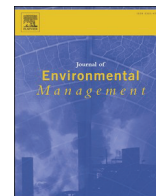




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Emerged macrophytes to the rescue: Perfluoroalkyl acid removal from wastewater and spiked solutions

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ABSTRACT

This study evaluated the potential for three emergent aquatic macrophytes to remove perfluoroalkyl acids (PFAAs) from contaminated waters in constructed wetland systems. Three plants (*Iris pseudacorus* L., *Phragmites australis* (Cav.) Trin. Ex Steud., and *Typha latifolia* L.) were exposed to an effluent from a tannery wastewater treatment plant (WWTP) that contained residual PFAAs, and to three spiked solutions with increasing concentrations of 11 perfluorocarboxylic acids (PFCAs) and three perfluorosulfonic acids (PFSA) (500, 2500, and 5000 ng L⁻¹, each). Thirty-six lightweight expanded clay aggregate- and vegetation-filled tanks (0.35 × 0.56 × 0.31 m) were exposed to the tested solutions at the Acque del Chiampo SpA WWTP in Arzignano (NE Italy). Throughout the experiment, PFAA concentrations and physicochemical water parameters were monitored via measures of the clay material, plastic tank inner surfaces, and below- and above-ground biomasses (after harvest). Vegetation growth was shown to be unaffected by increased PFAA levels in the spiked solutions. Alternatively, total biomass was significantly reduced when WWTP water was used, although we attribute this finding to the relatively high salinity that mainly restricted *Typha* and *Iris* development. The tested macrophytes were found to remove a significant PFAA mass from the contaminated waters (36% to ca. 80%, on average) when *Phragmites* was subjected to the highest PFAA concentrations. Such large accumulations were primarily associated with long C-chain PFAA stabilization in belowground biomass (26%, on average). Most PFAA translocations were observed in *Typha*, which accumulated mostly short perfluorinated C-chain PFBA, PFPeA, and PFHxA in the aboveground biomass (16%, on average). Despite some growth limitations, *Iris* was still the most efficient macrophyte for translocating PFBS under WWTP.

1. Introduction

Perfluoroalkyl acids (PFAAs) are synthetic chemicals that can be found into aquatic environments (Wang et al., 2017). This family of xenobiotic compounds with hydrophobic perfluoroalkyl moieties and a hydrophilic functional group (De Voogt and Sáez, 2006) has attracted global interest due their easy entry into the food chain (Sunderland et al., 2019). Several characteristics of the compounds are particularly worrisome: high persistence (Krafft and Riess, 2015), high potential for bioaccumulation (Ding and Peijnenburg, 2013), and toxicity (Lau et al., 2007).

Conventional wastewater treatment plants (WWTPs) are often inefficient at removing PFAAs (Ahrens, 2011), so much so that it is not uncommon for 'treated' effluents to contain PFAA concentrations of hundreds of ng L⁻¹ (Higgins et al., 2005). Moreover, some conventional

activated sludge treatment plants have actually increased PFAA levels (Becker et al., 2008; Houtz et al., 2016) by degrading fluorinated precursors (e.g., fluorotelomer alcohols, FTOHs) (Li et al., 2018), and 6:2 fluorotelomer sulfonate (FTS) (Sun et al., 2011). Sonochemical treatment (Moriwaki et al., 2005), membrane technology (Tang et al., 2006), and electrochemical oxidation (Niu et al., 2012) represent technologies tested for removal of PFAAs from the aqueous matrix, but their high energy demand and high construction and maintenance costs make them less practical (Vecitis et al., 2009). Indeed, most innovative treatments for real-world WWTPs face significant challenges due to scaling and mass-transfer limitations (Lenka et al., 2021). Some authors suggest that effective water treatment may require technique combinations (Lenka et al., 2021; Mahinroosta and Senevirathna, 2020). Utilizing the uptake and transport of contaminant compounds into aboveground vegetation may represent one part of a viable passive

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