PFOA and PFOS in soil, water and crops**

154 PFOA and PFOS were analyzed in soil, water and vegetables using the analytical method reported by
155 Choi et al. (2018). In brief, soil was dried at room temperature and passed through a 2 mm sieve. One
156 gram of soil was extracted with 10 mL of aqueous acetic acid (1.0%) with mechanical shaking for an
157 hour before and after sonication for 20 min. The extracts were centrifuged, and supernatants were
158 collected in a new PP tube. 10 mL of a mixture solvent with methanol and 1.0% aqueous acetic acid
159 (9/1, *v/v*) was added to the original soil, and the extraction was repeated three times. The combined
160 extract was concentrated to 15 mL under N_2 gas on Hurricane-Eagle (Chungmin-Tech Co. Ltd., Seoul,
161 Korea) and diluted with DW to a 50 mL. The diluted extract was vortexed and loaded to an HLB SPE
162 cartridge preconditioned with 10 mL methanol, followed by 10 mL DW. Extract was loaded at a rate
163 of 1.3-1.6 mL min^{-1}, and washed with 5 mL of 30 % methanol in DW. The cartridge was eluted with
164 10 mL methanol, and eluent concentrated and re-dissolved with methanol to a final volume of 1.0 mL.
165 The extract was cleaned up with 20 mg of powdered ENVI-Carb^{TM}, then filtered with a nylon syringe
166 filter. Ten microliters of 0.01 mg L^{-1} $^{13}C_8$-PFOS and $^{13}C_8$-PFOA were added to the clean-up extracts
167 prior to analyses as internal standards. Water samples, collected from Nakdong River, were allowed
168 to settle for two hours prior to extraction. 500 mL of water sample was passed through an HLB
169 cartridge, and the extraction was processed using the same method described above. The method

developed by Choi et al. (2018), was used to extract PFOS and PFOA from vegetables. Briefly, the crops were washed gently under running water to remove soil and the samples were ground with dry ice. 10.0 g of sample was extracted with 90 % (v/v) methanol in DW (10 mL x 3) by mechanical shaking for an hour and sonication for 20 min. The extracts were centrifuged and supernatants were collected in a new PP tube. Additionally the crop sample was re-extracted with 75 % (v/v) tetrahydrofuran in DW. The combined extracts were then concentrated to 10 mL under nitrogen and re-diluted with DW to a volume of 50 mL. These samples were then extracted with HLB SPE cartridges and the subsequent process was followed the method described above.

Instrumental analyses

Samples were analyzed using high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). This was performed on an Agilent 1200LC liquid chromatograph coupled to a 4000 QTrap triple-quadrupole mass spectrometer (AB Sciex Ltd., MA, USA) operated in negative electrospray ionization mode with multiple reaction monitoring (MRM). A FluoroSep-RP Octyl column (5 μm, 150 mm x 2.1 mm; ES Industries, NJ, USA) for analyte separation and a Restek C_{18} column (5 μm, 50 mm x 2.1 mm, Restek, Bellefonte, PA, USA) for the prevention of PFAS contamination from solvent impurity were used for the analysis. The optimized instrumental parameters and HPLC mobile phase gradient are described in detail by Choi et al. (2017).

Quality control

Spike recovery tests were performed using a $^{13}C_4$-PFOS and $^{13}C_4$-PFOA solution resulting in a final sample concentration of 0.05 μg L^{-1} for water, 0.50 μg kg^{-1} for soil and crop. Samples were tested in triplicate, and returned acceptable recoveries (69.4-76.3%) for soil, water and vegetables. The method limit of quantification (MLOQ) was determined to be 0.00002 μg L^{-1} for water, 0.010 μg kg^{-1} for soil and 0.001 μg kg^{-1} for crops. Linearity was recorded throughout the analyses by running the calibration

195 series (0.010 to 1.00 μg L^{-1}), and the inter-day precisions were below 10 %. All quality control results
196 are presented in Table S2 in the supporting information.
197
198 **Calculation on PUF and estimated daily intake (EDI)**
199 Crop and soil samples, used in the calculation of PUF and EDI of PFOA and PFOS, were collected in
200 2017. PUF, expressed as the ratio between concentrations of a chemical analyte determined in plant
201 tissue and soil (Liu et al. 2019), was calculated by dividing the concentration in the crop by the
202 concentration recorded in the soil (Equation 1):
203
204 $$PUF = \frac{Concentration\ in\ crop\ (\mu g\ kg^{-1})}{Concentration\ in\ soil\ (\mu g\ kg^{-1})}$$
205 ***Equation 1: Calculation for plant uptake factor (PUF)***
206
207 EDI was calculated using the concentration recorded in each crop, and an estimate of the daily intake
208 of crops for Korean adults, assuming an average body weight of 60 kg (Equation 2). Food intake data
209 were obtained from the 2017 National Food & Nutrition Statistics provided by the Korean Health
210 Industry Development Institute (KHIDI, 2017).
211
212 $$EDI\ (ng\ kg_{bw}^{-1} day^{-1}) = \frac{[(Daily\ intake\ of\ crop\ per\ person\ (g\ day^{-1})\ x\ (Residual\ concentration\ (ng\ g^{-1})]}{Average\ body\ weight\ (60\ kg)}$$
213 ***Equation 2: Calculation for estimated daily intake (EDI)***
214
215 **Results and discussion**
216 **PFOA and PFOS residues in irrigation water in Nakdong River**
217 PFOA and PFOS were detected in water samples from all study sites. The average PFOA and PFOS
218 concentrations in 48 irrigation waters sampled throughout the study period were 0.042 ± 0.042 μg L^{-1}

and 0.027 ± 0.068 μg L^{-1}, respectively (Table 1). The average of the sum of PFOA and PFOS in 2013 and 2015 were highest in winter at 0.101 μg L^{-1}, followed by 0.070 μg L^{-1} in summer and 0.060 μg L^{-1} in autumn, with the lowest concentrations of 0.047 μg L^{-1} recorded in spring (Table S4 in the supporting information). The biennial (2013–2015) average concentrations of the sum of PFOA and PFOS in the southern sites (downstream sites A, B, E, and F, 0.080 μg L^{-1}) were twice as high as for the northern sites (upstream sites C and D, 0.048 μg L^{-1}). Concentrations peaked during winter for the southern sites, and at the beginning of summer for the northern sites in 2013 (Fig. 2). PFOA and PFOS residues varied seasonally in the southern site in 2013, with the greatest PFOA and PFOS concentrations in winter (0.129 and 0.107 μg L^{-1}, respectively), followed by PFOS concentrations in autumn (0.094 μg L^{-1}), PFOA and PFOS concentrations in summer (0.089 and 0.033 μg L^{-1}, respectively), and PFOA (0.029 μg L^{-1}) and PFOS (0.023 μg L^{-1}) in spring. The average PFOA and PFOS concentrations in the southern sites were 0.067 and 0.064 μg L^{-1} in 2013, respectively; this decreased to 0.019 and 0.009 μg L^{-1}, respectively, in 2015. The average PFOA and PFOS concentrations in the northern sites in 2013 were 0.059 and 0.016 μg L^{-1}, respectively; this decreased to 0.020 and 0.003 μg L^{-1}, respectively, in 2015.

Industrial activities involving paint, metal, and recycling factories were located near sites A–C during sampling, whereas other sites were at least a 100 m away from industrial activities. Thus, contamination in site A could be attributed to localized disposal of pollutants into irrigation waterways of the Nakdong River. The average PFOA concentrations at all sites (A–F) decreased by a factor of 3 from 2013 (0.064 μg L^{-1}) to 2015 (0.019 μg L^{-1}). Similarly, the PFOS concentrations decreased by a factor of 7 from 2013 (0.048 μg L^{-1}) to 2015 (0.007 μg L^{-1}). Based on the differences in the observed residue patterns in Fig. 2 for 2013 and 2015, the decrease in concentrations could be attributed to a positive impact of the enforcement of the POPs Control Act in 2013. Additional six samples from the sites were analyzed from June 2017; the results indicated that PFOA concentrations continued to decline (0.017 μg L^{-1}), and PFOS concentrations remained relatively stable (0.005 μg L^{-1})

High concentrations of PFOA and PFOS corresponded with elevated levels of rainfall documented in Busan from 2013 to 2015. Sites (C–F) showed a decrease in PFOS and PFOA residues in September, but this trend was not observed in sites A and B which were near heavily industrialized zones. This could be attributed to the heavy rainfall observed during summer (206.7–316.9 mm/month). With heavy rains, PFOS and PFOA may be washed away, removing some of the local contamination sources. In 2013, PFOA residues increased in all sites studied in June, which could be attributed to contamination from the main river, although local contamination sources may have partially contributed to this increase.

From previous studies, PFOA and PFOS concentrations detected in the Nakdong River (0.0065–0.101 μg L^{-1}) are relatively similar to those reported in this study, considering differences in study sites, extent of contamination, and sampling season (Cho et al. 2010; Hong et al. 2013; Lam et al. 2014). The annual mean concentrations of PFOA (0.064 and 0.019 μg L^{-1} for 2013 and 2015, respectively) and PFOS (0.048 and 0.007 μg L^{-1} for 2013 and 2015, respectively) in surface irrigation water of the Nakdong River exceeded the advisory guideline by Office of Environmental Health Hazard Assessment (OEHHA) in California (0.0051 μg L^{-1} for PFOA and 0.0065 μg L^{-1} for PFOS) (OEHHA, 2019), indicating that PFOA and PFOS in the Nakdong region may have an adverse effect on human health.

PFOA and PFOS residues in agricultural soil around Nakdong River

Table 2 shows the average PFOS and PFOA residue concentrations in soil samples collected from agricultural sites A–F around the Nakdong delta. A 100% detection frequency was observed in all soil samples over the five-year study period (2013–2017), with the average total PFAS concentrations ranging between 0.443 and 2.717 μg kg^{-1}. The detected PFOA and PFOS residues were 0.141–0.841 and 0.059–2.785 μg kg^{-1} in the soil, respectively, with respective averages of 0.377 and 0.763 μg kg^{-1} for the entire period. The average PFOA and PFOS concentrations in the soil samples were consistent

with the relative concentrations in water samples obtained from the same locations. The average residues of PFOA and PFOS were ranged on 0.336-0.485 μg kg^{-1} and 0.496-1.024 μg kg^{-1} in the southern site (A, B, E, and F) and 0.273-0.411 μg kg^{-1} and 0.219-1.016 μg kg^{-1} in the northern site (C and D), respectively (Table S5 in the supporting information). Higher average concentrations of PFOA (0.406 μg kg^{-1}) and PFOS (0.790 μg kg^{-1}) in the entire period were determined in the southern soil, in comparison to the northern locations where average concentrations were 0.322 and 0.710 μg kg^{-1} for PFOA and PFOS, respectively. Interestingly the PFOA residue in the site A and B appeared to increase with time, while the residues in other sites remained relatively constant. This differed from the trends for PFOS where residues in the soil of all sites tended to decrease over time (Figure 3). These opposing trends might be a result of the difference in the restriction guidelines for the use of PFOA and PFOS by the POPs Act. The restriction for PFOS was listed in 2013 but PFOA was only listed in 2019. Average soil concentrations in all sites were below the proposed Canadian Federal quality guideline for agricultural soil (10 μg kg^{-1}; Xiang et al. 2020).

Plant uptake of PFOA and PFOS

In addition to soil, irrigation water from the Nakdong River is an important source of PFOA and PFOS that may influence plant uptake of PFAS. Six crop types (white cabbage, rice, green onions, parsley, lettuce, and plums) and the cultivated soils were collected in 2017 throughout the delta area. Concentrations of PFOA and PFOS recorded in soil, and the crops are presented in Table 3, along with the calculated plant uptake factor (PUF). The highest levels of PFOA were identified in green onions and white cabbage at 0.809 and 0.476 μg kg^{-1}, respectively. PFOS residues were the highest in white cabbage (0.115 μg kg^{-1}) and lettuce (0.087 μg kg^{-1}). Both PFOA and PFOS concentrations were lowest in plums and parsley.

Leafy vegetables had higher PUFs for PFOA than other crops (green onions, 0.962; white cabbage, 0.592; rice (whole), 0.435; plums, 0.355; lettuce, 0.252; parsley, 0.154). Lettuce had the highest PFOS

PUF (0.286), followed by white cabbage (0.086), parsley (0.067), rice (whole, 0.057), green onions (0.017), and plums (<0.004). The uptake of PFOA from soil to crop was greater than that of PFOS, however the extent of this difference varied for each crop.

Dietary exposure assessment of PFOS and PFOA from Nakdong region

A human health risk assessment was performed to calculate the EDIs of PFOA and PFOS from the edible crops analyzed in this study. The results showed that the intake of rice, leafy vegetables, and fruits grown in the Nakdong delta contributed the most to PFAS exposure (Table 4). Rice was identified as the main source of both PFOA (0.247 ng kg_{bw}^{-1} day^{-1}) and PFOS (0.086 ng kg_{bw}^{-1} day^{-1}). Notable contributions of PFOS were also recorded in white cabbage (0.018 ng kg_{bw}^{-1} day^{-1}), green onions (0.011 ng kg_{bw}^{-1} day^{-1}), and Chinese chives (0.010 ng kg_{bw}^{-1} day^{-1}). Notable contributions for PFOA were also recorded in white cabbage (0.076 ng kg_{bw}^{-1} day^{-1}), green onions (0.059 ng kg_{bw}^{-1} day^{-1}), onions (0.057 ng kg_{bw}^{-1} day^{-1}), lettuce (0.039 ng kg_{bw}^{-1} day^{-1}), tomatoes (0.023 ng kg_{bw}^{-1} day^{-1}), and spinach (0.019 ng kg_{bw}^{-1} day^{-1}).

In comparison to the revised EFSA RfD guideline values (0.8 ng kg_{bw}^{-1} day^{-1} for PFOA and 1.8 ng kg_{bw}^{-1} day^{-1} for PFOS), the EDI contributions of the revised RfDs from crops in this study were 66.4% for PFOA and 7.9% for PFOS, of which rice contributed up to 30.9% and 4.8% of the RfDs, respectively. This indicates that crops might be a more important exposure pathway than has previously been considered, although both of the EDIs of PFOA and PFOS from crops alone did not exceed the RfD. However, when combined with other sources from recent reports (1.052 ng kg_{bw}^{-1} day^{-1} for PFOA, 1.190 ng kg_{bw}^{-1} day^{-1} for PFOS), such as tap water, beverages, dairy, fish and shellfish, and meat and its products (Heo et al. 2014; Park et al. 2018), the Korean EDIs for PFOA and PFOS exceeded the RfDs. The detailed EDIs values are presented in Table S6 in the supporting information.

The major source of PFAS in most human diets is assumed to be from meat and fish based products, as low bioaccumulation factors have been reported for PFAS in plants (Lechner and Knapp 2011;

Blaine et al. 2013; Garcia-Valcarcel et al. 2014; Choi et al. 2018; Ghisi et al. 2019). This present study shows this may not always be the case, as approximately 70% of the RfD of PFOA arose from consumption of crops. From reviewing available literature, it would appear that this issue is not limited to this study site. South Korean EDI values for PFOA from crops and foods were comparable to reported values from China, Japan, Germany, and the United States (0.72 – 10.5 ng kg_{bw}^{-1} day^{-1}), but higher than those from Norway and Sweden (0.35 – 0.69 ng kg_{bw}^{-1} day^{-1}) (Liu et al. 2017).

Conclusions and recommendations

This study explored the influence of PFOA- and PFOS-contaminated water and soil on plant uptake and its impact on dietary exposure in and around one of the largest rivers in South Korea, the Nakdong River, over a five-year period (2013–2017). The annual average concentration of the sum of PFOA and PFOS concentrations in the irrigation water exceeded the Californian OEHHA's advisory guidelines for inland surface water. Although the accumulation rates for crops would likely be lower than those of animal products, this study identified that plant uptake of PFOA and PFOS can be a significant pathway for human exposure. Plant uptake factors greatly vaired with different crop types ranging from < 0.4 % (plum) to 96 % (green onion) and with leafy vegetables appearing to accumulate the highest concentrations of PFOA and PFOS.

The calculated EDI contributions of the proposed EFSA RfDs from crops in this study were 66.4% for PFOA and 7.9% for PFOS, of which rice contributed up to 30.9 and 4.8% of the total PFOA and PFOS exposure, respectively. Although the PFOA and PFOS residues in soil did not exceed the advisory Canadian guidelines for agriculture, the PFOA EDI values of the local crops almost reached the proposed RfD. When combined with estimated inputs from other sources, the EDIs of PFOA and PFOS for people consuming vegetables grown in the study site would likely exceed both of the RfDs.

It is not currently clear whether the PFOS and PFOA recorded in these samples were predominantly due to plant uptake from soil and pore water, or from PFAS introduced to the surface of the plants by

irrigation water. Further studies are needed to establish this so that effective mitigation measures can be introduced. The results of our research point towards the positive impact legislation can have in reducing environmental concentrations of PFOA and PFOS, however, not all PFAS are regulated to the same extent. Therefore, the decrease in concentrations in PFOA and PFOS identified here may be offset by increased use of emerging PFAS, such as the C8 replacements hexafluoropropylene oxide dimer (HFPO-DA), hexafluoropropylene trimer acids (HFPO-TA), and 6:2 chlorinated polyfluorinated ether sulfonic acid (6:2 Cl-PFESA). Future PFAS monitoring campaigns should include an assessment of emerging perfluorochemical contaminants in local foods and in agricultural environments to help establish more robust PFAS management guidelines.

Conflicts of Interest

The authors declare no conflicts of interest

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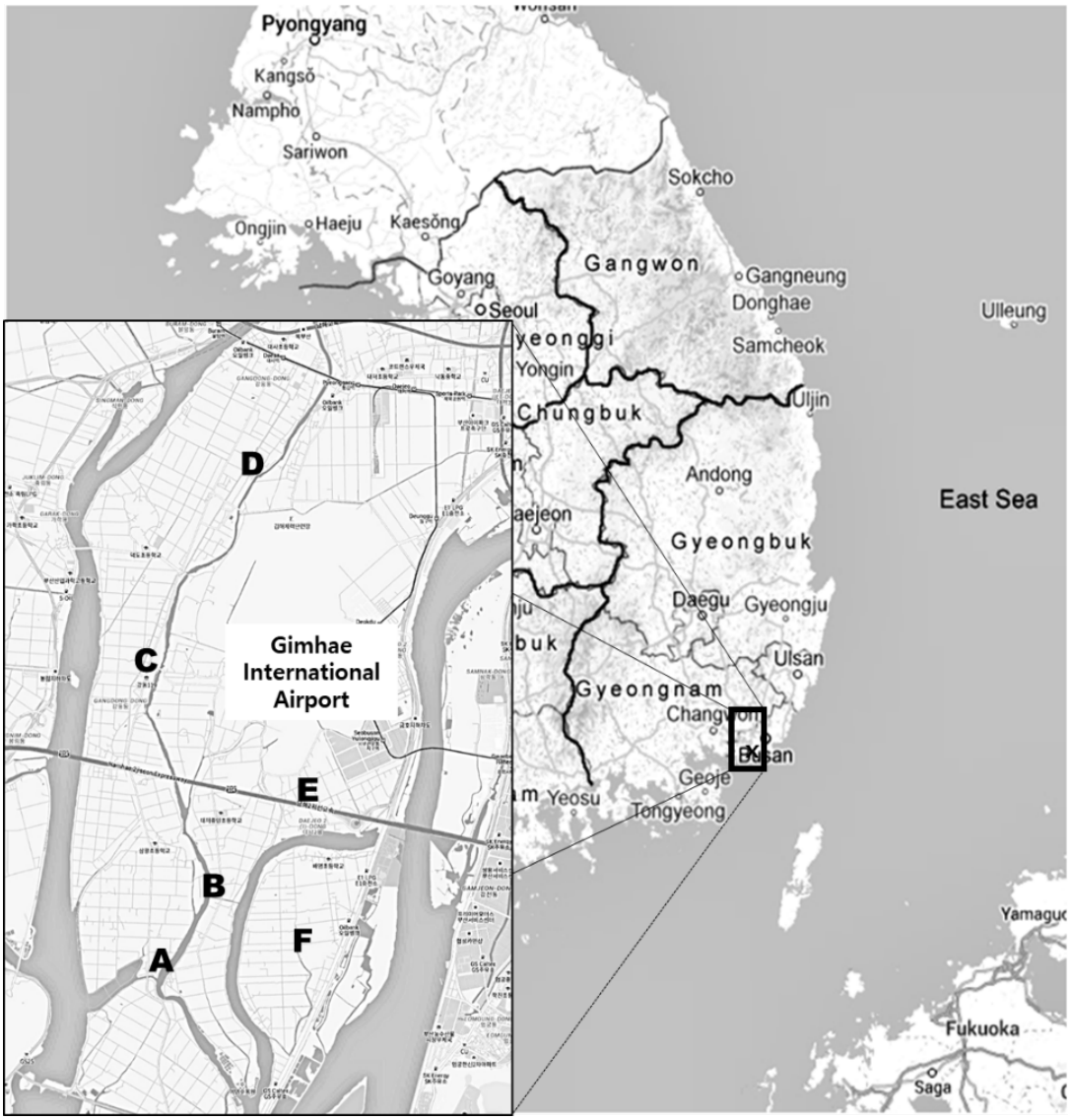

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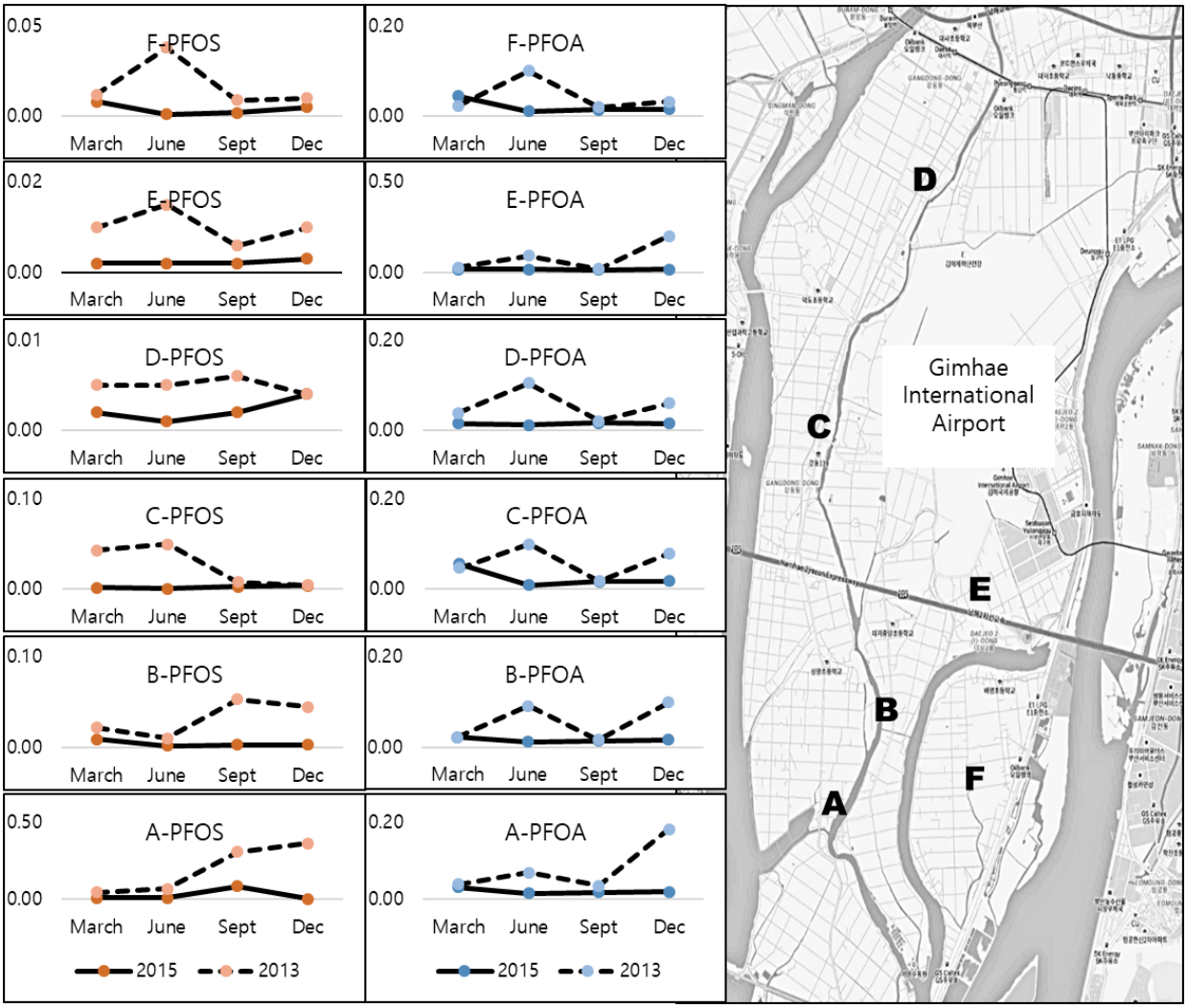
542 **Fig. 1** A map showing the study area, Nakdong River, and sampling points within and around the river.

543 Sampling points are referenced from A-F

544



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546 **Fig. 2** Temporal changes in PFOA and PFOS concentrations (μg L^{-1}) in surface water from Nakdong
547 River from March to December 2013 and 2015
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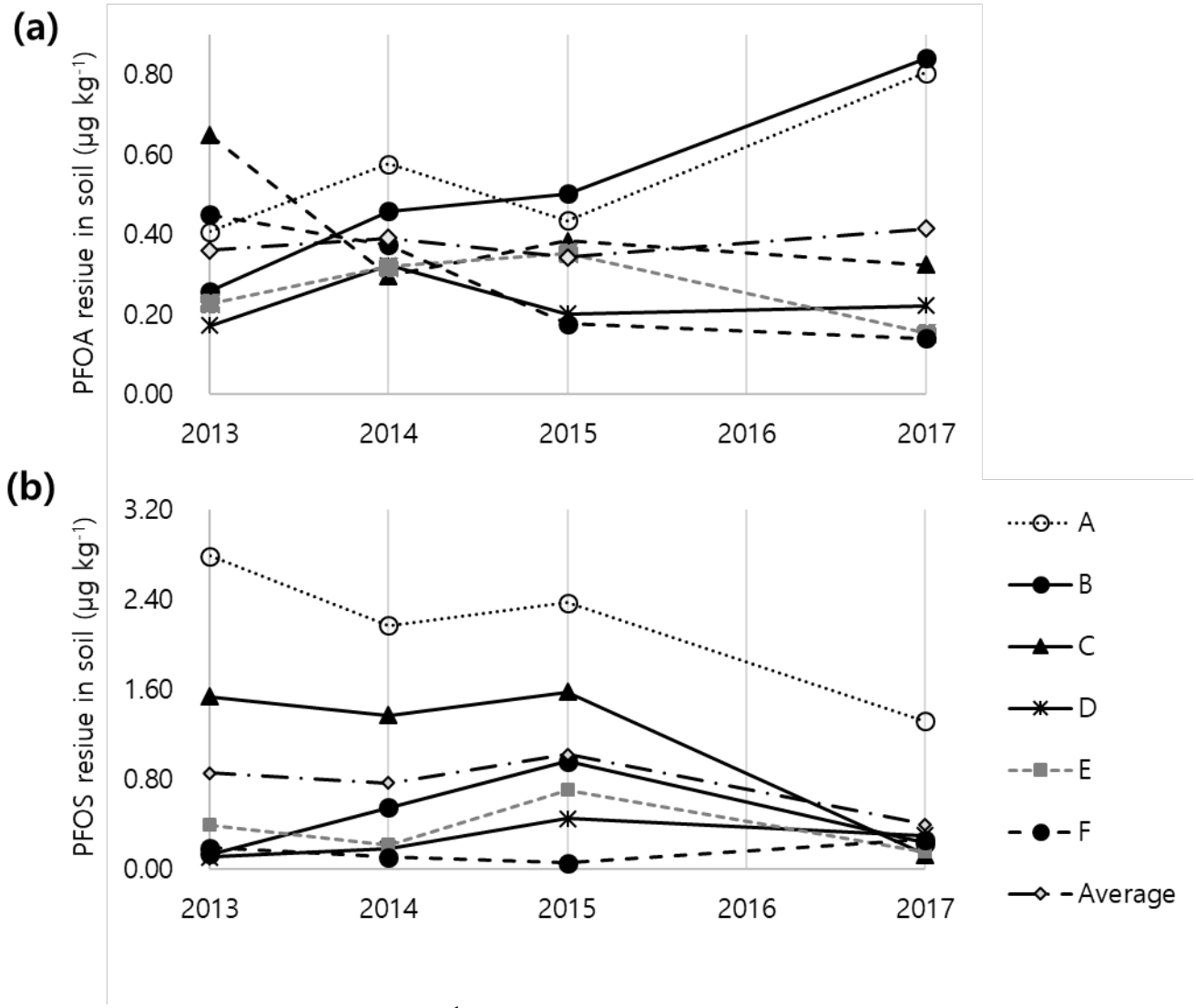

549
550 **Fig. 3** Temporal residue changes (μg kg^{-1}) in PFOA (a) and PFOS (b) in the soil of the each sampling
551 site (A-F) from Nakdong River from 2013 to 2017

552 **Table 1.** Temporal changes of PFCs residual concentration (μg L^{-1}) in irrigation water on the delta
553 area of the Nakdong-river.

Site		Average ± SD (2013)	Average ± SD (2015)	Average ± SD (All)
A	PFOA	0.082 ± 0.063	0.022 ± 0.006	0.052 ± 0.053
	PFOS	0.196 ± 0.148	0.026 ± 0.036	0.111 ± 0.137
	Sum	0.278 ± 0.210	0.048 ± 0.039	0.163 ± 0.186
B	PFOA	0.058 ± 0.040	0.017 ± 0.004	0.037 ± 0.035
	PFOS	0.033 ± 0.018	0.004 ± 0.003	0.019 ± 0.019
	Sum	0.091 ± 0.043	0.021 ± 0.007	0.056 ± 0.047
C	PFOA	0.061 ± 0.033	0.025 ± 0.019	0.043 ± 0.032
	PFOS	0.027 ± 0.021	0.003 ± 0.001	0.014 ± 0.019
	Sum	0.087 ± 0.050	0.028 ± 0.021	0.057 ± 0.048
D	PFOA	0.056 ± 0.033	0.015 ± 0.002	0.035 ± 0.031
	PFOS	0.005 ± 0.001	0.002 ± 0.001	0.004 ± 0.002
	Sum	0.062 ± 0.036	0.017 ± 0.003	0.039 ± 0.034
E	PFOA	0.086 ± 0.076	0.017 ± 0.002	0.051 ± 0.063
	PFOS	0.010 ± 0.003	0.002 ± 0.001	0.006 ± 0.005
	Sum	0.096 ± 0.084	0.019 ± 0.002	0.057 ± 0.069
F	PFOA	0.044 ± 0.034	0.021 ± 0.015	0.032 ± 0.028
	PFOS	0.017 ± 0.013	0.004 ± 0.003	0.011 ± 0.011
	Sum	0.061 ± 0.052	0.025 ± 0.019	0.043 ± 0.041
Southern (A,B,E,F)	PFOA	0.067 ± 0.057	0.019 ± 0.008	0.043 ± 0.047
	PFOS	0.064 ± 0.106	0.009 ± 0.020	0.037 ± 0.081
	Sum	0.132 ± 0.085	0.028 ± 0.016	0.080 ± 0.086
Northern (C,D)	PFOA	0.059 ± 0.032	0.020 ± 0.014	0.039 ± 0.032
	PFOS	0.016 ± 0.018	0.003 ± 0.001	0.009 ± 0.014
	Sum	0.075 ± 0.043	0.023 ± 0.015	0.048 ± 0.041
Average (All)	PFOA	0.064 ± 0.050	0.019 ± 0.011	0.042 ± 0.042
	PFOS	0.048 ± 0.090	0.007 ± 0.017	0.027 ± 0.068
	Sum	0.112 ± 0.117	0.026 ± 0.020	0.069 ± 0.094

554

555

556 **Table 2.** Temporal changes of PFOA and PFOS residue (μg kg^{-1}) at different sampling sites (A-F) in
557 the farmland soil around Nakdong River.

Site	Contaminant	Average±SD (2013-2017)
A	PFOA	0.556 ± 0.171
	PFOS	2.161 ± 0.587
	Sum	2.717 ± 0.441
B	PFOA	0.516 ± 0.223
	PFOS	0.472 ± 0.338
	Sum	0.988 ± 0.432
C	PFOA	0.414 ± 0.150
	PFOS	1.156 ± 0.631
	Sum	1.570 ± 0.770
D	PFOA	0.230 ± 0.062
	PFOS	0.263 ± 0.136
	Sum	0.493 ± 0.153
E	PFOA	0.264 ± 0.085
	PFOS	0.370 ± 0.225
	Sum	0.634 ± 0.313
F	PFOA	0.286 ± 0.138
	PFOS	0.158 ± 0.084
	Sum	0.443 ± 0.169
Southern (A,B,E,F)	PFOA	0.406 ± 0.208
	PFOS	0.790 ± 0.888
	Sum	1.196 ± 1.039
Northern (C,D)	PFOA	0.322 ± 0.150
	PFOS	0.710 ± 0.638
	Sum	1.031 ± 0.761
Average (All)	PFOA	0.377 ± 0.190
	PFOS	0.763 ± 0.803
	Sum	1.141 ± 0.878

558

559

560 **Table 3.** PFOA and PFOS residues in soil and crops, and the PUF in crops.

	Soil (μg kg^{-1})		Crop (μg kg^{-1})		PUF	
Name	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS
White cabbage	0.804	1.322	0.476	0.115	0.592	0.086
Green onion	0.841	0.236	0.809	0.004	0.962	0.017
Parsley	0.324	0.134	0.050	0.009	0.154	0.067
Lettuce	0.222	0.304	0.056	0.087	0.252	0.286
Rice (whole plant)	0.154	0.159	0.067	0.009	0.435	0.057
Plum	0.141	0.268	0.050	<0.001	0.355	<0.004

561

562 **Table 4.** EDI of PFOA and PFOS from the collected crops

Crop	EDI (ng kg^{-1} day^{-1})		Reference
	PFOA	PFOS	
Apricot	<0.001	<0.001	This study
White cabbage	0.076	0.018	This study
Chinese chive	0.005	0.010	This study
Green onion	0.059	0.011	This study
Parsley	<0.001	<0.001	This study
Lettuce	0.039	0.008	This study
Onion	0.057	<0.001	This study
Plum	0.002	<0.001	This study
Raspberry	<0.001	<0.001	This study
Rice (grain)	0.247	0.086	This study
Spinach	0.019	0.008	This study
Tomato	0.023	0.003	This study
Sub-total	**0.530**	**0.144**	This study
Beverage	0.069	0.011	Heo et al. (2014)
Dairy	0.396	<0.001	Heo et al.(2014)
Meat and its product	<0.001	0.797	Heo et al. (2014)
Fish and shellfish	0.033	0.314	Heo et al. (2014)
Tapwater	0.555	0.068	Park et al. (2018)
Total	**1.582**	**1.334**	

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564