

## Distribution of PFASs on leaching depth using rice paddy lysimeter

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### Introduction

Rice is the staple food of more than half of the world's population – more than 3.5 billion people depend on rice for more than 20% of their daily calories needs [1]. Especially, Asia accounts for 90% of global rice consumption, paddy cultivation is the main farming of rice in the East Asian region. Paddy rice is grown in flooded conditions with water. Therefore, it turns out that the way rice is grown, in the soil with a lot of water makes it particularly able to soak up hazardous chemicals such as Perfluoroalkyl substances (PFASs) including perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) which were groups of emerging persistent organic pollutants (POPs). It is well known that shorter alkyl chain PFASs were relatively more water soluble than that of longer alkyl chain PFASs [2, 3]. Thus, the mobility of PFASs has been concerned about the uptake of PFASs in rice and leaching through paddy field into groundwater.

In this study, the properties of PFASs in the paddy lysimeter were to examine their mobility, leaching behavior, and the relationship to the chain length and functional group. The mobilization potentials of the different PFASs in the paddy field may provide the important informations for the retention and release of these chemicals in the agro-environment and aquatic environment

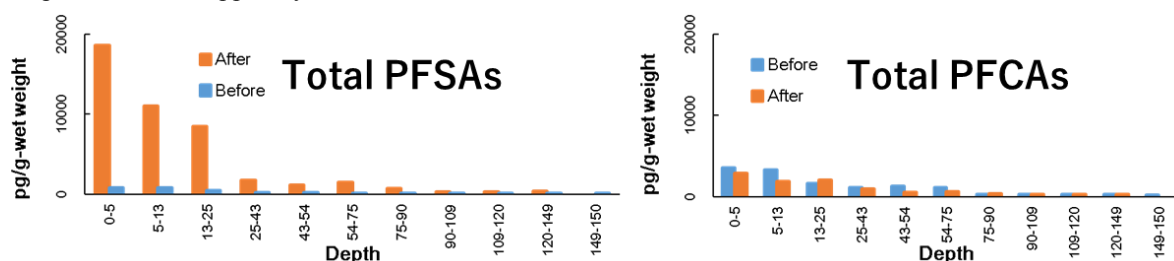
### Materials and methods

The lysimeter was a square-shaped surface area of 4 m<sup>2</sup> (2 x 2 m) and a depth of 1.8 m [4]. The type of soil was "Kanto loam" (a kind of volcanic cohesive soil). As irrigation water, river water and tested water were mixed. Soil sample and leached water sample were collected from lysimeter experiment from May 2015 to November 2015. The six months lysimeter experiment included collecting pre- and post-experimental soil and irrigating water were conducted. The lysimeter water (leachate) was collected through seven drain-pipes with depths of 5, 40, 75, 110, 145 and 180 cm. Approximately 100 mL of the leached water was extracted using Oasis WAX cartridges. Water

samples were analyzed by following the modified International Standard Method [5] described elsewhere and the Japanese Industrial Standard Method [7]. 5 g of soil sample spiked with 0.1 mL of 10 ppb PFAS internal standard solution consisting of  $^{13}\text{C}$  and 20 mL of Methanol together with 4 mL of 50 mM Ammonium acetate was added to 50 mL centrifuge tube for extraction twice. The extract was combined into a new pp tube and was added to 100 mL Milli-Q water. Then, raw extract was extracted using Oasis WAX cartridges and cleaned by Envi-Carb cartridges. The eluant was concentrated to 1 mL for LC-MS/MS analysis under nitrogen gas. Six perfluoroalkane sulfonic acids (PFDS, PFOS, PFHxS, PFBS, PFPrS, PFEtS), fourteen perfluoroalkyl carboxylic acids (PFOcDA, 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). HP1100 liquid chromatography (Agilent Technologies, Palo Alto, CA) interfaced with a Micromass (Beverly, MA) Quattro Ultima Pt mass spectrometer.

## Results and discussion

Approximately 4 months after irrigation, the concentrations of PFASs were remarkably increasing in the soil of lysimeter. PFASs were remained mainly in the upper layer soil (depth 0-25 cm). Especially, the concentration of PFHxS increased, because the high concentration of PFHxS was primarily derived from irrigation water. It is clear that PFASs residual in paddy soil depends on the PFASs components of irrigation water. The water solubility of PFHxS was known to be about  $1.49 \times 10^{-6}$  to  $5.69 \times 10^{-1}$  mol/L. Kanto loam is well characterized and represents a typical agricultural soil in Japan. The total carbon contents (TC) of upper layer soil in this study was determined higher (about 5%) than that of lower layers (1.7-2.8%). Thus, PFHxS was strongly absorbed with relatively high TC soil particles in the upper layer.

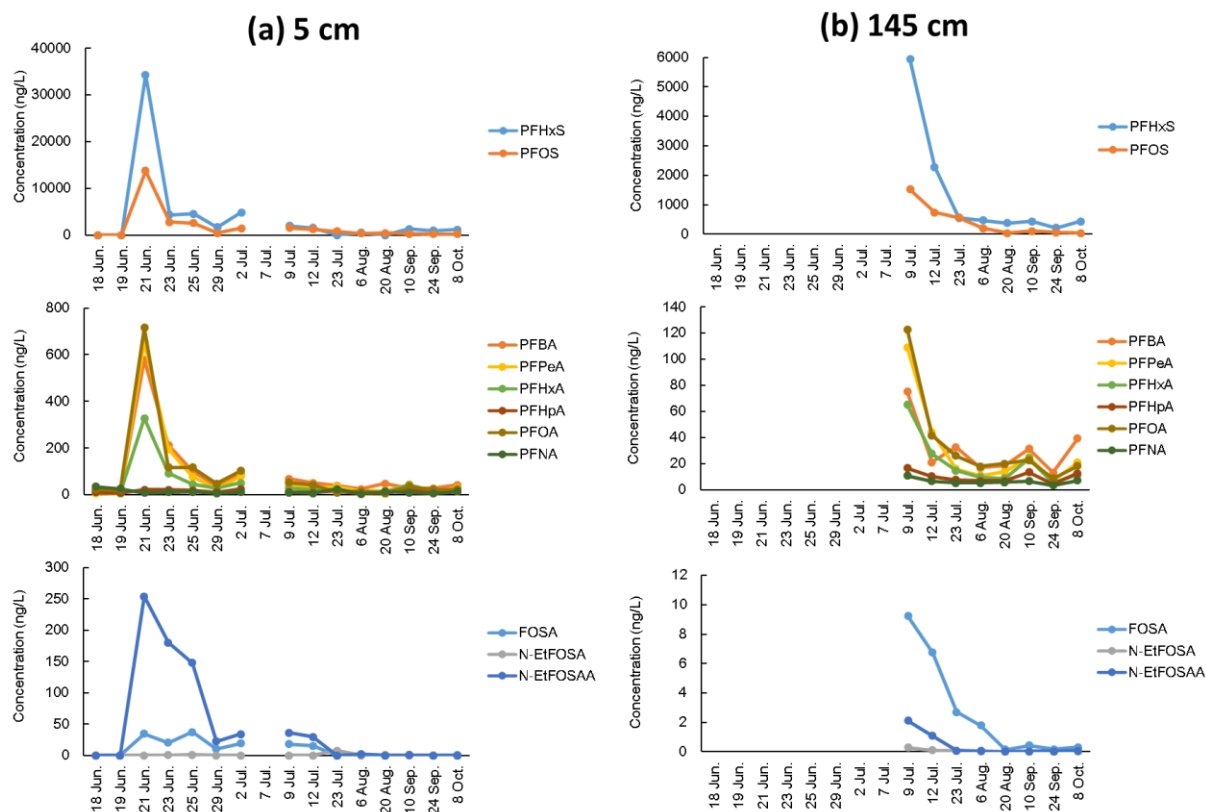


**Figure 1. Total concentrations (pg/g-wet weight) of PFASs (C3-C18) in soil before and after irrigation water (PFASs; perfluoroalkane sulfonates, PFCAs; perfluoroalkyl carboxylic acids)**

Indeed, the middle and longer chain PFASs remained easily in the upper layer by their water solubility and the

property of TC in the soil. On the contrast, since the shorter chain PFASs have relatively higher water solubilities, their migration will not have been strongly affected by the TC of adsorption to soil but would have been controlled by the migration of the soil water. It revealed that PFEtS and PFPrS were not detected in the soil, PFBS was detected almost in all layers.

Compared with results of PFASs, the distribution of PFCAs in the soil of lysimeter showed diversity. Except for longer chain PFCAs (PFDA to PFOcDA), the rest of PFCAs were distributed all layers of lysimeter. In the case of carboxylates, the migration of PFCAs can not explain the soil profile simply by its carbon number. Stahl et al. [7] reported that PFOA is transported rapidly by water passing through the soil, whereas PFOS travels much more slowly in leachate from a lysimeter experiment. Therefore, the migration behavior of PFASs in paddy field is associated with their functional groups such as carboxylates or sulfonate.



**Figure 2. Time trend of PFASs concentrations (ng/L) in leachate (a) 5cm and (b) 145 cm depth**

Fig. 2 shows the time trend of PFASs in leachate between upper layer and bottom layer for the lysimeter. After irrigation (21 June, 2015), the concentration of PFASs in leachate reached its peak value at 5cm. But the bottom leachate showed peak value on July 7 2015. It takes only 2 weeks. It should be noted here that paddy field was filled with irrigation water during the cultivation. It revealed that the migration speed of PFASs in paddy is faster than any other farming forms. Therefore, the mechanisms and kinetics of the migration of PFASs are different from upland cultivation.

The PFASs distributions in the paddy soils were influenced by migration in water and adsorption to the soil. It was difficult to identify the separate effects of diffusion in the water and adsorption–desorption to the soil, because PFASs chemical properties and carbon contents in the soil in each layer of the lysimeter were different.

## References

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