



Evaluation of perfluoroalkyl substances in field-cultivated vegetables

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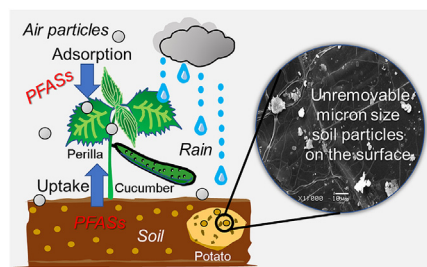
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HIGHLIGHTS

- This is the initial report of PFAS analysis in leafy, fruit and root vegetables cultivated in an open-field in Japan.
- Short-chain PFCAs under C9 were mainly detected in the vegetables.
- PCA indicates that PFASs residue in vegetables shows different composition profiles in soil, air, and rainwater.
- Although potatoes were washed with water, the unremovable soils on peel affected the concentrations of PFASs residues.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluoroalkyl substances (PFASs) were investigated in three types of vegetables (fruit, leafy, and root vegetables) that were cultivated and harvested from 2014 to 2017. The cultivated soil was mainly affected by perfluoroalkyl carboxylic acid (PFCAs; 91.8% detection rate) rather than perfluoroalkyl sulfonic acids (PFASs; 8.2%). The cultivated soil (i.e., a volcanic cohesive soil) had a high total organic carbon (TOC = 3.4%) and therefore showed strong adsorption of long-chain PFASs. Short-chain PFCAs (i.e., under C9) were mainly detected in vegetables; specifically, PFBA showed high concentration in tomato shoots. Principal component analysis (PCA) plots clearly showed that PFASs in vegetables were different from those of cultivated soil, air, and rainwater. Interestingly, the whole potato (i.e., including peel) was in the same group as soil, indicating that the whole potato can easily be affected by the cultivated soil. Energy Dispersive X-ray Spectrometry-Scanning Electron Microscope (EDS-SEM) results showed that presence of unremovable micron-sized cultivated soil particles on the potato surface. Comparing the regional

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differences between the cultivated area of Tsukuba city (East Japan) and Osaka city (West Japan), PFASs patterns were similar in cucumber but differed in green perilla and potato.

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1. Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are commonly-known substances in a group of perfluoroalkyl substances (PFASs), which include perfluoroalkyl sulfonic acids (PFASs), perfluoroalkyl carboxylic acid (PFCAs) and many other compounds. Strong carbon-fluorine bonds are present in PFASs and are hydrophobic, lipophobic, and dissipate with extreme heat (Krafft and Riess, 2015). Thus, PFASs have been widely used as adhesives, coatings, and in fire-fighting foams (Buck et al., 2011). However, PFOS and PFOA are persistent, bioaccumulative, and toxic to different organisms including humans (Kannan et al., 2001; Yamashita et al., 2005). Therefore, they were included in Annex B of the Stockholm Convention on Persistent Organic Pollutants in 2009 (Secretariat, 2009). Consequently, manufacturing and importing has been prohibited, and the use of PFOSs and the associated salts for nonessential purposes has been prohibited in Japan, after PFOSs were designated as a class 1 specified chemical substance by the chemical substances control law (effective on May 2010). An exception to this is that the use of PFOS (or its salts) is permitted for the production of etching agents, resistors for semiconductors, and commercial photographic film.

After 3M ceased the manufacturing of PFOS in 2003, China commenced large-scale production until recent years (Zhang et al., 2012). Due to their persistence, toxicity, and atmospheric transport, PFASs present a growing concern in Japan. Water and food consumption are generally considered the two major sources of PFASs in humans, although air and air-suspended dust, food packaging, and cookware also contribute to the overall PFAS load in the human body (Tittlemier et al., 2007).

Although many other sources of PFASs (e.g., air and dust) contribute to PFAS exposure to humans, ingestion via food and drinking water are considered to be the major routes of human exposure (Tittlemier et al., 2007). Among food types, fish is considered one of the most important sources of PFASs in humans (Brambilla et al., 2015; Christensen et al., 2017). Thus, vegetable consumption has been considered to be a less important source of PFASs intake (Domingo et al., 2012), although vegetables have been demonstrated to bioaccumulate short-chain fluorinated chemicals when grown in contaminated soil (Lechner and Knapp, 2011). However, the presence of PFASs residues in edible parts of vegetables have mainly been observed in a basket study and there remains limited knowledge about PFASs in agricultural environments. Vegetables may represent a non-negligible source of human intake of PFASs, even in the absence of bioaccumulation. In addition, the basket study included limited geographical regions, and the variety of vegetables consumed in typical Asian and Western diets are generally quite different. Only a few studies have so far reported on the occurrence of PFASs in agricultural soils in Asia (Li et al., 2010; Kim et al., 2014; Choi et al., 2017). Since vegetables are arguably the important ingredient of the human diet for the maintenance of health, the toxicity, mobility, and bioaccumulation potential of PFAS pose potential adverse effects to human health, as well as the environment.

The objective of the present study was thus to investigate the presence of PFASs in field-cultivated vegetables. The profiles and concentrations of PFASs in three types of vegetables (fruit, leafy,

and root vegetables) were assessed to investigate their accumulation. To investigate regional difference, the differences of PFASs in vegetables between Tsukuba city (East Japan) and Osaka city (West Japan) were also evaluated.

2. Materials and methods

The cultivated field used in the study was the Institute for Agro-Environmental Sciences, NARO (NIAES) agricultural experimental station in Tsukuba city, Japan. Plant species in this study were; tomato (*S. lycopersicoides*), cucumber (*Cucumis sativus*), eggplant (*Solanum melongena*), green pepper (*Capsicum annuum*), zucchini (*Cucurbita pepo*), green perilla (*Perilla frutescens*), crown daisy (*Glebionis coronaria*), spinach (*Spinacia oleracea*), carrot (*Daucus carota subsp.*), sweet potato (*Ipomoea batatas*), and potato (*Solanum tuberosum*). Sufficient fertilizer (N10P10K10) was added to the cultivated field. Each vegetable was planted on five stumps which had been collected in the periods of spring to summer in 2014–2017. Each vegetable sample was harvested from each of the five stumps at its appropriate time and transported to the laboratory as quickly as possible. The individual sample was well-mixed to produce final composite sample as per the analysis.

To compare and evaluate the general differences between the cultivated area (Tsukuba city, east Japan) and Osaka city (west Japan), three different types of vegetables: cucumber (fruit vegetable), green perilla (leafy vegetable), and potato (root vegetable) were collected in Osaka city, which is the 3rd city and industrial area in Japan. The direct distance between Tsukuba city and Osaka city is approximately 500 km. In Osaka city, PFOA in wastewater were at the highest concentration of 570 ng/L in 2007 and decreased to <67 ng/L in 2009 (Murakami and Takizawa, 2010).

Analysis of total organic carbon (TOC) in the cultivation soils was carried out on a Sumigraph NC analyzer NC-22F (Sumika Chemical Analysis Service, Osaka, Japan). The air-dried fine soil (<2 mm) used for measuring the carbon concentration was oven-dried at 105 °C for 24 h and weighed to determine the soil moisture content. The carbon concentration of fine soil was determined using the dry combustion method.

Samples of composite soil using ten points in all directions of the field were taken and mixed. Water extraction of the soils was carried out in accordance with the standard batch sorption test method. Twenty-five milliliters of Milli-Q water was added to 20 g dry weight (dw) of soil in a 50-mL polypropylene (PP) centrifuge tube. The tubes were agitated on a thermostat shaker (TAITEC, Saitama, Japan) for 24 h at 25 ± 2 °C in the dark. After shaking, the mixtures were centrifuged at 1200×g for 30 min. This extraction procedure was repeated three times. In addition, 25 mL of methanol was added to the remaining sample. The collected supernatant was evaporated in a rotary evaporator to reduce the volume to approximately 4 mL and was then used to quantify the methanol extracts.

All samples were analyzed following the modified International Standard Method ISO25101 and ISO/CD 21675 (ISO25101., 2009; ISOC21675., 2017). The method used the same reagents, methods, and instrument conditions as described previously (Yamazaki et al., 2019).

Briefly, 5-g portions of vegetable and fruit samples were mixed

with 25 mL of acetonitrile for extraction. The sample was then homogenized for 30 s at 11000 rpm to remove plant tissue. Following centrifugation (3000 rpm for 20 min), the supernatant was transferred into an unused PP tube, and ^{13}C -labeled internal standard reagents were added to calculate the recovery of surrogates using standard detection methods. Extracts were evaporated to ~5 mL under a nitrogen stream. Envi-Carb (100 or 200 mg) cartridges were previously conditioned with 3 mL of methanol (3 x 1-mL aliquots) and were loaded with samples and eluted with 3 mL of methanol (3 x 1-mL aliquots) and Milli-Q water to a final volume of 100 mL. Samples were cleaned by solid-phase extraction using solid phase extraction weak anion exchange cartridges (Oasis WAX 150 mg). This cleaning procedure and determination of PFASs were derived from our previous work. The QA/QC criteria was based on the ISO method (ISO25101., 2009). To detect PFAS compounds, RSpak JJ-50 2D column (2.0 mm i.d., 150 mm length, 5 μm ; Shodex, Showa Denko K.K., Kawasaki, Japan) and Keystone Betasil C18 column (2.1 mm i.d., 50 mm length, 5 μm , 100 Å pore size, endcapped) were used. The external calibration curves were constructed using a concentration series of 10, 50, 200, 1000, 5000, and 20000 $\mu\text{g mL}^{-1}$. The limit of quantification (LOQ) is the lowest analyte concentration at which quantitative results can be reported with a high degree of confidence. The range of matrix recoveries for soil, soil water and vegetables, was 84–112%, 84–105% and 55–119%, respectively. Six perfluoroalkane sulfonic acids (PFDS, PFOS, PFHxS, PFBS, PFPrS, PFETs), fourteen perfluoroalkyl carboxylic acids (PFODa, PFHxDA, PFTEda, PFTrDA, PFDoDA, PFUnDA, PFDA, PFNA, PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA), Perfluoroalkane sulfonamides (FOSA), N-Ethyl perfluoroalkane sulfonamides (N-EtFOSA), N-Ethyl perfluoroalkane sulfonamidoacetic acids (N-EtFOSAA), and unsaturated fluorotelomer carboxylates (8:2FTUCA) were analyzed by high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) using HP1100 liquid chromatography (Agilent Technologies, Palo Alto, CA) interfaced with a Micromass (Beverly, MA) Quattro Ultima Pt mass spectrometer.

2.1. Scanning electron microscopy/energy dispersive X-ray (SEM/EDS) analysis

The morphological features of the potato and soil particles on the surface were analyzed by scanning electron microscopy (SEM; JEOL JSM-5610 LV, Tokyo, Japan). The elemental analysis on the surface utilized energy dispersive X-ray (EDS). We detected 11 elements (C, O, Na, Al, Si, Fe, Mg, Cl, K, Ca and Ti) in the samples.

2.2. Principal components analysis (PCA)

Principal component analysis (PCA) is described by inter-correlated quantitative dependent variables. Thus, PCA can be display the pattern of similarity of the observations and of the variables as points in maps. In the study, PCA was performed to observe the dispersal patterns of all samples and their relationship. Therefore, we used the method based on the correlation matrix. The data were analyzed by the BellCurve for Excel (Social Survey Research Information Co., Ltd., Japan) and MS Excel.

3. Results and discussion

The cultivated area is located in Tsukuba city, which was designated as a special city with a center for research and education in Japan, and is the location of the majority of public research institutes and organizations. Thus, there is no large industrial emission source of PFASs. The open field-vegetables are commonly grown method in Japan. In particular, in the case of open field-

vegetables, it is a common practice to cultivate depending on the rainwater without special water irrigation supply. In this study, vegetables were planted in May and harvested from June to July. During this period, the water in the field soil is sufficient due to rainwater. In particular, June is a rainy season, the soil has as much moisture as the vegetable cultivation. Thus, the tested field can keep soil moisture enough to grow vegetables in normal cultivation. Since the volumetric water content of volcanic ash soil is 50–60% on average per year (Okuyama, 1988), vegetables can be cultivated without irrigation. Therefore, special irrigation was not performed in this test. In other words, only rainwater was the source of irrigation for cultivation. Indeed, the used the experimental station on the cultivation test site has no history of adding PFASs so far, and it has never been irrigated since. Therefore, the high possibility is only the PFASs accumulation in the soil and vegetables by PFASs through air and rainwater.

Concentrations of PFASs in cultivated soil and vegetable groups cultivated and harvested from 2014 to 2017 are shown in Fig. 1. The detection rates (%) show that the cultivated soil was mainly affected by PFCAs (91.8%) rather than PFSAs (8.2%). The order of detection rates of PFAS in the cultivated soil was PFNA (15.3%) > PFBA (13.8%) > PFHpA (12.2%). Ge et al. reported that PFHxA, PFHpA, PFOA, and PFNA were mainly detected in air particles in the area (Ge et al., 2017). In addition, the major PFASs found in rainwater are PFBA, PFNA, and PFOA (Taniyasu et al., 2013). In the past, PFNA production was primarily in Japan (Prevedouros et al., 2006), and the source of PFNA is also known that a degradation product derived from fluorotelomer alcohols (FTOHs) e.g., 8:2 FTOH can decompose into C5–C9 PFCAs through OH radical oxidation (Ellis et al., 2004).

There is a high possibility that the cultivated soil was mainly affected by PFASs in air and rainwater. Interestingly, PFASs in soil extracted with water were in the order of PFBA > PFHpA > PFPeA, whereas those in soil extracted with methanol was in the order of PFUnDA > PFNA > PFOS. In soil extracted with water, PFSAs were relatively insoluble in water, whereas PFCA (under C9) compounds exhibited high water solubility. The result indicated that high carbon content in cultivated soil can capture PFSAs and PFCA (over C10) compounds. In this regard, the soil was exposed to more PFCAs, however, alternatively, it may have been detected at this level due to leaching into the ground as a result of high water solubility. Indeed, the cultivation soil is a volcanic cohesive soil, i.e., it has a high TOC content, which is one of the most important parameters which provide an assessment of PFASs in agricultural soils.

The organic carbon content is generally known as a dominant parameter affecting PFAS adsorption in soil (Zhao et al., 2016), which is correlated with adsorption of PFASs in sewage sludge and sediments (Gellrich et al., 2012; Zhao et al., 2016). It may be inferred that long-chain PFASs were strongly adsorbed in soil with high organic carbon content, making it difficult to dissolve in the water phase and leading to the limited transfer of long-chain PFAS into plant tissues. In the present study, the TOC in the cultivation soil was high (3.4%). This can be partially explained in that organic carbon of the cultivation soil may easily capture relatively water-insoluble PFSAs and longer chain PFCAs.

The range of detection rates of PFOA was 0.1% in green perilla to 14.3% in spinach; PFOS was not detected in leafy vegetables. For PFBA, the percentage of total PFASs was high, at 35.1% in spinach and 88.8% in crown daisy. In particular, PFCAs (over C10) compounds were detected more frequently in leafy vegetables compared with fruit and root vegetables. A well-known pathway of PFAS accumulation in plants is aerial transport of volatile or particle-bound precursors, which can be absorbed by plant leaves with further metabolization to PFCAs and PFSAs (Yoo et al., 2011;

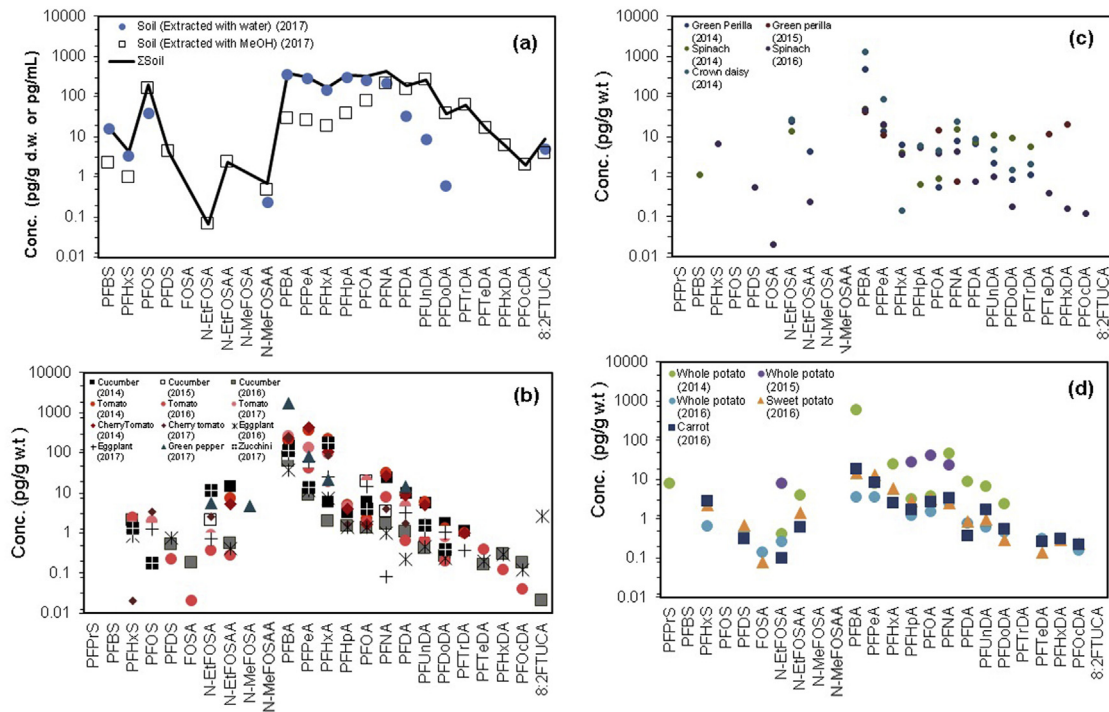


Fig. 1. Concentration of PFAS in cultivated soil (a) and vegetable groups such as leafy (b), fruit (c) and root (d) vegetables cultivated and harvested from 2014 to 2017.

Rankin et al., 2016).

In fruit vegetables, the percentage range of PFCAs was 93.9% in cucumber to 99.2% in tomato. This is similar to the results of several previous studies (Blaine et al., 2014; Navarro et al., 2017), where high rates of PFBA accumulation in fruits of tomato plants grown in amended soil were reported. The same effect of chain length on PFAS distribution across vegetables were also found in tomato and zucchini, with those with shorter-chain lengths being found in leaves and fruits.

In particular, PFASs in fruit vegetables showed relatively similar patterns with the soil extracted with water compared with leafy and root vegetables. In general, the pathway of many chemical residues (such as organic chemicals) in fruit is known to be via uptake of water from soil. In this respect, the accumulation of PFASs in fruit can be explained through uptake of water-soluble PFASs in soil.

In Fig. 2, the principal component analysis (PCA) plot clearly showed that PFASs in vegetables were different from those of cultivated soil, air, and rainwater. The PCA plot separated cultivation and environmental factors (soil 1 [extracted with ethanol], air, rainwater, and soil 2 [extracted with water]) and divided vegetables into four groups; group 1 represented the cultivation-environmental factors (soil 1 [extracted with ethanol] and air (Ge et al., 2017), group 2 represented rainwater (Taniyasu et al., 2013), group 3 represented soil 2 (extracted with water), and group 4 included vegetable samples. Initially, the approaches used for groups 1, 2, and 4 were completely separated; group 3 was separated and was located in the middle of groups 1, 2 and 4. The water-extracted cultivation soil sample (group 3) was distinct from groups 1 and 2. It was found that cultivated soil was mainly affected by particle-bound PFASs in the air. Although the major compounds of PFASs (PFNA, PFBA, and PFHpA) in soil were similar to those of rainwater (PFBA, PFNA and PFOA), the PCA result of PFASs shows similarity with air (PFHxA, PFHpA, PFOA and PFNA).

The results obtained from the PCA indicates that the residual PFASs in vegetable differed with the cultivation soil, air, and

rainwater, namely, each vegetable has its own.

Interestingly, whole potato (i.e., without peeling) were in group 1, indicating that the whole potato can be easily affected by the cultivation soil. In Fig. 3, the SEM images displayed the comparative morphological features of the potato peel and soil particles. The EDS analysis of potato peel was conducted to determine the presence of elements on the potato peel surface. The elements of the point 1 (potato peel) were mainly C, O, etc. (Fig. 3[a]). On the contrary, the elements of the point 2 (the white particle) were mainly Al, Si, O, Fe, etc; these were typical soil compounds such as alumina (Al₂O₃) and silica (SiO₂). It was clear that the white particles on the potato peel surface were micron-sized soil particles. Carrot and sweet potato also showed unremovable cultivated soil particles on their surfaces (data not shown). Helsing et al. reported that PFASs sorb to alumina surfaces (positively charged), forming a hydrated layer on soil (Helsing et al., 2016). In addition, PFOA and PFOS did

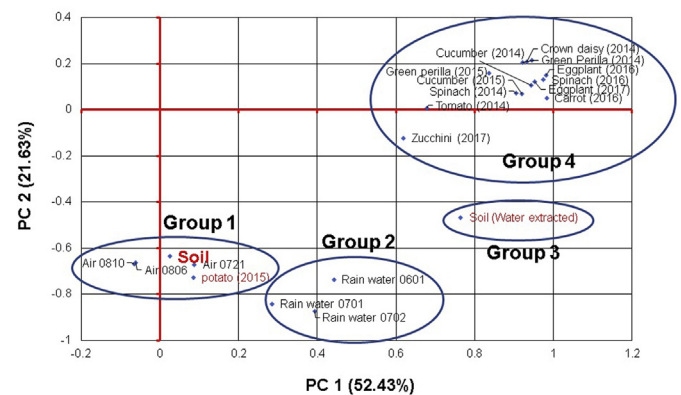


Fig. 2. Principal component analysis (PCA) score plot for all vegetables and its cultivated environment (soil, air and rainwater). PFASs data in air and rainwater in the cultivated area from Taniyasu et al. and Ge et al.'s results were used.

not sorb to silica (i.e., negatively charged) surfaces on soil, since the electrostatic interaction is the driving force in the sorption process. Therefore, our result indicates that unremovable cultivated soil particles remaining on root vegetables peel may greatly affect the risk posed to humans by PFASs.

For cucumbers, the percentage of PFASs distributed were 75% in Tsukuba city and 74% in Osaka city by PFBA (Fig. 4). This indicated that cucumber readily uptakes highly soluble short-chain PFCAs from soil-water. The toxicity of PFBA is similar to PFBA and PFOA in the liver (Gomis et al., 2018). Except for N-EtFOSA in Tsukuba city, PFASs were not detected in cucumbers in either study area. Furthermore, longer chain PFCAs and PFNAs were not detected. Cucumber plants mainly transport and accumulate these types of compounds from soil-water through their roots. The order of PFASs in green perilla (leafy vegetable) was PFBA (42%) > PFHxDA (20%) > PFOA (14%) in Tsukuba city, and PFHxDA (51%) > PFBA (17%) > PFOcDA (8%) in Osaka city; PFASs were not detected in samples from Tsukuba city.

Generally, the surface of leafy vegetables was directly affected by air and rainwater. Taniyasu et al. and Ge et al. reported the time-trend of rainwater and atmospheric monitoring about PFASs (Taniyasu et al., 2013; Ge et al., 2017). Based on their results, short-chain and long-chain PFASs in air and rainwater were detected in the Tsukuba area. Although the emission source of PFASs in Osaka city remains unclear, the general differences between Tsukuba city and Osaka city are likely to be due to different PFASs emission.

In potato, the patterns of PFASs were remarkably different between Tsukuba city and Osaka city; the order of PFASs was; PFOA (40%) > PFHpA (28%) > PFNA (23%) in Tsukuba city, and PFNA (49%) > PFPeA (35%) > PFOA (15%) in Osaka city. In this study, although potato samples were washed by brushing with water, soil particles remained on the surface of the potato peel. Hence, the pattern of PFASs may reflect differences in the soils of the two cultivated fields. Therefore, these results suggest that if vegetables

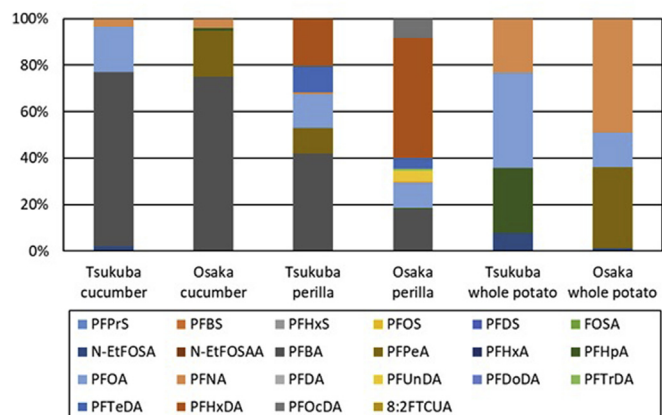


Fig. 4. PFAS composition profiles in cucumber (fruit vegetable), green perilla (leafy vegetable), and potato (root vegetable) in tested cultivated area (Tsukuba city, East Japan) and Osaka city (West Japan).

are peeled, the risk of toxicity from PFASs will decrease.

The distribution of PFASs in vegetables was found to depend on physicochemical and bio-accumulative properties of each vegetable. The results will contribute to the development of further studies on these compounds in vegetables as a response to current human health demands. Our results indicate that unremovable cultivated soil particles that remain on vegetable peel may greatly influence the risk posed by PFASs.

In this study, PFCAs under C9 were detected in all vegetables, and PFBA showed high accumulation; it has been shown that PFBA has similar toxicity as PFOA (Ge et al., 2017). Thus, further studies should investigate the accumulation pathway of PFASs in vegetables.

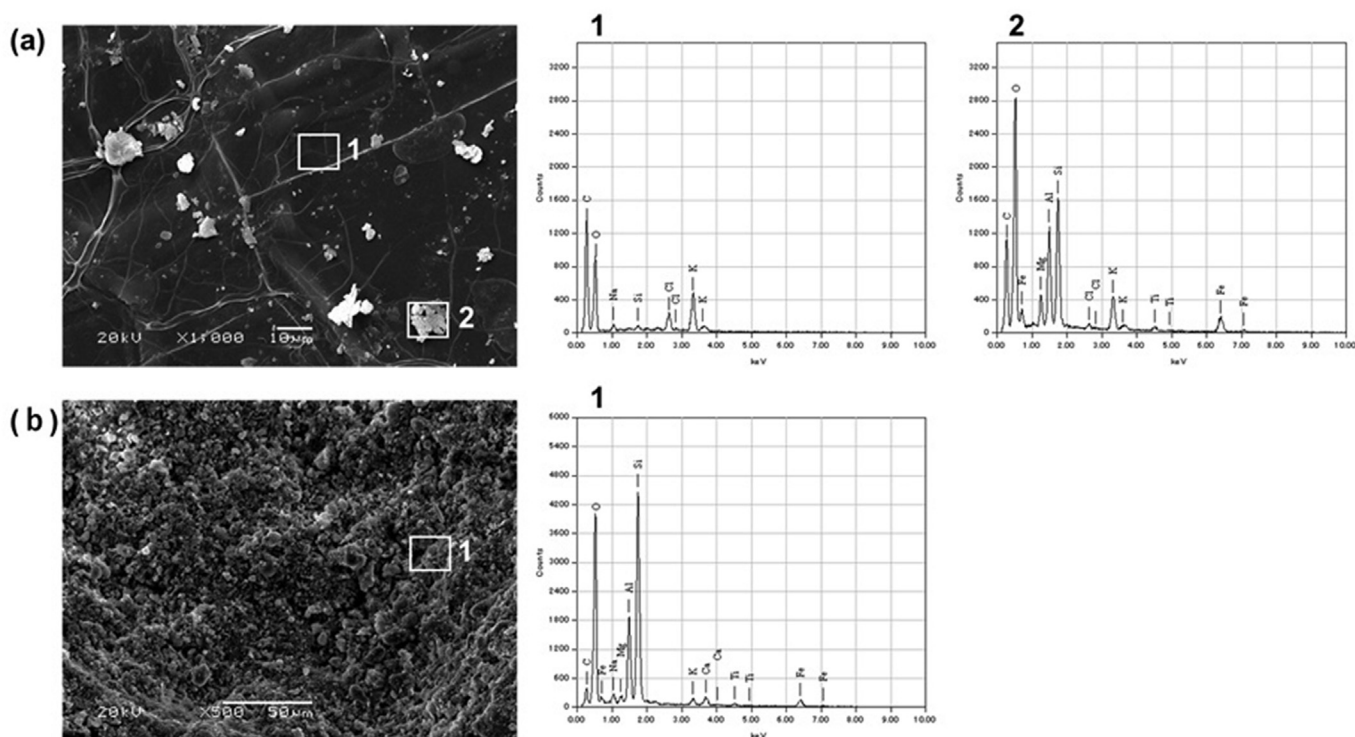


Fig. 3. Scanning electron micrographs (SEM) along with energy dispersive X-ray spectroscopy (EDS) of the outer epidermis of potato skin (1000X) (a) and cultivated soil (b) (500X).

4. Conclusions

Uptake of PFASs in food is related to physicochemical properties such as molecular structure and water solubility. Although PFASs compounds are no longer manufactured in Japan, many PFASs are used in numerous industrial products. The result demonstrates ultra-trace levels of PFAS residues in vegetables and cultivated soils. This is mainly due to the circulation of PFAS in the atmosphere and rainwater from various emission sources across the border. For vegetables cultivated and harvested in Japan, the PFAS residual pattern was similar for each kind of vegetable analyzed in this study, with the exception of unpeeled potato samples, for which the SEM analyses showed soil particles which were not removed by washing the skin surface. This study shows that PFCAs under C9 were mainly detected in all vegetables, with the highest accumulation of PFBA. Further studies are needed to understand the accumulation pathways of PFASs in vegetables and so enable mitigation of human health effects from consumption of contaminated vegetables.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124750>.

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