# Formation and Degradability of Per- and Polyfluoroalkyl Substances in River Soils around a Fluoropolymer Manufacturing Plant in Osaka, Japan

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## Abstract

Our previous studies reported that perfluorooctanoic acid (PFOA) contamination decreased in well, tap, and surface water around a fluoropolymer plant in Osaka, Japan between 2003 and 2016. In this study, we evaluated the degradability of PFOA and perfluorohexanoic acid in river soils to identify the influence of the degradation on the perfluorocarboxylic acids (PFCAs) in the Yodo River Basin. We also investigated the influence of abiotic oxidation on the formation of PFCAs in soils and measured the fluorotelomer alcohols (FTOHs) as precursors of PFCAs in the soil and air samples collected at Osaka and Kyoto, respectively. No major changes were observed in soils contaminated with PFCA during the 24-week experimental period, while the PFOA levels increased only in the control group. The PFCA levels significantly increased after oxidation in this group. The dominant FTOH in soils was 10:2 FTOH, whereas 6:2 FTOH was dominant in the air samples. These findings suggest that PFOA was rapidly removed from water system but persist in soils. Moreover, the results indicate the need to evaluate not only the PFCAs, but also the FTOHs and other precursors for the accurate prediction of PFCA accumulation and fates in the environment.

## Introduction

Per- and polyfluoroalkyl substances (PFASs) are a large group of chemicals that have been used since the 1950s. They are ingredients or intermediates of surfactants and surface protectors for assorted industrial and consumer applications. Several PFASs have been recognized as highly persistent, bio-accumulative and toxic (Banzhaf et al., 2017; Boiteux et al., 2017; Daly et al., 2018; Guelfo & Adamson, 2018; Harada et al., 2005; Sunderland et al., 2019) In particular, perfluorooctanoic acid (PFOA) is concerning because it is easily bioaccumulated and has a long half-life of 3.8 years in humans (Harada et al., 2005). Recent studies have found elevated levels of perfluorocarboxylic acids (PFCAs) in house dust; these findings strongly suggest there are indoor sources of these compounds (Banzhaf et al., 2017; Boiteux et al., 2017; Daly et al., 2018; Guelfo & Adamson, 2018; Guo et al., 2009). Previous epidemiological studies have reported the toxicity (Kennedy Jr. et al., 2004; Washino et al., 2009) and carcinogenicity (Barry et al., 2013; Vieira et al., 2013; Wen et al., 2020) of PFOA. In Japan, high levels of PFOA contamination have been reported in environmental samples and residents’ serum samples in the Kansai area (J. Liu et al., 2010b). Discharged water samples from sewage treatment plants (STPs) and findings from an ecological study show strong evidence that a fluoropolymer (FP) plant (Daikin in Settsu City, Osaka Prefecture) is the primary source of PFOA contamination (Ye et al., 2014). Consequently, the company has reduced use and emissions of PFOA. The plant has replaced PFOA with other PFCAs with shorter carbon-chain such as perfluorohexanoic acid (PFHxA) (Daikin Industries Ltd., n.d.; USEPA, n.d.).

In our previous study, we found that the PFOA concentrations in surface water and groundwater around the FP plant substantially decreased during 2003 to 2015 in the Yodo River Basin (Shiwaku et al., 2016). The decline of PFOA in the water environment may be due to decomposition of PFOA in soils and transfer of PFOA to other locations via river flow.

There are a few studies investigating PFAS degradation in soil (Luo et al., 2018; Zabaleta et al., 2018). A previous study of water samples collected from STPs in 2003 showed that wastewater from the FP plant in Settsu was released into surface water (6.6 t year$^{-1}$), air (2.3 t year$^{-1}$) and soil (1.2 t year$^{-1}$)(Niisoe et al., 2010). Therefore, when considering the trend of PFCA contamination in this area, it is necessary to clarify the current levels of PFCAs in the air and soil, as well as in the aquatic environment. Moreover, PFCA contamination is not only caused by PFCAs themselves, but also affected by the decomposition of precursors such as fluorotelomer alcohols (FTOHs)(C. Liu et al., 2010; Martin et al., 2005). Thus, it is necessary to consider the influence of the precursors on levels of PFCA contamination. Previous studies have reported that 8:2 FTOH is mainly biotransformed to PFOA and PFHxA. 6:2 FTOH is decomposed to PFHxA, PFPeA, and PFBA by biotransformation (J. Liu et al., 2010a; Remde & Debus, 1996; Wang et al., 2009). Furthermore, it has been reported that C4- to C11-PFCA concentrations increased by 121–220% an average (Ye et al., 2014) through the oxidation process in water samples. In this study, we collected soil from impacted sites. The aim of the study was to investigate the biotransformation of PFOA and PFHxA in the river soil at the major fluoropolymer (FP) plant (Daikin, Osaka Prefecture) experimentally. We also evaluated the influence of precursor FTOHs on the contamination of the area.

## Materials and Methods

**Sampling.** Artificially treated surface soils were collected at two locations: 1) along the Ai River in Osaka Prefecture at the major FP plant (Daikin) (Saito et al., 2004; Shiwaku et al., 2016) (OS, Figure 1) (N 34.759645°, W 135.533303°) on February 23, 2016, and 2) along the Kamo River, Kyoto Prefecture on March 20, 2016 (KS, Figure 1) (N 35.023752°, W 135.771872°). Polyethylene bags and metal scoops were used to collect the soil samples. The soil samples were used for the degradation experiment. Vegetation, large soil fauna, and stones were removed from the soil prior to passing it through a 2-mm sieve (OECD 2002). The collected soil samples were uniformly mixed and stored at 4°C until analysis. Air samples were collected at the Higashi-Yodogawa area in Osaka (OA, Figure 1) (34.7532929, 135.5539568) between November 15-17, 2016, and the Sakyo area in Kyoto (KA, Figure 1) (N 35.023530°, W 135.776898°) between November 30 and December 2, 2016. These air sampling sites were downwind from the FP manufacturing facility. Air sampling and treatment of sampling media were conducted as previously reported (Oono et al., 2008). In brief, quartz fiber filters (QF, 8 inch × 10 inch; QR-100, Sibata, Tokyo, Japan) were used to obtain the particulate matter. For the gaseous phase, we used glass columns (90 mm i.d.) with a polyurethane foam (PUF, 50 mm) followed by activated carbon fiber felts (ACF, 10 mm; KF-1700F, Toyobo, Osaka, Japan) as well as high-volume air samplers (HV-700F, Sibata, Tokyo, Japan) at approximate flow rates of 700 L $\text{min}^{-1}$ for 48 hours (h). Field blanks (ACF, PUF and QF) were carried to the sampling sites with each set of samples. After the collection, the samples were delivered to the laboratory immediately and kept at 4°C until analysis.

**Insert Fig. 1 here**

### Experimental Methods.

*Reagents*

Native and mass-labelled PFAS mixtures, PFAC-MXB and MPFAC-MXA (Wellington Laboratories, Guelph, ON, Canada) were used for external standards and recovery surrogates for PFCA analysis, respectively. 11H-perfluoroundecanoic acid was purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as internal standard for PFCA analysis. 4:2 FTOH (purity >98%), 6:2 FTOH (purity >98%), 8:2 FTOH (>97%) and 10:2 FTOH (>96%)

were purchased from Alfa Aesar (Ward Hill, MA). 8:2 FTOAcryl (>96%), was purchased from Lancaster Synthesis (Lancashire, UK). 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-1-nonanol (8:1 FA; >98%) was purchased from Wako Pure Chemicals and used for internal standard for FTOH analysis. 1D,1D,2D,2H,3$^{13}$C-perfluorodecanol (mass labelled 8:2 FTOH) was donated by the Environmental Protection Agency of the U.S.A. (originally synthesized by DuPont, Wilmington, DE) and used for recovery surrogate for FTOH analysis.

*Degradation tests*

Degradability tests were conducted following the method of Russell and colleagues (Russell et al., 2008) A total of 42 glass serum vessels were prepared and capped with crimp-sealed aluminum foil-lined closures. The vessels were incubated statically at 20 ± 2°C. Approximately 25 g dry weight equivalent of test soil were added to 21 vessels for each of the Kyoto and Osaka samples. Bacteriostatic treatments were performed with 5,000 µg of both chloramphenicol and cycloheximide to inhibit further microbial growth. Sodium acetate (2 µg/g) was used as positive control of biodegradation.

*Extraction and analysis of PFCAs*

We had three different types of soil preparation: 1) addition of PFOA (100 ng PFOA per 25 g soil in dry weight; 2) addition of PFHxA (300 ng PFHxA per 25 g soil in dry weight); and 3) no treatment (controls). Vessels from Groups 1, 2, and 3 were extracted and analyzed at 0, 1, 2, 4, 8, 16, and 24 weeks using the following method: 125 ml of acetonitrile, 10 ml of 200 mM NaOH and 10 µl of a $^{13}$C-labeled compound were added to each bottle to calculate the recovery rate. Each bottle was stirred for 3 h on a swing shaker (Powley et al., 2005). After filtration, the filtrate was concentrated with an evaporator. After evaporating the solvent, 5 ml of tetrabutyl ammonium buffer was added and transferred to a 15-ml tube. Next, 10 ml of MTBE was added, and the mixture was treated for 3 min at 1500 rpm using a centrifugal separator. The organic solvent layer was transferred to a glass test tube. The extract and internal standard solution (1 ng of 11H-PFUnDA) were dried at 60°C for 30 min while blowing nitrogen gas. Then, 100 μl of benzyl bromide/toluene was put in the glass test tube and transferred to a vial, heated at 100°C for 60 minutes. The concentrations of PFCAs in the soil were analyzed using gas chromatography-mass spectrometry (GC-MS) (Agilent 6890 GC/5973 MSD, Agilent Technologies Japan, Ltd., Tokyo, Japan)(Fujii, Yan, et al., 2012). PFCA benzyl esters were separated on a DB-5MS column (30 m length, 0.25 mm i.d., 1 μm film thickness; Agilent Technologies Japan, Ltd.) with a helium carrier gas (99.9999 % purity; Air Liquide Japan Ltd., Tokyo, Japan). Splitless injections (1 μL) were performed with an injector temperature of 220 °C, and the split vent was opened after 1.5 min. The initial oven temperature was 70 °C for 2 min, after which it was increased to 100 C° at 20 °C $min^{-1}$, and then to 280 °C at 30 °C $min^{-1}$. Negative chemical ionization (NCI) was used to quantify the PFCA benzyl esters. Methane (99.9999 % purity; Air Liquide Japan Ltd.) was used as the reagent gas (2 mL $min^{-1}$). The ion source and quadrupole temperatures were maintained at 150 °C and 106 °C. PFCA benzyl esters gave abundant fragment ions $[M\text{-}C_7H_7]^-$ in NCI mode and used as quantification ions. Fragment ions $[M\text{-}C_7H_7+1]^-$ were used as confirmation ions.

Standard stock solutions (2 μg $mL^{-1}$) were diluted to seven working standard solutions (4, 2, 1, 0.8, 0.4, 0.2, and 0.1 ng $mL^{-1}$) by serial dilution with acetone. Quantification was conducted using an internal standard, 11H-PFUnDA when target/confirmation ion ratios were within 20% of the standard values. Linear fitting of calibration curve was conducted, and linearity was confirmed at more the r>0.999 for PFCAs. $^{13}C_2$-labeled PFHxA,$^{13}C_4$-labeled PFOA, $^{13}C_5$-labeled PFNA, and $^{13}C_2$-labeled PFDA were used as recover surrogate standards for the

PFCAs. The MDL is defined as the concentration that produces a signal three times that of the blank. The extraction recoveries of PFCAs were examined for soil samples (n=7 fortified with PFCAs). Mean recovery rates of PFCAs were 94%, 88%, 95%, 98% and 93% for PFHxA, PFHpA, PFOA, PFNA and PFDA, respectively. Control experiments were conducted using agar powders (n=5) while no significant contaminations were observed. Limits of detection were calculated as the mean blank concentration within 3 standard deviations with 10 repetitions, ranging from 0.02 ng/g (PFHxA) to 0.15 ng/g (PFDA). QC samples (extracts from spiked soils) were analyzed in every 12 samples. Coefficient of variation (CV) of QC samples was 11.4%.

*Total oxidative precursor assay (TOP Assay) for PFCAs*

The Total Oxidizable Precursor (TOP) Assay is an oxidative sample pretreatment method aimed at converting the PFAS within a sample into the stable perfluoroalkyl acids. The levels of stable perfluoroalkyl acids can be quantified by conventional analytical techniques. This provides a greater understanding of the extent of PFAS within a sample. The oxidation is achieved by hydroxyl radicals. Radicals are formed under heated alkaline conditions from prescribed amounts of potassium persulfate and sodium hydroxide (NaOH) added to the sample prior to incubation.

In the oxidation test (Bolan et al., 2021; Houtz & Sedlak, 2012), 12 subsamples were taken from each soil sample. We analyzed levels of PFCAs (PFHxA, PFHpA, PFOA, PFNA, and PFDA) both before ($n$ = 6) and after ($n$ = 6) oxidation. The oxidation method was as follows: 25 mL of acetonitrile and a 10-mL aliquot of 200 mM NaOH was added to each sample. Samples were extracted for 3 h using a gyratory shaker table set at 250 rpm. One fifth of eluate was passed through filter paper. The eluate was evaporated to 0.5 mL to avoid the loss of the target compounds during the drying process. Then 5 ml ultrapure water with

0.5 g of potassium persulfate and 1 mL of 5N KOH were added. The pH of the samples was adjusted between 5 and 9 using NaOH prior to the extraction. Then the samples were then heated at 85°C for 6 h. Prior to analysis, samples were cooled at room temperature, and then analyzed with GC-MS as described above.

Fluorotelomer alcohols (*FTOH) analysis*

Analysis of FTOHs in soil samples was conducted using the same soil samples. Two glass bottles were prepared. Then 25 g dry weight of each soil was added. Then, 120 ml of 25% ethyl acetate in hexane and 1 ml of $^{13}$C-labeled FTOH were added. Next, the mixture was stirred with a swing shaker for 3 h. After filtration, the filtrate was concentrated using an evaporator. Hexane was added until the total amount reached about 30 ml, leaving about 2 ml of solvent. The extract was then washed with a silica gel column (Presep®-C Silica Gel, Wako Pure Chemicals), eluted in a glass test tube with 3 ml of 25% ethyl acetate/hexane, and evaporated to 0.5 ml under high purity nitrogen. 8:1 FA was added as an internal standard just prior to the GC-MS analysis.

The GC-MS analysis was based on the previous report (Mahmoud et al., 2009). GC-MS (Agilent 6890GC/5973MSD) in electron impact ionization (EI) mode was employed (GC-EI-MS). Analytes were separated on an HP-5MS column (30 m length, 0.25 mm i.d., 0.25 µm film thickness, Agilent Technologies Japan, Ltd.) with a helium carrier gas (99.9999 % purity; Air Liquide Japan Ltd., Tokyo, Japan). Splitless injections (1 µL) were performed with the injector set at 200 °C, and the split vent was opened after 1.5 min. The initial oven temperature was 50 °C for 4 min, ramped at 20 °C min$^{-1}$ to 140 C°, and then at 40 °C min$^{-1}$ to 240 °C, followed by a 1 min hold. The ion source and quadrupole were 230 °C and 150 °C, respectively. Fragment ions $[M\text{-}HF]^+$ for 4:2 to 10:2 FTOH and $[M]^+$ for 8:2 FTOAcryl were monitored as quantification ions in EI mode. Fragment ions $[M\text{-}2HF\text{-}F]^+$ for 4:2 to 10:2

FTOH and $[M+1]^+$ for 8:2 FTOAcryl were monitored as confirmation ions. Quantification was performed using standard curve analysis and the internal standard 8:1 FA when target/confirmation ion ratios were within 20% of the standard values. Standard stock solutions (2 μg $mL^{-1}$) were diluted to seven working standard solutions (100, 30, 10, 3, 1, 0.3, and 0.1 ng $mL^{-1}$) by serial dilution with ethyl acetate. Linear fitting of calibration curve was conducted, and linearity was confirmed at more the $r>0.999$ for FTOHs. The extraction efficiencies of FTOHs were evaluated by spiking the standard solutions of FTOHs on a soil sample (n=7). Mean recovery rates of analytes were 82%, 89%, 95%, 94% and 92% for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, and 8:2 FTOAcryl, respectively. Control experiments were conducted using agar powders (n=5). No significant contamination was observed. Limits of detection were calculated as the mean blank concentration within 3 standard deviations with 10 repetitions (Table 1). QC samples (extracts from spiked soils) were analyzed in every 12 samples and the CV of QC samples was 13.1%.

The FTOH analysis in air was conducted as previously reported (Oono et al., 2008). Air samples were collected on quartz fiber filters (QF 8″ x 10″; QR-100, Sibata, Tokyo, Japan) and in glass columns (90 mm i.d.) with a polyurethane foam (PUF 50 mm, Sibata) followed by activated carbon fiber felts (ACF 10 mm; KF-1700F, Toyobo, Osaka, Japan), using high-volume air samplers (HV-700F, Sibata) at flow rates of 700 L $min^{-1}$ for 24 hrs. For extraction of samples, the three sampling media were soaked for 10 min in 50 mL of ethyl acetate three times (150 mL total). The aliquots were combined and dried with sodium sulfate. Isotope-labeled 8:2 FTOH was added to all extracts to determine recoveries. The extracts were evaporated, and reconstituted into hexane. The concentrates were cleaned on a silica gel column (Presep®-C Silica Gel, Wako Pure Chemicals). The eluates were combined with 5 mL of 25% ethyl acetate in hexane. Finally, 8:1 FA was added as an internal standard just prior to the GC-MS analysis to correct for volume differences. The eluates were evaporated to 0.5 mL under high purity nitrogen. Then we analyzed the samples using GC-MS as described above. The LODs were shown in Table 1. To evaluate recovery in extraction, ACF spiked with target analytes (50 ng) were analyzed (n=5). Mean recovery rates were 79%, 85%, 93%, 92% and 88% for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, and 8:2 FTOAcryl, respectively.

**Insert Table 1 here**

## Results and Discussion

### *Degradability of PFCAs in Soil Samples*

Sodium acetate as a positive control showed 86.2±8.9% degradation after 24 weeks of observation. In the PFOA and PFHxA addition groups, no remarkable changes were observed in PFOA and PFHxA concentrations within 24 weeks (Fig. 2 (a)). Even after 24 weeks of measurement, the concentrations of PFOA and PFHxA were almost the same as those of Week 0. After 24 weeks, concentrations of PFOA were the same in Osaka (Ai River) soil concentration at baseline and 0.8 times the Kyoto (Kamo River) soil concentration at baseline. After 24 weeks, concentrations of PFHxA were 0.9 times the Osaka (Ai River) soil concentration at baseline and the same in Kyoto (Kamo Rivers) soil concentration at baseline. These results showed that PFOA and PFHxA are not easily decomposed in soil within a short period. Thus, this study supports the hypothesis that the short-term decline of PFCAs in the Yodo River Basin can be explained by transfer of PFCAs via river flow and diffusion into groundwater rather than by decomposition in river soil. Our previous study suggested that PFOA was distributed within the groundwater in the Yodo River Basin (Shiwaku et al., 2016). In addition, another study reported PFCA contamination downstream of the Ai River and estuary of Osaka Bay (Takemine et al., 2014). Therefore, this study suggests that PFCAs released into Ai River through STPs eventually flows out into Osaka Bay.

In contrast to PFCA addition soil groups, we observed increasing trends of PFOA concentrations in the control soil group. At 24 weeks, the PFOA concentrations were 1.8 times the Osaka (Ai River) soil concentration at baseline and 1.7 times the Kyoto (Kamo River) soil concentration at baseline (Fig. 2 (b)). These results suggest that the precursors contained in the soil may have decomposed into PFCAs over the 24-week study period.

**Insert Fig. 2 here**

### *Oxidation in Soil Samples*

The concentrations of PFCAs in soil increased significantly after oxidation in both Osaka soil (Ai River) and Kyoto soil (Kamo River) samples (Fig. 3 (a) and (b)). In the Osaka soil samples, the concentrations of PFHpA and PFOA increased significantly after oxidation. Similarly, PFHxA, PFHpA, PFOA, PFNA and PFDA were significantly increased in the Kyoto soils (Fig. 3 (a), (b)). The presence of precursors in the soil samples could indicate that PFCAs increased as a result of the decomposition of the precursors.

**Insert Fig. 3 here**

### *Fluorotelomer alcohols* (*FTOHs) in Soil and Air Samples*

In the Osaka (Ai River) soil samples, 10:2 FTOH (8.76 ng $g^{-1}$) was the dominant substance among the FTOHs followed by 8:2 FTOH (2.16 ng $g^{-1}$), 4:2 FTOH, and 6:2 FTOH, respectively. However, 8:2 FTOAcryl was not detected. In the Kyoto (Kamo River) soil samples, 10:2 FTOH (11.83 ng $g^{-1}$) was predominate, followed by 8:2 FTOH (2.63 ng $g^{-1}$), 6:2 FTOH (0.10 ng $g^{-1}$) and 8:2 FTOAcryl (0.005 ng $g^{-1}$). However, 4:2 FTOH was below the LOD (Table 2).

**Insert Table 2 here**

The highest concentrations of airborne FTOHs in Osaka near the Yodo River Basin were the 6:2 FTOH (122.3 pg $m^{-3}$), followed by 8:2 FTOH (75.3 pg $m^{-3}$), 4:2 FTOH (16.3 pg $m^{-3}$), 10:2 FTOH (14.5 pg $m^{-3}$), and 8:2 FTOAcryl (2.03 fmol $m^{-3}$). In Kyoto, near the Kamo river Basin, 6:2 FTOH (77.2 pg $m^{-3}$) was the most abundant compound among the FTOHs, followed by 8:2 FTOH (29.8 pg $m^{-3}$), 10: 2 FTOH (4.9 pg $m^{-3}$), and 8:2 FTOAcryl (0.23 pg $m^{-3}$), while 4:2 FTOH was below the detection limit (Table 3).

**Insert Table 3 here**

In this study, FTOHs were detected in both air and soil samples, but there were differences in ratios between the air and the soil. The most dominant FTOHs in soil samples were 10:2 FTOH, followed by 8:2 FTOH and 6:2 FTOH. In contrast, 6:2 FTOH was the most prevalent in the air samples, followed by 8:2 FTOH and 10:2 FTOH. We presume that the precursors of PFCAs with large molecular weights tend to be adsorbed to soils (J. Liu & Lee, 2007). Moreover, a previous study of the FTOHs in the air samples conducted at the Yodo River Basin in 2005 showed that the most prevalent FTOHs were 8:2 FTOH, followed by 10:2 FTOH, and 6:2 FTOH(Oono et al., 2008). In contrast, 6:2 FTOH was dominant in the air samples in the current study. This demonstrates differences in the mixture profiles between air and soil. The air samples reflect the recent situation in which the manufacturer has reduced the use of long-chain PFCs and switched to PFAS. However, the soil samples show the previous situation in which long-chain PFCs were frequently used, since it takes a long time for FTOHs in air to accumulate in the soil.

### *Formation of PFCAs in the Soil Samples*

Various organic fluorine compounds have been reported to be sources of PFCAs. Recent surveys have shown that concentrations of PFCAs increased due to biological treatment of wastewater containing FTOHs from a STP (Takemine, n.d.). Many studies also indicate that the metabolic oxidation of 8:2 FTOH leads to formation of PFOA (Butt et al., 2014). Yet, there is not a mass balance between the sum of the FTOHs before oxidation and the sum of the increase in PFCAs post-oxidation. This suggests that FTOHs could be changed into different carbon chain or shorter carbon chain PFCAs such as PFBA and PFHpA (Janda et al., 2019; Xu et al., 2021). However, we did not measure different carbon chain or shorter carbon chain in this study.

We compared two quantities: 1) the total molar concentration for the sum of the: a) concentration of FTOHs (pre-oxidation), which are precursors of PFCAs, and b) the concentration of PFCAs in non-oxidized soils, with 2) the total molar concentration of PFCAs after oxidation (Fig. 4). In the Osaka (Ai River) soil, the concentrations of PFHxA (C6) after oxidation were higher than the sum of PFHxA and 6:2 FTOH in non-oxidized soils. But the sum of the concentrations of PFOA (C8) and FTOHs of PFOA (C8) were substantially higher than the concentrations of PFOA (C8) in both the Osaka (Ai River) and Kyoto (Kamo River) soil samples. Similarly, the sum of the concentrations of PFDA (C10) and FTOHs of PFDA (C10) in non-oxidized soils were much higher than the concentrations of PFDA (C10) after oxidation in both the Osaka (Ai River) and Kyoto (Kamo River) soil samples.

The sum of the C8 and C10 concentrations of the PFCAs and FTOHs in non-oxidized soils was much higher than PFCAs concentrations after oxidation. In the case of 8:2 FTOH, the concentrations of PFOA after oxidation tended to be higher in the Osaka (Ai River) soil than the Kyoto (Kamo River) soil, even though the concentrations of 8:2 FTOH in the soil samples collected in the Ai River and Kamo River were almost the same. This showed that 0.70 pmol $g^{-1}$ (15.1% of 8:2 FTOH in the soil) were formed by oxidation in the Osaka (Ai River) soil, while and 0.28 pmol $g^{-1}$ (4.9% of 8:2 FTOH in the soil) were formed by oxidation in the Kyoto (Kamo River) soil. These results indicate that substances other than 8:2 FTOH in Ai River soil may have been degraded to PFOA by the oxidation process. Based on these results, we suggest that the transformation degradation of 8:2 FTOH to PFOA is about 5% in soil samples. Recently, a modified TOP assay that works without prior extraction has been conducted (Göckener et al., 2021; Meng et al., 2021).

In general, degradation and formation kinetics of substances in soil largely depend on the properties of soils and surrounding environmental conditions. Therefore, the dynamics of PFCAs in studied soils may not be generalized to other regions. Moreover, unmeasured substances, such as PFBA, PFPeA and other PFCAs or precursors, may affect the results in the oxidation process, which was not considered in this study. We conducted extraction of soil samples by acetonitrile for oxidation experiments. However, this type of extraction is not necessarily effective to extract acrylate-linked fluorotelomer polymer (AFTP) (Washington et al., 2009). In this case, potential PFCAs from AFTP may be underestimated.

Taken together, this study suggests that it is necessary to consider the influence of precursors when examining environmental pollution by PFCAs. Moreover, the results suggest that is possible to predict the potential environmental pollution of PFCAs by oxidizing the soil samples.

## Conflicts of Interest

The authors have no financial conflicts of interest regarding the publication of this paper.

## Author Contributions

Phayong Thepaksorn-reviewing, writing, editing. Pureum Lee- reviewing, writing, formal analysis, data management, Yoko Shiwaku- reviewing, writing, formal analysis, data management, Bo Zheng- reviewing, writing, formal analysis, data management, Akio Koizumi- conceptualization, data curation, funding acquisition, investigation, methodology, project administration, resources. Kouji H. Harada- conceptualization, supervision, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources.

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**Table 1** Detection limit of fluorotelomer alcohols in air and soil samples.

| | Limit of detection | |
|---|---|---|
| | Air (pg $m^{-3}$) | Soil (ng $g^{-1}$) |
| 4:2 FTOH | 8 | 0.1 |
| 6:2 FTOH | 4 | 0.07 |
| 8:2 FTOH | 2 | 0.05 |
| 10:2 FTOH | 3 | 0.1 |
| 8:2 FTOAc | 0.2 | 0.002 |

**Table 2** Concentrations of soil FTOHs in the Keihan area (pmol $g^{-1}$).

| Place | Latitude | Longitude | Date | 4:2 FTOH | 6:2 FTOH | 8:2 FTOH | 10:2 FTOH | 8:2 FTOAcryl | ΣFTOH |
|---|---|---|---|---|---|---|---|---|---|
| OS | 34.760047 | 135.53644 | 23 Feb. 2016 | N.D. | N.D. | 4.65 | 15.53 | N.D. | 20.19 |
| KS | 35.023171 | 135.771854 | 7 Mar. 2016 | N.D. | 0.27 | 5.67 | 20.97 | 0.01 | 26.92 |

N.D. = not determined.

**Table 3** Concentrations of airborne FTOHs in the Keihan area (fmol $m^{-3}$).

| Place | Latitude | Longitude | Date | 4:2 FTOH | 6:2 FTOH | 8:2 FTOH | 10:2 FTOH | 8:2 FTOAcryl | ΣFTOH |
|---|---|---|---|---|---|---|---|---|---|
| OA | 34.75329 | 135.553957 | 15 Nov.–17 Nov. 2016 | 61.91 | 335.79 | 162.26 | 25.66 | 3.93 | 589.56 |
| KA | 35.022858 | 135.776804 | 30 Nov.–2 Dec. 2016 | N.D. | 212.11 | 64.29 | 8.56 | 0.46 | 285.42 |

N.D. = not determined.

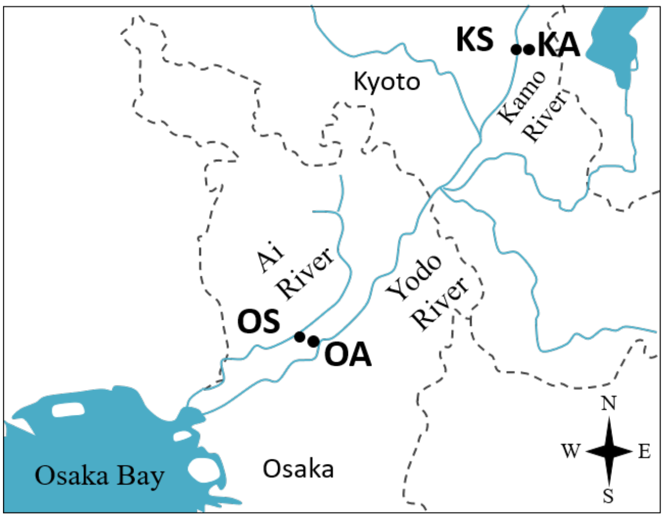


**Fig. 1** Sampling locations in Osaka and Kyoto, Japan. Blue lines represent rivers in this area. Sites OS (Osaka Soil) and KS (Kyoto Soil) represent soil sampling points, and OA (Osaka Air) and KA (Kyoto Air) represent air sampling points.

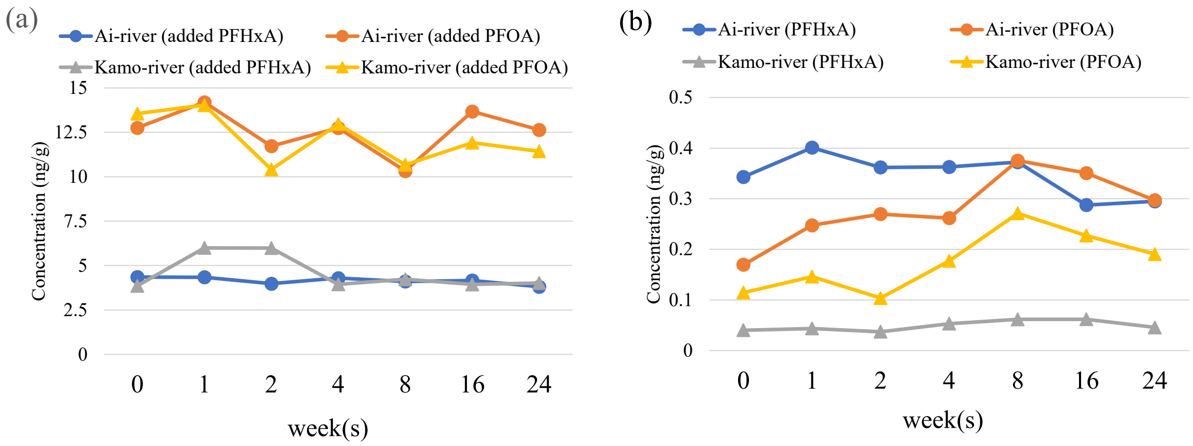
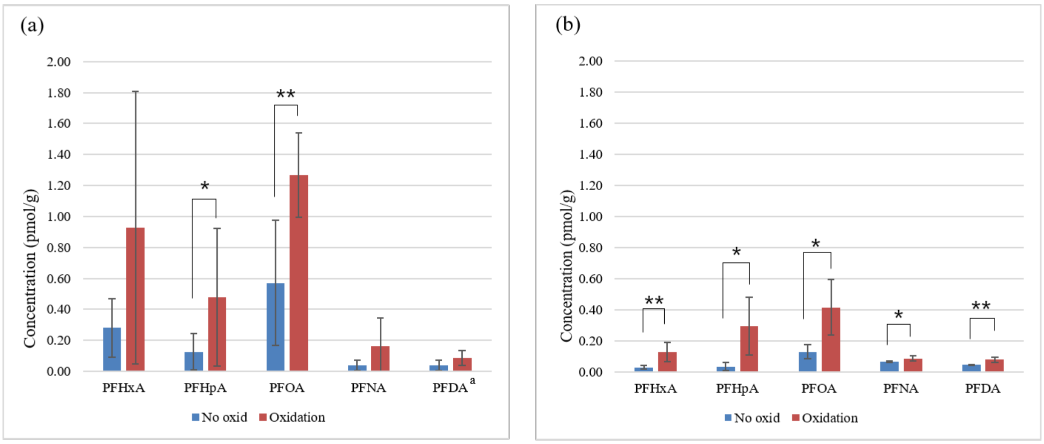


**Fig. 2** Degradability of PFCAs in Ai River and Kamo River soil. (a) PFCA addition groups (b) controls. OS and KS represent Osaka soil and Kyoto soil, respectively.



| **PFCAs** | **Oxidation (Ai-river soil)** | | **p** |
|---|---|---|---|
| | **Before (n=6)** | **After (n=6)** | |
| | mean (±SD) | mean (±SD) | |
| PFHxA | 0.28 (±0.19) | 0.93 (±0.88) | 0.075 |
| PFHpA | 0.28 (±0.12) | 0.48 (±0.44) | 0.047* |
| PFOA | 0.57 (±0.40) | 1.27 (±0.27) | 0.007** |
| PFNA | 0.04 (±0.03) | 0.16 (±0.18) | 0.098 |
| PFDA | 0.04 (±0.03) | 0.08 (±0.05) $^{a}$ | 0.148 |

| **PFCAs** | **Oxidation (Kamo-river soil)** | | **p** |
|---|---|---|---|
| | **Before (n=6)** | **After (n=6)** | |
| | mean (±SD) | mean (±SD) | |
| PFHxA | 0.03 (±0.01) | 0.13 (±0.06) | 0.009** |
| PFHpA | 0.03 (±0.03) | 0.30 (±0.19) | 0.011* |
| PFOA | 0.13 (±0.04) | 0.41 (±0.18) | 0.016* |
| PFNA | 0.06 (±0.01) | 0.09 (±0.02) | 0.012* |
| PFDA | 0.04 (±0.00) | 0.08 (±0.02) | 0.001** |

**Fig. 3** Concentrations of PFCAs in soil before and after oxidation (a) Ai River (b) Kamo River.

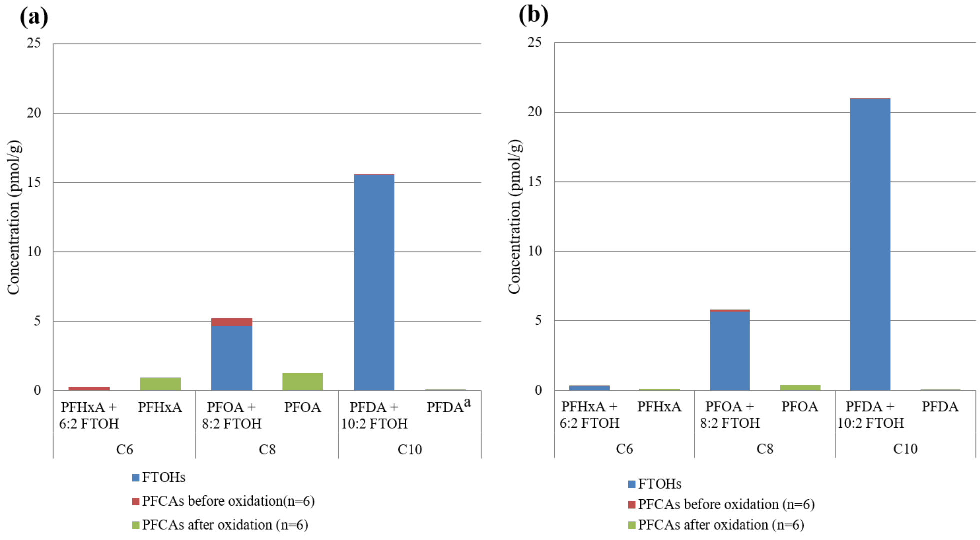


**Fig. 4** Comparison of concentrations of FTOHs and PFCAs in soil from (a) Ai River and (b) Kamo River.