Comparison of the plant uptake factor of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) from the three different concentrations of PFOA and PFOS in soil to spinach and Welsh onion

Deuk-Yeong Lee¹ · Geun-Hyoung Choi² · Jin-Ho Rho² · Hyo-Sup Lee² · Sang-Won Park² · Kyeong-Yeol Oh¹ · Jin-Hyo Kim¹

Received: 31 July 2020 / Accepted: 3 September 2020 / Published Online: 30 September 2020
© The Korean Society for Applied Biological Chemistry 2020

Abstract The long-chained perfluoroalkyl acids (PFAAs), perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are a potential exposure risk in the environment, specifically for humans due to high levels of bioaccumulation, persistence, and toxicity. In the current study, the plant uptake factors (PUFs) of spinach and Welsh onion were investigated on the three different concentration levels of PFOA and PFOS in soil. Spinach and Welsh onion were divided into three residue groups, a control group and two levels of PFOA and PFOS. The PFAAs spiked soils were aged for six months and the extractable residue of PFOS in the aged soil was reduced to 30–59% of the initial spiked concentrations for PFOS, while PFOA showed almost the same initial spiked concentrations. The PUFs for PFOA and PFOS were 0.111–2.821 and 0.047–3.175 for spinach, and 0.203–0.738 and 0.035–0.181 for Welsh onion, respectively. The highest PUF values in both vegetable were displayed when the residual concentration of PFAAs were part-per-billion (ppb) or sub-ppb in soil.

Keywords Perfluorooctanesulfonic acid · Perfluorooctanoic acid · Plant uptake factor · Spinach · Welsh onion

Introduction

Perfluoroalkyl acids (PFAAs) have been widely used for industrial or consumer products for more than 50 years, and short chain PFAAs are still used to the products [33]. However, the residue risk of the long-chained PFAAs such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in environment and food are constantly raised due to their potent physico-chemical stability, bioaccumulation and toxicity. Especially, PFOA, PFOS and those related compounds have been listed on persistent organic pollutants (POPs) in Stockholm Convention [17,18,29,31,32]. Although the POPs had been banned to produce and use in commercial products, there were frequently detected in environment, crops and wildlife as well as in human [2,14,20,24–26,28,30]. To know the current exposure level of PFOA and PFOS in human, many scientists reported the exposure assessment and scenarios from air, water, food and living environment [1,4,13,37,38]. From these researches, the dietary exposure was identified as a major exposure route for human, and the importance of the risk management in food crops was addressed to reduce the exposure risk of PFOA and PFOS. However, there were still lack of the information for the residues and the exposure risk assessment for human. To study of the advanced research for the risk management of PFOA and PFOS in food crops, firstly, the national survey of the residues could be performed in agricultural environment and in locally produced food crops. Then the bioaccumulation properties in various food crops should be investigated to establish an environmental safety guidelines for irrigation water and soil.

Deuk-Yeong Lee and Geun-Hyoung Choi are contributed equally to this work.

Jin-Hyo Kim (✉)
E-mail: jhkim75@gnu.ac.kr

¹Department of Agricultural Chemistry, Institute of Agriculture and Life Science (IALS), Gyeongsang National University, Jinju 52828, Republic of Korea

²Chemical Safety Division, Agro-Food Safety and Crop Protection Department, National Institute of Agricultural Sciences, RDA, Wanju 55365, Republic of Korea

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Recently, the residues of PFOA and PFOS were surveyed in agricultural environment by Choi et al. [6] and most of the residue distribution of the sum of PFOA and PFOS were reported below $0.05 \mu\text{g L}^{-1}$ (92%) in the irrigation water and below $1.0 \mu\text{g kg}^{-1}$ (88%) in the farmland soil. In addition, some of the PFAAs residue surveys for food in Korea were investigated by a few researchers [13,27]. However, the exposure risk of PFOA and PFOS for Korean from the recent food survey would be expected to exceed the recent reference doses (RfDs, $0.8 \text{ ng kg}_{\text{bw}}^{-1} \text{ day}^{-1}$ for PFOA and $1.8 \text{ ng kg}_{\text{bw}}^{-1} \text{ day}^{-1}$ for PFOS) by European Food Safety Authority [35]. However, it would be difficult to propose the environmental guideline for agricultural soil and water unless the study on crops uptake of PFOA and PFOS from soil environment is supported. To solve this problem, plant uptake factors (PUFs) or bioconcentration factors of PFOA and PFOS were reported in several crops such as carrot, cucumber, lettuce, maize, potato, radish, rice and wheat [7,11,19,22,37]. However, the plant uptake potentials of PFAAs were studied limitedly and there was still needed to study on various food crops.

Spinach and Welsh onion are important vegetables in Korea and Asia. Their daily dietary intakes were reported to 6.38 g for spinach and 10.98 g for Welsh onion in Korea National Health and Nutrition Examination Survey in 2017 [16] and they were listed on top 20 crops in Korea. Spinach was cultivated 73,239 metric tons in 2018 and it was a major food source for supplying vitamin A and vitamin C [21]. Unlike lettuce, spinach was grown in soil and had a smaller growth rate and weight than lettuce [5]. Welsh onions, along with garlic and onions, are representative crops belonging to the *Allium* genus and are produced at an annual rate of 490,000 metric tons in Korea [21]. And strong antimicrobial, antioxidative and anti-obesity activities of the onion extract had been studied recently [23]. Due to the importance of these vegetables, PUF studies on various POPs have recently been conducted, however, there have been no reports of research on the PFAAs. In here, the PUFs on the three different PFOA and PFOS concentrations in soil were investigated and compared in spinach and Welsh onion.

Materials and Methods

Standards and reagents

^{13}C -labelled and native analytical standards for PFOA and PFOS were from Wellington Laboratories, Inc. (Guelph, ON, Canada) and reagent grade of PFOA and PFOS for soil contamination was

purchased from TCI Co., Ltd. (Tokyo, Japan). Acetonitrile (ACN), acetic acid, ammonium acetate, methanol and tetrahydrofuran were used a high-performance liquid chromatography grade from Merck (Darmstadt, Germany). Powdered ENVI-Carb™ (Supelco, Bellefonte, PA, USA), hydrophilic-lipophilic balance (HLB) cartridges (0.5 g, 6 mL, Oasis, Waters Co., Dublin, Ireland) and membrane filter and syringe filter (nylon, Silicycle Inc., Quebec, Canada) were purchased.

Soil preparation and vegetable cultivation

The experimental soil was collected on the top soil from an aerial field and used below 5 mm particle for pot preparation. The physicochemical properties of the experimental soil were described in Table 1. The experimental pot was divided to three groups; non-spiked, low-contaminated, and high-contaminated groups. The initial residues of PFOA and PFOS were ideally spiked to 1000 and $5000 \mu\text{g kg}^{-1}$ in spinach cultivation soil (Group SB and SC), and 50 and $500 \mu\text{g kg}^{-1}$ in Welsh onion cultivation soil (Group WB and WC) with the reagent grade standards. After the soil homogenization for 4 days, aging process was performed for six months in 1/5000 a of Wagner pot. For prevention of the leaching of the contaminants, the pot was closed on the bottom. For spinach and Welsh onion cultivation, the seeds were purchased from Asia Seed Co. (Seoul, Korea). The vegetables were cultivated in green house. Spinach was sown in February and harvested in June, and Welsh onion was sown in March and harvested in July. The pot cultivation of each treatment was performed with eight replications. The spinach and Welsh onion were harvested whole plant and the residue soil was washed under running tap water gently. The harvested vegetable blended with dry ice and stored at -20°C until the residue analysis.

Analytical sample preparation for residual PFAAs in soil

The analytical soil sample preparation was followed by Choi et al. [6]. Briefly, 1% aqueous acetic acid (10 mL) was added to 1.0 g air-dried soil sample, then it was shaken for 30 min, sonicated for 15 min and centrifuged at 3000 rpm. The supernatant was collected and the original soil was re-extracted three times using 10 mL of 90% (v/v) methanol in 1% acetic acid. All the extracts were combined and concentrated under nitrogen, then diluted with dH_2O . The diluted extract was loaded to pre-cleaned HLB cartridge, then washed with 30% methanol (5 mL) and eluted with methanol (10 mL). The eluent was concentrated and re-dissolved in 1.0 mL of methanol then 20 mg of powdered ENVI-Carb™ was added. The mixture was vortexed and filtered using nylon

Table 1 Physico-chemical properties of experimental soil for pot experiment

Crop	Texture	pH (1:5)	Organic matter (g kg^{-1})	Avail. P_2O_5 (mg kg^{-1})	Exchangeable Cations ($\text{cmol}_\text{c kg}^{-1}$)		
					K	Ca	Mg
Spinach	Sandy clay loam	5.38	19.6	138.1	1.1	6.9	3.2
Welsh onion	Sandy clay loam	6.28	55.1	497.3	2.0	16.2	4.7

syringe filter then $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_4$ -PFOS were added to the filtrate as internal standards.

Analytical sample preparation for residual PFAAs in vegetables

The cleanup and quantitation procedure for PFAAs was followed by Choi et al. [7] with slight modification. Briefly, 10.0 g vegetable was extracted with 75% methanol (10 mL×3) then centrifuged at 3000 rpm and the supernatant was collected. The extracted vegetable was re-extracted using 75% of aqueous tetrahydrofuran (10 mL). All extracts were combined and concentrated to 10 mL under nitrogen stream. The extract was diluted to 50 mL dH₂O then extracted with HLB cartridge as follow as the above described. The eluent was concentrated and re-dissolved with 1.0 mL methanol-then added 20 mg of powdered ENVI-CarbTM. The mixture was vortexed and filtered using syringe filter then isotope labeled internal standards were added to the filtrate.

Instrumental analysis

The instrumental analysis of PFOA and PFOS was performed with liquid chromatography (LC)-triple quadrupole mass spectroscopy (API 3200 QTRAP, AB Sciex LLC., Framingham, MA, USA) with a C18 column (3 μm , 150 mm×2.1 mm, Silicycle Co., Quebec, Canada) for analysis and a C18 column (5 μm , 50 mm×2.1 mm, Phenomenex, Inc., Torrance, CA, USA) for separation of solvent impurity. The eluent and detailed instrumental conditions were described in Table 2.

Quality assurance

Linearities of PFOA and PFOS from concentrations of 0.010 to

5.000 $\mu\text{g L}^{-1}$ were 0.9992 and 0.9993, respectively. Both of the limit of quantification (LOQ) for PFOA and PFOS were 0.010 $\mu\text{g kg}^{-1}$ for soil and 0.001 $\mu\text{g kg}^{-1}$ for vegetables. Recovery were measured two spiked concentrations on each of 0.05 and 0.5 $\mu\text{g kg}^{-1}$ of the $^{13}\text{C}_8$ -PFAAs in spiked soil and vegetables and ranged from 69 to 78%. The precisions of PFOA and PFOS were determined to 9.1-9.8% for soil, and 8.4-9.9% for vegetables, respectively.

PUF of vegetables for PFAAs

PUF was calculated with the followed equation. The PFAAs concentration was used an initial level as before plantation in soil and a harvest level in vegetables.

$$\text{PUF} = \frac{C_{\text{vegetable}}}{C_{\text{soil}}}$$

Results and Discussion

PUFs for PFOA and PFOS residues in soil

The estimated soil contamination level was designed to three groups; non-spiked, low-concentration spiked and high-concentration spiked of PFOA and PFOS groups were prepared. Before the contamination of PFOA and PFOS in the collected soil, the initial residues of PFOA and PFOS were analyzed and the residues were determined to 0.381 and 0.099 $\mu\text{g kg}^{-1}$ in spinach cultivation soil (Group SA), and 4.230 and 3.251 $\mu\text{g kg}^{-1}$ in Welsh onion cultivation soil (Group WA), respectively.

For the spinach cultivation, each of PFOA and PFOS was

Table 2 The instrumental condition of LC-MS/MS for quantitative analysis of PFOA and PFOS

LC	Agilent HP1100 (Agilent Technologies, Inc., Santa Clara, CA, USA)	
Column	Siliachrom C18 (3 μm , 150 × 2.1 mm)	
Injection volume	10 μL	
Mobile phase	A: 2 mM NH ₄ OAc in 5% MeOH B: 2 mM NH ₄ OAc in 75/25/5 (v/v/v, MeOH/ACN/dH ₂ O)	
Flow rate	0.2 mL/min	
Gradient	Time (min)	Mobile phase
	0	100% A
	2	100% A
	3	90% A/ 10% B
	5	50% A/ 50% B
	9	10% A/ 90% B
Mass spectrometry	API 3200 system (AB Sciex LLC., Framingham, MA, USA)	
Source temperature	600 °C	
Ion spray voltage	−4.2 kV	
Ionization mode	ESI negative	
Detection	412→369 for native PFOA; 417→372 for $^{13}\text{C}_4$ -PFOA; 421→376 for $^{13}\text{C}_8$ -PFOA 498→79 for native PFOS; 503→99 for $^{13}\text{C}_4$ -PFOS; 507→99 for $^{13}\text{C}_8$ -PFOS	
MS/MS condition	Declustering potential -15V (PFOA), -80V (PFOS); Collision cell entrance potential -20V (PFOA), -28V (PFOS); Collision energy -14V (PFOA), -68V (PFOS); Collision cell exit potential -4V (PFOA), 0V (PFOS)	

spiked on a part-per-million (ppm) level of concentrations to $1000 \mu\text{g kg}^{-1}$ for low concentration spiked group (Group SB) and $5000 \mu\text{g kg}^{-1}$ for high concentration spiked group (Group SC) in the soil. And the real concentrations of PFOA and PFOS were detected to 816.3 and $392.6 \mu\text{g kg}^{-1}$ on Group SB and 4916 and $1521 \mu\text{g kg}^{-1}$ on Group SC, respectively (Table 3). On the other hand, the soil for Welsh onion cultivation were spiked on a part-per-billion (ppb) level of concentrations to 50 and $500 \mu\text{g kg}^{-1}$ as initial spiked concentrations for Group WB and Group WC; this spiked concentrations were designed based on the current environmental residue concentrations and the worst contamination scenario. The PFOA and PFOS residues were 51.80 and $27.62 \mu\text{g kg}^{-1}$ on Group WB and 483.1 and $295.4 \mu\text{g kg}^{-1}$ on Group WC. Interestingly, the PFOS residues after aging process were detected lower than the initial spiked concentration, respectively (Tables 3, 4). And this residue reduction of PFOS in soil was expected to the adsorption and immobilization of PFOS in soil clay from the previous immobilization studies [10,12,36,39]. These studies reported on the adsorption mechanism of clay minerals like montmorillonite and/or kaolinite with perfluorinated sulfonate and the interaction Al/Fe ions with PFOS, while PFOA didn't show these immobilization process [3,39]. Thus, the diminution of extractable PFOS residue could be expected in aged soil without change of the total residue in soil due to its potent stability in soil [39]. In this experiments, the soil aging for six months decreased the extractable PFOS to 30-59% of the initial spiked concentration, while the PFOA residue was recorded to almost of the initial spiked concentration in soil. These immobilization effect of soil might expect to help the diminution of plant uptake ratio from soil to crop.

PUFs for PFOA and PFOS residues in spinach

The PFOA and PFOS residues in spinach were detected 1.077 and $0.316 \mu\text{g kg}^{-1}$ on Group SA, 171.5 and $18.32 \mu\text{g kg}^{-1}$ on Group SB and 544.5 and $73.58 \mu\text{g kg}^{-1}$ on Group SC, respectively. Based on the residue in spinach and soil, the PUFs of PFOA and PFOS were estimated to 0.111 - 2.821 and 0.047 - 3.175 , respectively (Table

3). Interestingly, the highest PUFs were recorded on the lowest PFOA and PFOS residues in the soil, and the PUFs for PFOA were gradually decreased on the increasing of the residue concentration in soil. On the other hand, the PUFs for PFOS showed a consistent value, not dependent on over hundreds ppb of the residues in soil. In addition, the residue in spinach and their PUFs for PFOS showed lower than those of the PFOA. In the cultivation experiments, the experimental PFAAs concentration in soil didn't affect to spinach growth and production in all of the groups.

PUFs for PFOA and PFOS in Welsh onion

In the cultivated Welsh onion, the highest PFOA and PFOS were detected 124.0 and $24.19 \mu\text{g kg}^{-1}$ on Group WC that was found the highest soil residues, respectively. Based on the residue in Welsh onion, the PUFs of PFOA and PFOS were calculated to 0.203 - 0.738 and 0.035 - 0.181 , respectively (Table 4). As with the results of spinach, the highest PUFs on Welsh onion were recorded on the several ppb-level of PFOA and PFOS concentrations in the soil, and the Welsh onion uptake and accumulate PFOA more than PFOS.

The highest PUF for PFOA and PFOS in the test vegetables was found 2.821 and 3.175 in spinach, respectively. Although both of the plant uptake experiments were not performed on the same soil condition, the PUFs for PFOA and PFOS in spinach were similar values with the previously reported in rice straw (0.769 - 1.474 for PFOA and 1.749 - 4.700 for PFOS) [7]. In addition, the PUFs for the PFAAs were at least 10-fold higher than those for endosulfan and other organochlorine POPs [5,8,9,15]. Due to the ionic functional group of PFOA and PFOS, the PFAAs have higher hydrophilicity and ionic charges than the organochlorine POPs and these chemical properties would result to higher PUFs in crops through a different pathway for the uptake and accumulation with non-polar organochlorine POPs [22,34].

The highest PUFs for PFOA and PFOS in spinach and Welsh onion showed up to 2.821 and 3.175 in ppb or sub-ppb level of the residues in soil, respectively. And the PUFs of PFOA and PFOS

Table 3 PFOA and PFOS residues (average $\pm$ SD) in the soil, spinach and the PUFs

	Soil ($\mu\text{g kg}^{-1}$)		Spinach ($\mu\text{g kg}^{-1}$)		PUF	
	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS
Group SA	0.381 ± 0.021	0.099 ± 0.003	1.077 ± 0.245	0.316 ± 0.058	2.821	3.175
Group SB	816.3 ± 54.89	392.6 ± 27.49	171.5 ± 28.35	18.32 ± 2.315	0.210	0.047
Group SC	4916 ± 342.2	1521 ± 118.5	544.5 ± 95.12	73.58 ± 10.77	0.111	0.048

Table 4 PFOA and PFOS residues (average $\pm$ SD) in the soil, Welsh onion and the PUFs

	Soil ($\mu\text{g kg}^{-1}$)		Welsh onion ($\mu\text{g kg}^{-1}$)		PUF	
	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS
Group WA	4.230 ± 2.867	3.251 ± 1.957	3.122 ± 0.606	0.589 ± 0.033	0.738	0.181
Group WB	51.80 ± 7.61	27.62 ± 6.07	10.53 ± 2.06	0.961 ± 0.147	0.203	0.035
Group WC	483.1 ± 87.4	295.4 ± 46.71	124.0 ± 35.27	24.19 ± 4.117	0.256	0.082

differed up to 20- and 60-folds in spinach, and 3- and 5-folds in Welsh onion according to the soil contamination level. The highest PUFs were found in the popular residues in Korean agricultural environment, and the residues of the cultivated vegetables in Korea would be below 2.821 and 1.588 $\mu\text{g kg}^{-1}$ in spinach and 0.738 and 0.181 $\mu\text{g kg}^{-1}$ in Welsh onion, respectively. Actually, the similar residues were reported the previously studied PFAAs residue monitoring of the retailed Korean foods ($<1.0 \mu\text{g kg}^{-1}$) by Heo et al. [13]. However, we were still not sure of the maximum and average residues of the PFAAs in crops due to the complexation of effects on the various factors such as the irrigation water contamination, soil condition, and vegetable growth condition. Recently, some of the exposure assessments for PFAAs were reported that the exposure risk of PFAAs from food and tap water was not exceeded the previously reported RfDs (1500 $\text{ng kg}_{\text{bw}}^{-1} \text{day}^{-1}$ for PFOA and 150 $\text{ng kg}_{\text{bw}}^{-1} \text{day}^{-1}$ for PFOS). However, the recent RfDs of the PFAAs were strengthened to 0.8 $\text{ng kg}_{\text{bw}}^{-1} \text{day}^{-1}$ for PFOA and 1.8 $\text{ng kg}_{\text{bw}}^{-1} \text{day}^{-1}$ for PFOS in 2018, and we didn't have the national residue survey data after the implementation of the strengthen of POPs Control Acts for PFAAs in Korea. Thus, the further approach of this research is needed the national level of the residue survey in crops and in soil for the dietary exposure risk assessment of crops and the establishment of agricultural environmental guidelines for the PFAAs.

Acknowledgment This study was supported by the “Cooperative Research Program for Agricultural Science & Technology Development (Project No. PJ01332102)”, Rural Development Administration and by the Ministry of Science and ICT (MSIT) through the National Research Foundation (NRF) of Korea (NRF-2019R1A4A1029125), Republic of Korea.

References

- van Asselt ED, Rietra RP, Romkens PF, van der Fels-Klerx HJ (2011) Perfluorooctane sulphonate (PFOS) throughout the food production chain. *Food Chem* 128: 1–6
- Bae JY, Lee DY, Choi IW, Lee JH, Kim JH (2019) Examination of commercial biochars to compare their endosulfan adsorption properties. *Korean J Pestic Sci* 23(3): 172–176
- Bao Y, Niu J, Xu Z, Gao D, Shi J, Sun X, Huang Q (2014) Removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from water by coagulation: mechanisms and influencing factors. *J Colloid Interface Sci* 434: 59–64
- Brambilla G, D'Hollander W, Oliaei F, Stahl T, Weber R (2015) Pathways and factors for food safety and food security at PFOS contaminated sites within a problem based learning approach. *Chemosphere* 129: 192–202
- Choi GH, Jeong DK, Lim SJ, Ro JH, Ryu SH, Park BJ, Moon BC, Kim JH (2017) Plant uptake potential of endosulfan from soil by carrot and spinach. *J Appl Biol Chem* 60: 339–342
- Choi GH, Lee DY, Jeong DK, Kuppusamy S, Lee YB, Park BJ, Kim JH (2017) Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in the South Korean agricultural environment: A national survey. *J Integr Agric* 16: 1841–1851
- Choi GH, Lee DY, Bae JY, Rho JH, Moon BC, Kim JH (2018) Bioconcentration factor of perfluorochemicals for each aerial part of rice. *J Appl Biol Chem* 61: 191–194
- Choi GH, Lee DY, Ryu SH, Park BJ, Moon BC, Kim JH (2018) Investigation of the bioconcentration factor of endosulfan for rice from soil. *Korean J Pestic Sci* 22: 25–28
- Choi GH, Lee DY, Seo DC, Kim L, Lim SJ, Ryu SH, Park BJ, Kim JH, Kim JH (2018c) Endosulfan plant uptake suppression effect on char amendment in oriental radish. *Water Air Soil Pollut* 229: 24
- Feng H, Lin Y, Sun Y, Cao H, Fu J, Gao K, Zhang A (2017) In silico approach to investigating the adsorption mechanisms of short chain perfluorinated sulfonic acids and perfluorooctane sulfonic acid on hydrated hematite surface. *Water Res* 114: 144–150
- Ghisi R, Vamerali T, Manzetti S (2019) Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review. *Environ Res* 169: 326–341
- Hale SE, Arp HH, Slinde GA, Wade EJ, Bjørseth K, Breedveld GD, Straith BF, Moe KG, Jartun M, Hoisæter Åse (2017) Sorbent amendment as a remediation strategy to reduce PFAS mobility and leaching in a contaminated sandy soil from a Norwegian firefighting training facility. *Chemosphere* 171: 9–18
- Heo JJ, Lee JW, Kim SK, Oh JE (2014) Foodstuff analyses show that seafood and water are major perfluoroalkyl acids (PFAAs) sources to humans in Korea. *J Hazard Mater* 279: 402–409
- Hong S, Khim JS, Park J, Kim M, Kim WK, Jung J, Hyun S, Kim JG, Lee Hm Choi HJ, Codling G, Giesy JP (2013) In situ fate and partitioning of waterborne perfluoroalkyl acids (PFAAs) in the Youngsan and Nakdong River Estuaries of South Korea. *Sci Total Environ* 445–446: 136–145
- Hwang JI, Lee SE, Kim JE (2015) Plant Uptake and Distribution of Endosulfan and Its Sulfate Metabolite Persisted in Soil. *PLoS One*. doi: 10.1371/journal.pone.0141728
- KHIDI (2017) Food intake in 2017. In Korea National Health and Nutrition Examination Survey, Korea Health Industry Development Institute (KHIDI). <https://info.khidi.or.kr/kps/dhraStat/result2?menuId=MENU01653&gubun=&year=2017>. Accessed 21 July 2020
- Kim JH, Jin CL, Choi GH, Park BJ (2015a) Sample Preparation Method for Perfluorochemicals with LC-Tandem Mass Spectrometry in Agricultural Water. *Korean J Pestic Sci* 19: 1–4
- Kim JH, Ok YS, Choi GH, Park BJ (2015b) Residual perfluorochemicals in the biochar from sewage sludge. *Chemosphere* 134: 435–437
- Kim H, Ekpe DO, Lee JH, Kim DH, Oh JE (2019) Field-scale evaluation of the uptake of Perfluoroalkyl substances from soil by rice in paddy fields in South Korea. *Sci Total Environ* 671: 714–721
- Kim SH, Kim JA, Im MH (2020) Residual characteristics of pesticide in banana from international pesticide residue monitoring data. *J Appl Biol Chem* 63(1): 9–22
- KOSIS (2018) Crop production survey. In Korean Statistical Information Service, Statistics Korea. <http://kosis.kr/publication/publicationThema.do>. Accessed 21 July 2020
- Lechner M, Knapp H (2011) Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plant and distribution to the different plant compartments studied in cultures of carrots (*Daucus carota* ssp. *Sativus*), potatoes (*Solanum tuberosum*), and cucumbers (*Cucumis Sativus*). *J Agric Food Chem* 59: 11011–11018
- Lee YH, Yang H, Lee SR, Kwon SW, Hong EJ, Lee HW (2018) Welsh onion root (*Allium fistulosum*) restores ovarian functions from letrozole induced-polycystic ovary syndrome. *Nutrients* 10: 1430
- Lim SJ, Oh YT, Yang JY, Ro JH, Choi GH, Ryu SH, Moon BC, Park BJ (2016) Development of Multi-residue Analysis and Monitoring of Persistent Organic Pollutants (POPs)-Used Organochlorine Pesticides in Korea. *Korean J Pestic Sci* 20: 319–325
- Lim SJ, Park JH, Ro JH, Oh YT, Joo HG, Lee MH, Yoon HI, Choi GH, Ryu SH, Park BJ (2018) Investigation of residual organochlorine pesticides in grape and peach orchard soils and fruits. *Korean J Pestic Sci* 22(4): 292–299
- Lim SJ, Park JH, Ro JH, Lee MH, Yoon HI, Choi GH, Ryu SH, Park BJ

- (2019) Investigation of residual organochlorine pesticides in apple and pear orchard soil and fruit. *Korean J Pestic Sci* 38(2): 110–118
27. Naile JE, Khim JS, Wang T, Chen C, Luo W, Kwon BO, Park JS, Koh CH, Jones PD, Lu Y, Giesy JP (2010) Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea. *Environ Pollut* 158: 1237–1244
 28. Naile JE, Khim JS, Hong SJ, Park JS, Kwon BO, Ryu JS, Hwang JH, Jones PD, Giesy JP (2013) Distributions and bioconcentration characteristics of perfluorinated compounds in environmental samples collected from the west coast of Korea. *Chemosphere* 90: 387–394
 29. Pan CG, Ying GG, Liu YS, Zhang QQ, Chen ZF, Peng FJ, Huang GY (2014) Contamination profiles of perfluoroalkyl substances in five typical rivers of the Pearl River Delta region, South China. *Chemosphere* 114: 16–25
 30. Ryu K, Kim JP, Park DW, Lee DV, Song NJ, Cho BS, Seo KW, Kim SH (2020) A statistical analysis of pesticide residues on leafy vegetables selling at agricultural wholesale markets in Gwangju. *Korean J Pestic Sci* 24(1): 91–104
 31. Scheringer M, Trier X, Cousins IT, de Voogt P, Fletcher T, Wang Z, Webster TF (2014) Helsingor statement on poly- and perfluorinated alkyl substances (PFASs). *Chemosphere* 114: 337–339
 32. Seong HJ, Kwon SW, Seo DC, Kim JH, Jang YS (2019) Enzymatic defluorination of fluorinated compounds. *J Appl Biol Chem* 62: 62
 33. Wang Z, Cousins IT, Scheringer M, Buck RC, Hungerbühler K (2014) Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ Int* 70: 62–75
 34. Wen B, Pan Y, Shi X, Zhang H, Hu X, Huang H, Lv J, Zhang S (2018) Behavior of N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) in biosolids amended soil-plant microcosms of seven plant species: Accumulation and degradation. *Sci Total Environ* 642: 366–373
 35. Xiang L, Li YW, Yu PF, Feng NX, Zhao HM, Li H, Cai QY, Mo CH, Li QX (2020) Food Safety Concerns: Crop Breeding as a Potential Strategy To Address Issues Associated with the Recently Lowered Reference Doses for Perfluorooctanoic Acid and Perfluorooctane Sulfonate. *J Agric Food Chem* 68: 48–58
 36. Zhang R, Yan W, Jing C (2014) Mechanistic study of PFOS adsorption on kaolinite and montmorillonite. *Colloids and Surf A Physicochem Eng Asp* 462: 252–258
 37. Zhao H, Guan Y, Zhang G, Zhang Z, Tan F, Quan X, Chen J (2013) Uptake of perfluorooctane sulfonate (PFOS) by wheat (*Triticum aestivum* L.) plant. *Chemosphere* 91: 139–144
 38. Zhao YG, Wong CK, Wong MH (2012) Environmental contamination, human exposure and body loadings of perfluorooctane sulfonate (PFOS), focusing on Asian countries. *Chemosphere* 89: 355–368
 39. Zhao L, Bian J, Zhang Y, Zhu L, Liu Z (2014) Comparison of the sorption behaviors and mechanisms of perfluorosulfonates and perfluorocarboxylic acids on three kinds of clay minerals. *Chemosphere* 114: 51–58