Mass balance analysis of PFASs in rice (*Oryza sativa subsp. Japonica)*

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Introduction

Perfluoroalkyl substances (PFASs) including perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) which were commonly used for industry were a groups of emerging persistent organic pollutants. It can be persistently remained in the water, soil, even food and seem to have potential threat to human health. Besides, PFASs were also serve as stable tracers for evaluating and monitoring environmental changes. Our previous works revealed distribution of PFASs in environment successively, e.g. dispersion of PFASs into open environment after the Great East Japan Earthquake [1]. Similar environmental discharge was found in the Kumamoto Erthquake in 2016. This suggested that PFASs can be useful tracer for soil chemistry [2]. Although recent report about accumulation and distribution of PFASs in lysimeter [3] [4], this is the first report about vertical transportation of PFASs in leached water through Kanto loam, special soil for paddy field in Japan.

Materials and methods

Two years lysimeter experiment in 2015 and 2016 were performed for monitoring the transportation of Perfluoroalkyl substances (PFASs) in soil, leached water and rice. Soil core and leached water sample were collected from lysimeter in Meiji University. Figure 1 shows schematic diagram of the field lysimeter facility. Dimension of lysimeter was 4 m^2 (2 x 2 m) and equipped at seven drain-pipes with depths of 5, 40, 75, 110, 145, 180 cm and bottom to collect leached water. Soils in lysimeter was consisted of low-humic andosol (from surface to 0.35 m deep) and Kanto loam (from 0.35 m to 1.75 m deep). During experiment periods (three months), relatively contaminated water from Tama River (17.42 L) in Tokyo was applied once on the day before transplanting of seedlings and tap water was used for irrigation. Two soil core (150 cm deep) were sampled before application of river water and after harvest of rice. Three months lysimeter experiment including collecting background soil, irrigating with Tama River water and planting rice was performed.

Prior to analysis, harvested rice was sectioned into five portions, root under soil, straws (ground to 20 cm, 20 cm to 40 cm, and higher than 40 cm) and rice husk and extracted by acetonitrile individually. Around one liter of water samples were analyzed by following the modified International Standard Method [5] described elsewhere [6] and the Japanese Industrial Standard Method [7]. 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 HPLC-MS/MS.

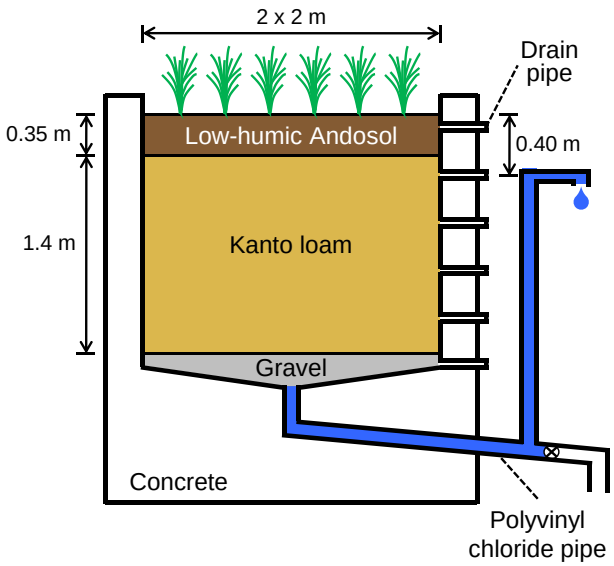

Figure. 1. Schematic diagram of the field lysimeter facility used in this research.

Results and discussion

The current trends of PFASs in soil core and leached water collected in 2015 were discussed in the previous report [8]. In this report, we focused into new finding, namely significant accumulation of PFASs in rice (Oryza sativa subsp. Japonica) harvested from above lysimeter experiments. Among analyzed chemicals, predominant PFASs in rice was PFBA followed by PFHxA and PFPeA. Highest concentration detected in rice was 2000 pg/g wet weight of PFBA in rice straw (>40 cm) after applied contaminated river water. Interestingly, residue concentration of PFBA was gradually increased from root to high portion of plant in control sample that was irrigated by tap water only. At the same time, mass balance analysis of all fluorinated chemicals using total fluorine analysis by combustion ion chromatography [9] couples with individual quantification of PFASs were carried out in rice samples. Possible risk of human exposure by organic and in-organic fluorochemicals will also be discussed.

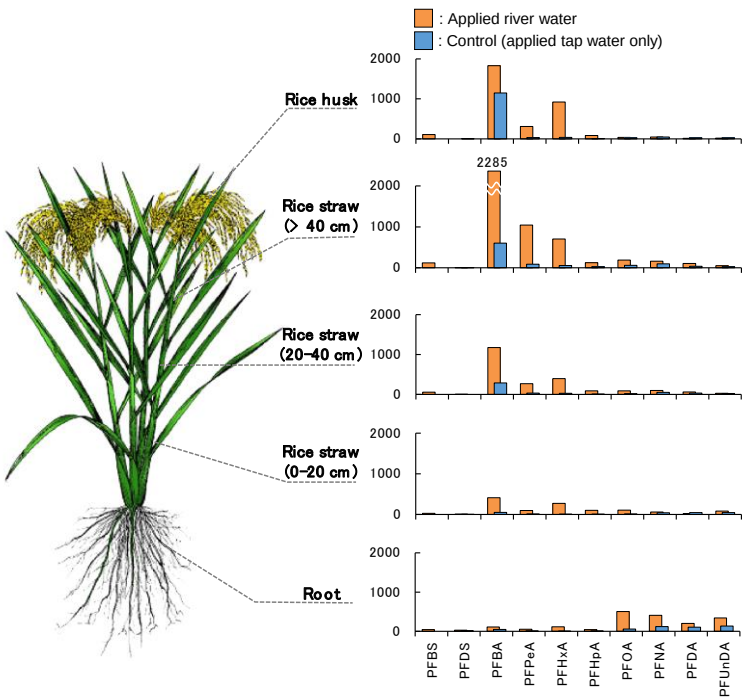

Figure. 2. PFASs concentrations (pg/g-wet weight) in rice husk, rice straw (>40 cm, 20-40 cm and 0-20 cm) and root collected from lysimeter applied river water and only tap water as control.

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