Cod: 8.6024

HUMAN DIETARY INTAKE OF PERFLUORINATED COMPOUNDS AND THEIR FORMATION POTENTIALS VIA CONSUMPTION OF CROP PLANTS, FISH AND OTHER FOOD ITEMS IN OSAKA, JAPAN

Y. Suzuki[1], S. Tanaka[1], S. Fujii[1], H. Ando[1], S. Yukioka[2], R. Kitao[2], N. Saito[3]

[1]*Graduate School of Global Environmental Studies, Kyoto University, Yoshida Campus, Kyoto, Japan*

[2]*Graduate School of Engineering, Kyoto University, Yoshida Campus, Kyoto, Japan*

[3]*Research Institute for Environmental Sciences and Public Health of Iwate Prefecture, Morioka, Iwate, Japan*

1. Introduction

Perfluorinated compounds (PFCs) are ubiquitous in the environment and detected even in human milk[1]. Their bioaccumulative potential and various adverse effects on human and wildlife are of great concern. Exposure to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), the representatives of PFCs, is considered to be correlated with infertility[2]. Potential routes of human exposure to PFCs are inhalation of air, ingestion of house dust, drinking water and one of the major pathways was said to be through diet[3]. It is reported that vegetables were identified to be the most important food category for exposure to perfluorohexanoic acid (PFHxA) and PFOA, with up to 69% of the total exposure[4,5]. In contrast, fish and seafood were also reported as the major contributors in some countries[6,7] . Information on PFCs in food and their dietary exposure is still not well understood.

Indirect exposure is also considered as a negligible route to human through intake of precursors, which have been suspected to exist in the environment including food market[8]. These precursors may be metabolized to PFCs and other transformation products once carried into human body. It is important to investigate on precursor's exposure to human since precursors such as carboxylates (FTCAs) were reported as more toxic than PFCs[9]. Due to precursors' degradability, their determination in food samples are difficult and reported knowledge is few. For the evaluation on the existence of possible precursors, our group has applied oxidative conversion method to environmental samples, which is defined as PFC formation potentials (PFC-FPs)[10]. Overview of this study is shown in **Figure 1**. Main objective of this study was to calculate human daily dietary intake (DDI) of PFCs and PFC-FPs in Osaka Japan, where relatively high PFCs concentration was detected in the previous study[11].

2. Materials and methods

2-1. Sample Collection: Details of total diet survey are shown in **Table 1**. Survey was conducted in winter 2015-2016 at local markets in Osaka. Food samples corresponding to each category were selected from locally grown and consumed items. In case of vegetables, Seven green vegetables and #ix other vegetables were purchased. In addition, tap water was collected in the market area. DDI was calculated by **Formula 1** and **Formula 2**. Data of daily intake (g) for 14 food groups were obtained from the report by Japanese Ministry of Health Labour and Welfare (2013)[12]. In this study, data for adults (> 20 years old) were applied. For TD-1, TD-2, maximum value in analyzed chemical were applied to estimate the upper bound intake. Solid food samples were freeze dried and crushed into powder before pre-treatment.

2-2. Sample Pre-treatment: PFCs in aqueous samples (water: 250 mL, others: 50 mL) were extracted by solid phase extraction (SPE) using Oasis® WAX cartridge (Waters). PFCs in dried samples (0.2 g) were extracted by ion-pair extraction method, which uses tetrabutyl ammonium hydrogen sulfate and sodium carbonate mixed with tert-butyl methyl ether. Extracts were treated by 0.2 μm syringe filter (Whatman®) and $ENVI_{TM}$-carb cartridge (Supelco). For the analysis of PFC-FPs, extracts from solid samples were replicated and diluted with 250 mL of PFCs-free Milli-Q water. All aqueous samples were then treated with $K_2S_2O_8$ (60 mM) and NaOH (150 mM) followed by heating for 24 hours under 95 °C. After this, samples were pre-treated in the same way of PFCs analysis in aqueous samples explained above.

2-3. Instrumental Analysis and Quantification: 12PFCs (C4A-C12A, C4S, C6S and C8S) were analyzed by LC-MS/MS (Agilent). Details of separation and quantification were shown in a previous literature[14]. Instrumental Detection Limits (IDLs) were 0.01-0.03 ng/mL. Recovery rates were ranged between 12% (PFHxA in cooking oil) - 126% (PFOS in groundnut) and their relative standard deviations were less than 30%. PFC-FPs concentration was calculated by differences between concentration before and after the oxidative conversion. Values less than LOD was assumed to be zero.

3. Results and discussion

3-1. Human DDI of PFCs and PFC-FPs in Osaka, Japan

Calculated DDI is shown in **Figure 2.** DDI of PFHxA (33.9 ng/kgbw/day), PFPeA (11.3 ng/kgbw/day) and PFBA(3.18 ng/kgbw/day) were highest. This suggested that more hydrophilic PFCs tend to be transferred to food via water. DDIs of PFOA and PFOS were 2.46 and 0.56 ng/kgbw/day, respectively. These values were comparable to previous studies[6, 7, 13]. In terms of PFC-FPs, DDIs were resulted in more than 1.0 ng/kgbw/day except for PFHpA-FP and PFDoDA-FP. DDI of PFOS-FP (12.8 ng/kgbw/day) was 22 times higher than that of PFOS. Thus, people in the studied area might be exposed to the precursors from diet despite the result that most of the PFCs contamination themselves were not clearly indicated. Moreover, DDIs of Σ12PFCs and Σ12PFC-FPs were calculated as 51.6 and 68.0, in total of 126.5 ng/kgbw/day, which was comparable to the provisional tolerable daily intake values (150 ng/kgbw/day) proposed by the European Food Safety Authority[14] . This value is applicable only to PFOS but occurrences of various PFCs and their possible precursors need to be regarded as a potential health risk.

3-2. Contribution of each food group to DDI

The ratio of each food group contribution to DDI is shown in **Figure 3**. In the figure, the food groups which contributed to DDI more than 10 % was emphasized by indicating the values. DDI of PFHxA was mainly from rice (26%), fruits (15%), green and other vegetables (14% and 11%). Crop plants accounted for 84% of the total DDI. Similarly, crop plants contributed to 67%, 78%. 84% of the total DDI for PFOA, PFOS and Σ12PFCs, respectively. Overall, vegetables and other crop plants were the major contributors to dietary exposure. In addition, drinking water contributed to 19 % of PFOA DDI. This might be due to high contamination of PFOA in the Yodo River, which is a main water source in the studied area[11]. In contrast, DDI of PFHxA-FP was mainly from pulses (36%), Fish (22%), green and other vegetables (12% and 11%). Fish also accounted for 19% of PFOA-FP DDI and 10% of Σ12PFC-FPs DDI. This indicated that fish consumption was one of the major pathways for PFCs precursors in this area.

3-3. PFOS-FP tends to be contained in fruit vegetables

Vegetables contributed to 90% of PFOS DDI (60 % from green vegetables and 30 % from other vegetables). **Figure 4** shows PFOS and PFOS-FP in different type of vegetables. PFOS was detected at 0.91 ng/g-dry in Japanese radish leaves (leaf vegetables) as maximum while PFOS-FP was detected more than that in five fruit vegetables and two leaf vegetables at 39.5 ng/g-dry in green pepper as maximum. PFOS-FP was detected from 33% (0/3) of root vegetables and 40% (2/5) of leaf vegetables while it was detected from 100% (5/5) of fruit vegetables. The tendency of higher concentration and more frequency of PFOS-FP detection in fruit vegetables may suggest a different translocation mechanism between PFOS and PFOS-related precursors depending on kinds of crop plants.

In this study, occurrences of PFC formation potentials (PFC-FPs) in food items in Osaka, Japan were demonstrated and their human dietary intake (DDI) were indicated. Data of PFCs and their precursors including PFC-FPs are expected to be accumulated more so that the route of exposure is elucidated.

Acknowledgements

This study was supported by JSPS KAKENHI(25289169) and Kurita WEF Grant (15E050).

References

1. Guerranti, C., Perra, G., Corsolini, S., et al. (2013). Food Chem, 140(1-2), 197-203.
2. Governini, L., Orvieto, R., Guerranti, C., et al. (2011). J Assist Reprod Genet, 28(5), 415-418.
3. D'Hollander, W., de Voogt, P., De Coen, W., et al. (2010). Rev Environ Contam Toxicol, 208, 179-215.
4. Klenow S., Heinemeyer G., Brambilla G., et al. (2013). Food Addit. Contam. A− 30 (12), 2141−2151.
5. Suzuki Y, Tanaka S, Fujii S., et al. (2015). Organohalogen Compounds, 77,663-667.
6. Ericson, I., Martí-Cid, R., Nadal, M., et al. (2008). J Agric Food Chem, 56(5), 1787-1794.
7. Haug, L. S., Thomsen, C., Brantsaeter, A. L., et al. (2010). Environ Int, 36(7), 772-778.
8. Tomy, G. T., Tittlemier, S. A., Palace, V. P., et al. (2004). Environ Sci Technol, 38(3), 758-762.
9. Phillips, M. M., Dinglasan-Panlilio, M. J., Mabury, S. A., et al. (2007). 41(20), 7159-7163.
10. Suzuki Y, Tanaka S, Fujii S., et al. (2014). J.JSCE,Ser G, 70(7), III_55-III_64. (in Japanese)
11. Suzuki Y, Tanaka S, Fujii S., et al. (2013). Organohalogen Compounds, 75, 1053-1056.
12. Japanese Ministry of Health, Labour and Welfare (2012).
http://www.mhlw.go.jp/bunya/kenkou/eiyou/dl/h25-houkoku.pdf (Accessed May 30, 2016, in Japanese)
13. Karrman, A., Harada, K. H., Inoue, K., et al. (2009). Environ Int, 35(4), 712-717.
14. EFSA (European Food Safety Authority) (2008). EFSA, Parma. EFSA J 653:1–131

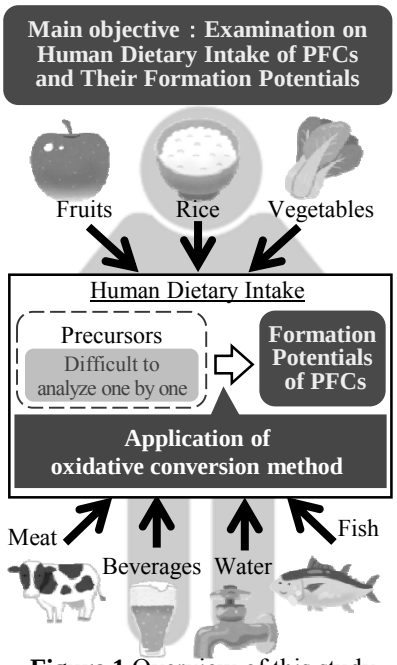

Figure 1 Overview of this study

Table 1 Analyzed food samples in 14 food groups in this study

ID	Food Groups		Daily intake by Japanese adults * (g/day/person)	Analyzed food samples
TD-1	Crop plants (Vegetables)	Green vegetables	90.9	Various (n=7)
TD-2		Other vegetables	286.5	Various (n=6)
TD-3	Crop plants (Others)	Rice and rice products	446.6	Rice
TD-4		Cereals and potatoes	54.5	Taro
TD-5		Pulses	61.6	Groundnut
TD-6		Fruits	109.8	Persimmon
TD-7	Drinks	Drinking water	1627.7	Tap water
TD-8		Beverages	672.3	Japanese Sake
TD-9	Others	Fish and shellfish	75.6	Gray mullet
TD-10		Meat and eggs	120.8	Beef
TD-11		Milk and dairy products	99.8	Yogurt
TD-12		Fats and oils	10.4	Cooking oil
TD-13		Seasonings	95.6	Pepper and salt
TD-14		Sugars and confectionery	31.5	Baked sweets

* National Health and Nutrition Survey by Japanese ministry of health labour and welfare (2013) [12]

Formula 1: $Dn = C \times En$

where, Dn : daily intake from TD-n
C: PFCs concentration in each food sample (ng/g)
En: daily intake of TD-n (g/day)

Formula 2: $T = \sum_{n=1}^{14} Dn / 50$

where , T = daily dietary intake of PFCs / 50 kgbw assuming 50 kg as average body weight (bw)

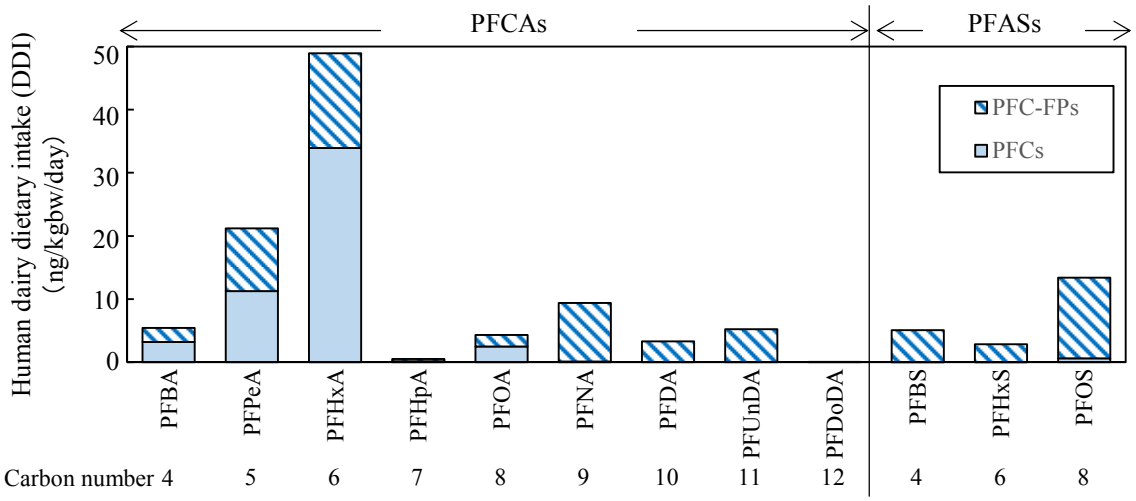

Figure 2 Human dairy dietary intake (DDI) of PFCs and PFC formation potentials (PFC-FPs) in Osaka, Japan 2015 - 2016

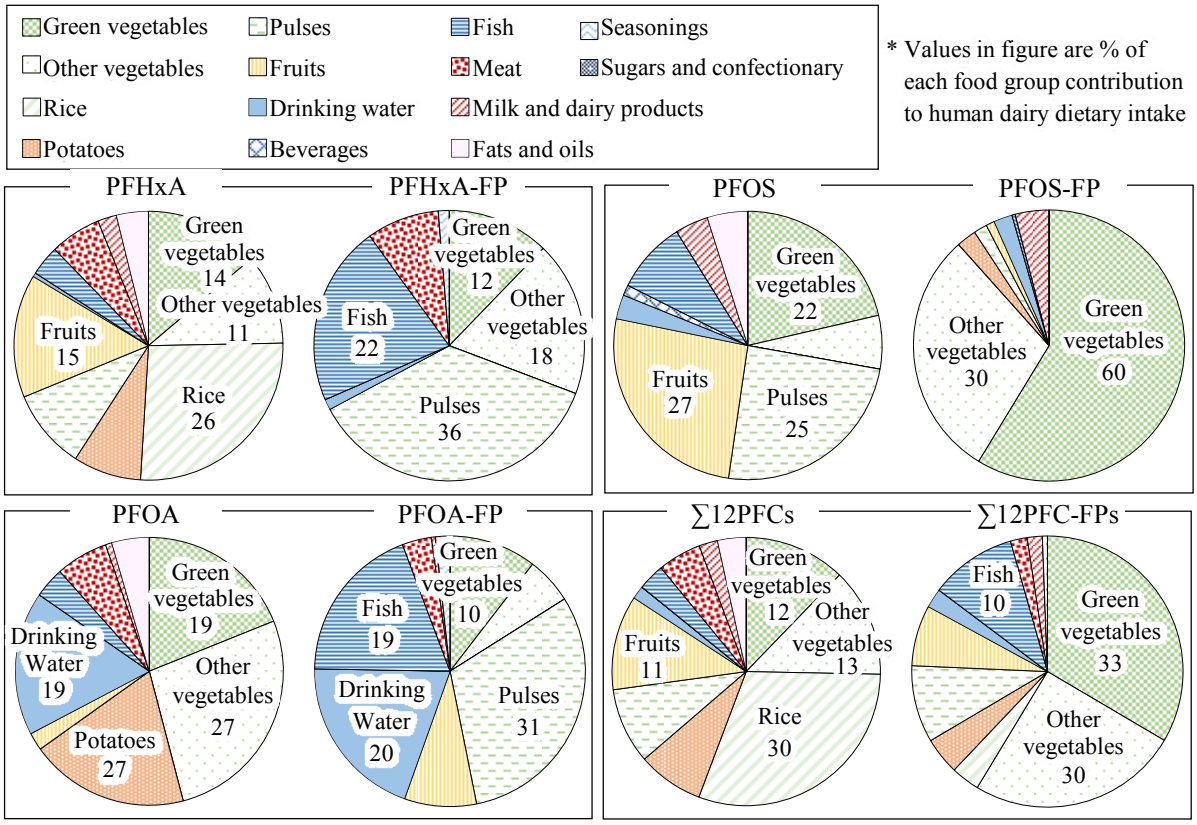

Figure 3 Contribution of each food group to dietary intake of PFCs and PFC formation potentials (PFC-FPs)

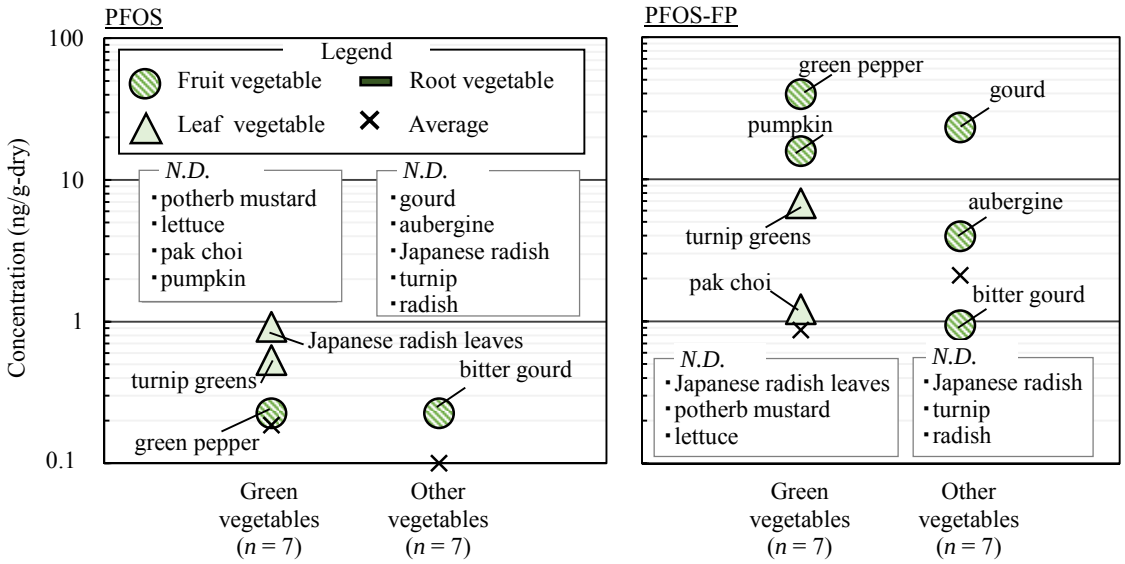

Figure 4 PFOS and PFOS formention potential (PFOS-FP) concentration in different types of vegetables