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EVALUATION OF PERFLUOROALKYL SUBSTANCES RESIDUES IN CUCUMBER, GREEN PERILLA, AND POTATO, JAPAN

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Introduction

In the last 50 years, commercial production of perfluoroalkyl substances (PFASs) have been widely used in industry as adhesives, coatings, in fire-fighting forms, etc. Until 3M stopped the manufacturing of PFOS in 2003, total production was about 100,000 tons from 1970 to 2002¹. After then, China began large scale production. Manufacturers increased their production dramatically in recent years. However, it was known that PFASs such as PFOS and PFOA were one of the persistent organic pollutants (POPs) under the Stockholm convention². Thus, numerous studies have been reported that PFASs widely affect the environment, wildlife and human beings around the world. Those studies reported increasing levels of PFASs in the environment within the food chain. There was a crucial need to gather database of food which assesses the potential risks associated with human exposure to PFASs. However, the data regarding PFASs residues in vegetables are still insufficient. And also the analytical methods for quantification of PFASs in food are necessary in order to understand and quantify dietary human exposure to PFASs. The aim of this study is to develop the clean-up method in vegetable samples and to determine concentrations of PFASs in different types of vegetables from Tsukuba city (East Japan) and Osaka city (West Japan) and to compare the regional difference of PFASs residues.

Materials and methods

We cultivated and collected samples from different types of vegetables, cucumber (fruit vegetable), green perilla (leafy vegetable), and potato (root vegetable) from Tsukuba city (East Japan) and Osaka city (West Japan). In order to develop the fast clean-up method in vegetable samples like a QuEChERS (Quick Easy Cheap Effective Rugged and Safe) pesticide multi-residue method, Supel Acetate, Supel Z-Sep+, and Supel PSA-C18-Envi-Carb were tested. To make it brief, 5 g portions of vegetable sample were mixed with 25 ml of acetonitrile for extraction. The sample is homogenized for 30 sec. at 11000 rpm /min to get rid of the plant tissue. After the centrifugation (3000 rpm, 20 min.), the supernatant was transferred in a new PP tube. ¹³C-labeled internal standard reagents were added into all samples to calculate the recovery of surrogates using standard detection method. Extractors were evaporated to ~5 mL by under a nitrogen stream. Envi-Carb (100 or 200 mg) cartridges, previously conditioned with 3 mL of methanol (3x 1mL) and loaded the analytical samples and eluted with 3 mL of methanol (3x 1mL) and Milli-Q water until 100mL. All collected samples were clean-up using by solid-phase extraction with solid phase extraction-weak anion exchange cartridge (Oasis WAX 150 mg). This clean-up procedure and determination of PFASs were derived from our previous work³. QAQC criteria is based on ISO method (ISO025101: Water quality). To detect the PFASs compounds only the RSpak-JJ50 column was used. The QC standard is under good condition if coefficient of variance (CV) is below 20% for every compound. Limit of Quantitation (LOQ) is the lowest analyte concentration at which quantitative results can be reported with a high degree of confidence. The acceptable range of recovery is 70% to 125%. The recovery range of compounds was in acceptable range except FOSA78 (C₈F₁₇SO₂NH₂), N-EtFOSA (C₁₀F₁₇SO₂NH₆), PFOcDA869 (C₁₇F₃₅CO₂H). The standard deviation (SD) of all compounds were below 30%, thus the repeatability of the experiment was acceptable.

Results and discussion

We conducted different clean-up procedures in order to develop a fast clean-up method suitable for vegetables. It was tested with Supel Acetate, Supel Z-Sep+, and Supel PSA-C18-ENVI-carb. Supel Acetate showed that the average recovery rate for PFASs was 80%. Supel Z-Sep+ was 80% for sulfonate compounds while 0% for carboxylate compounds. However, Supel PSA-C18-ENVI-carb for the removal of pigment such as chlorophyll showed that ¹³C-labeled internal standards of PFASs were very poor. It is

probably because Supel PSA-C18-ENVI-carb was strongly adsorbed for PFASs. Thus, ENVI-carb was employed as a pigment removal SPE, since ENVI-carb was relatively weaker adsorption material for PFASs than that of C18. ENVI-carb showed that the recovery rate ranged from 71% to 110%. Among the vegetables in this study, the extracts of green perilla, green pepper, pigment and Chinese cabbage showed the dark green color. When ENVI-carb (200 mg) was used in these extracts of vegetables, the recovery rate of PFASs was acceptable and the best removal efficiency of the color was achieved. It was reported that PFOA in the waste water at Osaka city detected the highest concentration of 570 ng/L in 2007, and decreased to under 67 ng/L in 2009⁴. The concerns about PFASs in food have been increasing in Japan, thus, this study provides some information about PFASs in vegetables. We selected three different types of vegetables, cucumber (fruit vegetable), green perilla (leafy vegetable), and potato (root vegetable), respectively. These types of vegetables have different cultivation thus the chemical effect can differ as well. The amount of cucumber, green perilla, and potato intake per day for Japanese⁵ was 31 g, 1.3 g, and 24.9 g, respectively.

Fig. 1 shows the concentration of sulfonate and of carboxylate PFASs compounds in cucumber, green perilla, and potato. Although the straight-line distance between Tsukuba city (East Japan) and Osaka city (West Japan) is approximately 500 km, there was no significant regional difference of PFASs residues in those vegetables. Especially, perfluoroalkyl sulfonic acids were in almost negligible quantities. The concentration of PFASs compounds in Osaka vegetables are relatively higher than that of Tsukuba except for PFOS80 ($C_8F_{17}SO_3H$), PFOA369 ($C_7F_{15}CO_2H$), PFOA169 and 10:2FTUCA ($C_8F_{16}CO_2H$) in cucumber, PFBA169 ($C_3F_7CO_2H$), PFPeA219 ($C_4F_9CO_2H$) and PFTeda669 ($C_{13}F_{27}CO_2H$) in green perilla, PFOS80, N-EtFOSA ($C_8F_{17}SO_2NH_2$), PFHpA319 ($C_6F_{13}CO_2H$), PFOA369, PFOA169, PFNA419 and PFNA219 ($C_8F_{17}CO_2H$) in whole potato. In cucumbers, the short-chain PFASs such as PFBA169 and PFPeA 219 ($C_4F_9CO_2H$) showed remarkably high concentration. It indicated that cucumber is easy to uptake the short-chain PFASs from soil-water by its high solubility. Especially, PFBA is known to have similar toxicity as PFDA and PFOS. The onset and duration of toxicity are dependent on the perfluoro chain length. PFNA419, PFPeA219, PFOA 169, and PFOA 369 are mainly detected in whole potato with its skin. Although the samples were pretreated with water, the skin of the potato absorbed the soil particles on its surface. (not shown here.) The observed pattern of PFASs probably indicated the difference of soil components between Tsukuba and Osaka cultivated field. Therefore, these results suggest that if root vegetables remove its skin, the risk of toxicity for PFASs will decrease. On the other hand, PFHxDA769 ($C_{15}F_{31}CO_2H$), PFBA169, PFPeA 219, PFOA 169, and PFOA 369 showed relatively high concentration in green perilla. Generally, leafy vegetables were directly affected on their surface from atmosphere and rain water. The result showed short-chain and long-chain perfluorinated chemicals residue in green perilla. Among them, PFOcDA869 ($C_{15}F_{31}CO_2H$) which has the highest concentration (478.6 pg/g wet weight) in this study. Although the emission source of PFASs is still not clear, cucumber, green perilla, and potato were mainly affected by perfluoroalkyl carboxylic acids. Finally, it would be useful to conduct further study to investigate the accumulation pathway of PFASs in vegetables.

References

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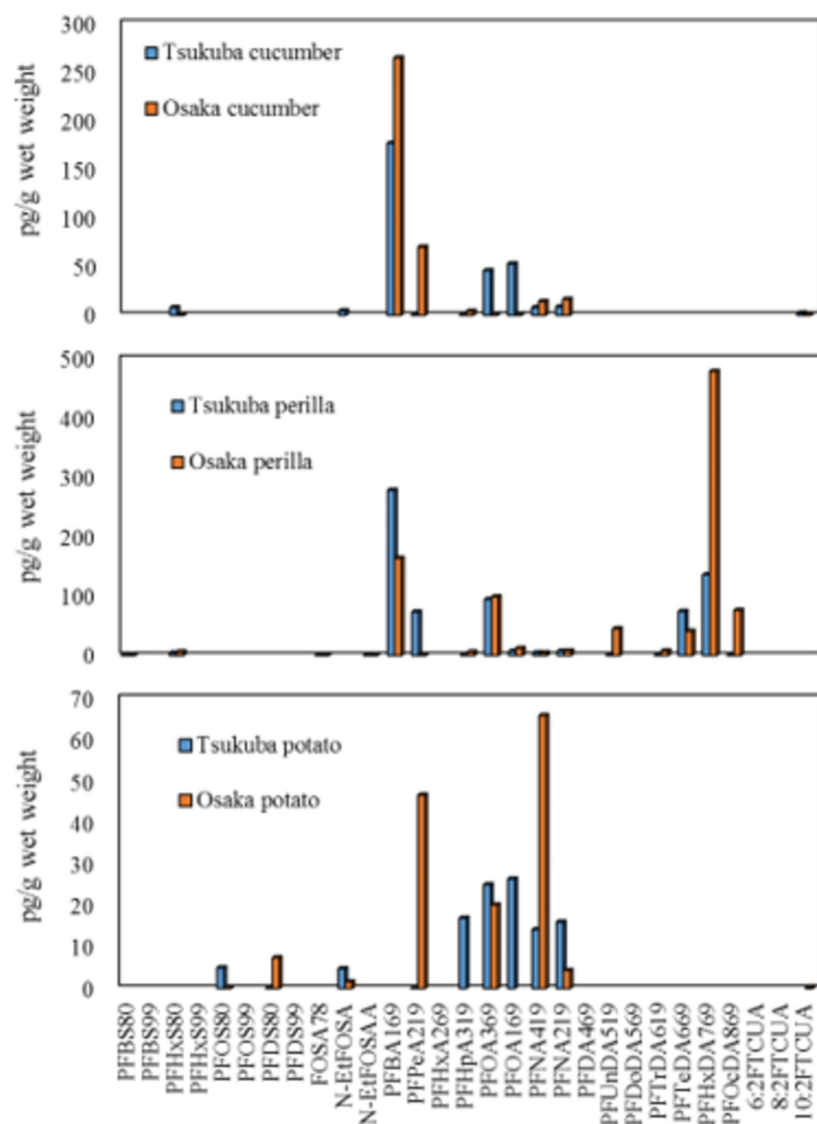


Fig.1. Comparison of PFASs between Tsukuba and Osaka