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# Uptake and elimination kinetics of perfluoroalkyl substances in submerged and free-floating aquatic macrophytes: Results of mesocosm experiments with *Echinodorus horemanii* and *Eichhornia crassipes*

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ABSTRACT

Studies investigating the bioaccumulation behavior of perfluoroalkyl substances (PFASs) in aquatic macrophytes are limited. The present study involved controlled mesocosm experiments to assess uptake and elimination rate constants ($k_u$, $k_e$), bioconcentration factors (BCFs) and translocation factors (TFs) of several perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) in two aquatic plant species, including one submerged species (*Echinodorus horemanii*) and one free-floating species (*Eichhornia crassipes*). The results indicated all PFASs were readily accumulated in these aquatic macrophytes. $k_u$ and BCFs increased with increasing perfluoroalkyl chain length. For PFCAs and PFSAs with identical perfluoroalkyl chain length, the corresponding PFSA exhibited higher bioaccumulation potential. On a whole-plant basis, the bioaccumulation potential of PFASs in submerged and free-floating macrophytes were comparable, indicating sorption to plant biomass is similar in the different species. Conversely, when considering accumulation in foliage, BCFs in the free-floating macrophyte were substantially lower compared to submerged species, especially for longer-chain PFASs. Compounds with shorter perfluoroalkyl chain length (PFBS, PFPeA and PFHxA) exhibited preferential translocation to leaf tissue (TFs >1). BCFs exhibited a sigmoidal relationship with pefluoroalkyl chain length, membrane-water distribution coefficients ($D_{mw}$), protein-water distribution coefficients ($D_{pw}$) and organic-water partition coefficients ($K_{oc}$). For these trends, maximum BCF values were exhibited by long-chain PFCAs, with a log $D_{mw}$, log $D_{pw}$ and log $K_{oc}$ of 6.47, 5.72 and 5.04, respectively. These findings are useful for future design and implementation of phytoremediation systems, as well for future develop of mechanistic models for predicting the environmental fate and distribution of these contaminants of concern.



## 1. Introduction

Perfluoroalkyl substances (PFASs) have been widely used in various industrial and commercial applications, mainly as surfactants, stain-repellants, coatings and aqueous film–forming foams (Kissa, 2001). Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are two important classes of PFASs that have been detected in environmental and biota samples, worldwide (Giesy and Kannan, 2001; Houde et al., 2006, 2011). PFCAs and PFSAs are commonly detected in the surface water and drinking water samples (Skutlarek et al., 2006; Quinete et al., 2009). PFCAs and PFSAs are also commonly detected in humans (Olsen et al., 2005; Lau et al., 2007), further highlighting the persistence and bioaccumulation potential of these substances.

Potential toxicological impacts of these compounds include hepatotoxicity, immunotoxicity, developmental toxicity, hormonal changes, cancer and gene alteration (Kennedy et al., 2004; Lau et al., 2007). In particular, PFOA and PFOS have been shown to induce functional alteration in cellular organelles (Panaretakis et al., 2001; Yang et al., 2001; Xie et al., 2003) and can cause neurotoxicity and hepatotoxicity (Nakayama et al., 2005; Tilton et al., 2008). The

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Science Advisory Board of United States Environmental Protection Agency (USEPA) has proposed PFOA be classified as a likely carcinogen in humans (Lau et al., 2007). Consequently, drinking water standards for PFOA and PFOS have been set to 0.4 and 0.2 μg/L respectively, in a provisional advisory established in the United States (USEPA., 2012).

Investigations of bioaccumulation behavior of PFASs in plants, especially aquatic plants, are limited. Previous studies have been conducted to assess uptake and bioaccumulation of PFASs in plants produce and grasses. Felizeter et al. (2012, 2014) recently investigated the uptake of PFASs in hydroponically grown vegetables. Yoo et al. (2011) investigated the uptake of PFCAs and PFSAs in grasses grown in contaminated biosolids. The available data indicate that PFCAs and PFSAs can accumulate extensively in plants and that perfluoroalkyl chain length and hydrophobicity are key determinants of PFAS bioaccumulation potential.

Aquatic macrophytes play an important role in aquatic ecosystems (Keddy, 2010). These plants are also key components of engineered phytoremediation systems. Phytoremediation involves use of plants to accumulate, sequester, transform, volatilize or otherwise detoxify contaminants. Direct uptake, accumulation and translocation of contaminants is an important mechanism in phytoremediation (Carvalho et al., 2014; Guittonny-Philippe et al., 2015; Lv et al., 2016). Phytoremediation studies focused on uptake of waterborne contaminants have included investigations on pesticides such as imazalil and tebuconazole (Lv et al., 2016), polyaromatic hydrocarbons such as phenanthrene and pyrene (Guittonny-Philippe et al., 2015), pharmaceuticals such as caffeine, ibuprofen, ofloxacin and sulfapyridine (Carvalho et al., 2014), and various trace metals (Rahman and Hasegawa, 2011; Guittonny-Philippe et al., 2015; Melignani et al., 2015).

A schematic illustration of contaminant uptake and elimination pathways for two different types of aquatic macrophytes, including a submerged species (*Echinodorus horemanii* Rataj) and free-floating species (*Eichhornia crassipes* (Mart.) Solms), is shown in Fig. S1. Direct exchange between water and plant tissues is a key process for uptake and elimination of contaminants in both submerged and free-floating aquatic macrophytes. Submerged macrophytes are typically rooted in sediments. Thus, uptake into these macrophytes will include direct exchange with leaf surface, as well as uptake via pore water in the bed sediments. For free-floating macrophytes, with root systems in the water column, transpiration and air-leaf exchange are likely important processes. Studies of semi-volatile organic contaminants in terrestrial vegetation have demonstrated the importance of a chemical's octanol-air partition coefficient ($K_{oa}$) in atmosphere-plant systems (McLachlan, 1999). Perfluoroalkyl acids (PFCAs and PFSAs) have been detected in bulk air at concentrations between approximately 8 and 16 pg/m$^3$ (gas + particulates), (Kim and Kannan, 2007). However, since these compounds exhibit relatively high water solubility and low Henry's low constants, atmospheric exchange processes are likely negligible. The formation of PFASs can occur via transformation of precursor compounds (e.g., perfluoroalkane sulfonamides), which provides an additional source of PFAS residues in macrophytes. It is important to note that many of these precursor compounds are semi-volatile organic compounds, which are present in surface waters and the atmosphere (Tomy et al., 2004; Young and Mabury, 2010), suggesting the potential importance of aerial exchange processes, especially for free-floating macrophytes.

The objective of the present study was to assess the bioaccumulation behavior of PFCAs and PFSAs in two different types of aquatic macrophytes, including a common submersed species (*Echinodorus horemanii*) and free-floating species (*Eichhornia crassipes*). Controlled mesocosm studies were conducted to determine key bioaccumulation metrics, including uptake and elimination rates, steady-state bioconcentration factors (BCFs) and translocation factors (TFs) of individual PFCAs and PFSAs in these plant species. In addition, the study aims to assess the influence of physical-chemical properties and differences between submersed and free-floating plant species on contaminant bioaccumulation behavior.

## 2. Material and methods

### 2.1. Mesocosm experiments

The bioaccumulation experiments were conducted at Singapore's Van Kleef Aquatic Science Centre, which offers a covered outdoor environment, with good growing conditions and shelter from rainwater interference. In total, nine plastic tanks, measuring 28 cm in length, 18 cm in width and 18 cm in height (total volume was 9072 cm$^3$), were used for the experiments. The plastic tank was selected based on the exactly capacity of 10 seedlings of *Eichhornia crassipes* per tank, with the total wet biomass between 90 and 110 g. As reported in previous studies, roots of a young plant display greater ability to absorb contaminants, such as heavy metals, compared to that of an old plant with similar size, therefore, use of young and healthy plants is very important for the efficient removal of contaminants (Tu et al., 2004; Tangahu et al., 2011). A previous study on the effects of plant age on the hyperaccumulation of arsenic in plants also indicated that its uptake reduced with plant age, and the highest accumulation was found in plants with age between 2 and 10 months (Gonzaga et al., 2007). The biomass and productivity of *E. crassipes* was estimated in 2001 and its fastest growth rate was suggested at the age smaller than 4 month (Gutiérrez et al., 2001). Based on those previous studies, as well as the aims of the present study, young (3 months) seedlings were selected.

Tanks were divided into three groups, including (i) *E. horemanii* (submerged macrophytes), *(ii) E. crassipes* (free-floating macrophytes), and (iii) controls. Each group had triplicate tanks. Thirty *E. crassipes* and *E. horemanii* (previously grown for 3 months), were purchased from a local supplier. The plants were allowed to acclimate for about 1 week, with a stocking density of 10 seedlings per tank. The control tanks contained no plants. Tanks were covered with aluminum foil on the sides to preclude photodegradation. Tanks were filled with 6 L of tap water, which was renewed every 2 days during the acclimation period.

Small plastic pots with net holes on the side, each had a dimension of 6 cm in diameter and 8 cm in height (total volume was 226 cm$^3$), were used in the exposure tanks (Fig. S1). The commercial available stones, pre-washed with tap water and methanol, were placed at the bottom of each pot, in order to immobilize the pot in the exposure medium. Then the plant of *E. horemanii* was placed in the pot, with one plant per pot, and the plastic string was used on the top of the pot, to support the plant up-straight and submerged in the medium (Fig. S1). Since the pots had net holes on the side, the root of *E. horemanii* was directly connected to the exposure medium in the tank (Fig. S1). The same pots were placed in the tanks of control and *E. crassipes* as well, with ten pots per tank, to ensure that the exposure setup was consistent for all groups.

After the acclimation period, the exposure experiments were initiated, starting with the exposure phase (day 0 to day 14), followed by the depuration period (day 15 to day 28). In exposure phase, a mixture of test compounds were spiked into the tank water (120 μg each), giving a nominal final concentration of 20 μg/L for individual PFCAs and PFSAs, and the real measured concentration of each compound in the exposure medium was between 19.21