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Ecological effect and risk towards aquatic plants induced by perfluoroalkyl substances: Bridging natural to culturing flora

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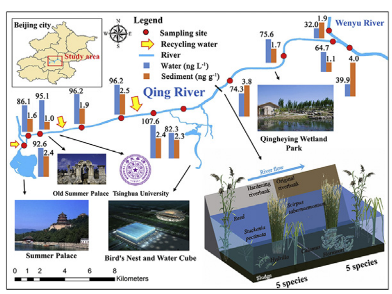
HIGHLIGHTS

- PFASs proportions in water of different seasons were mutative in the Qing River.
- Aquatic plants might have preference absorption for long-chain PFASs.
- Absorption effect of roots and foliage of emergent plants were obviously different.
- Capacity of tolerance and bio-accumulation towards PFOS of *hornworts* was good.
- *Hornworts* could be used as remediation flora to eliminate PFOS pollution in water.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, the concentrations and proportions of perfluoroalkyl substances (PFASs) in water and sediments (in different seasons) from the Qing River were investigated. The highest concentration of PFASs in water (207.59 ng L^{-1}) was found in summer. The composition of PFASs in water changed with time, perfluorobutane sulfonate (PFBS) was the predominant compound in spring and summer, while long-chain PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), started to increase in autumn and winter. The PFASs concentration in sediments ranged from 0.96 to 4.05 ng g^{-1} dw. The proportion of long-chain PFASs was higher than that of short-chain PFASs in sediments, the dominant component in sediments was PFOA with a contribution of 24.6–75.4% to total PFASs in sediments, followed by PFOS. The concentrations of PFASs in roots of emergent plants were relatively higher than those in submerged plants. However, the translocation effect of PFASs was not remarkable. Bioaccumulation factors (BAFs) of the aquatic plants indicated the absorption of PFASs were effective. BAFs in submerged plants basically increased with increasing chain length accordingly. In general, aquatic plants had the absorption preference for long-chain PFASs, especially PFOS, which was the predominant compounds in both submerged and emergent plants. Based on the results above, *hornworts* were selected to be cultivated indoor in the nutrient solution spiked gradient concentrations of PFOS to assess the general ecological risk. The results revealed that *hornworts* were resistant to PFOS and might be used as remediation flora to eliminate PFOS contamination.

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1. Introduction

Perfluoroalkyl substances (PFASs) which are difficult to biodegrade and easy to migrate, are now widespread all over the world including the North Pole, the tibetan plateau and other places that are far away from fluorine industries or human activities (Giesy and Kannan, 2001; Liu et al., 2010). For their ecotoxicity, PFASs have potential health or ecological risk to individual, population, community and even ecosystem, especially when the concentration of PFASs oversteps the critical micelle concentrations (CMC) (Yang et al., 2014). The two main approaches for PFASs to transport are atmospheric transmission (Taniyasu et al., 2013) and aquatic transmission, and the latter one contributes more for the reason that the polarity and solubility of ionic PFASs are relatively high (Armitage et al., 2009). So the concentration, transmission and other characteristics of PFASs in aquatic environment including waters, sediments, and aquatic biota attracted great interests of scientists, politicians and regulators.

Fluorine industry which releases PFASs in surrounding environment is regard as one emission source (Wang et al., 2015a; Zhu et al., 2015). The compounds of PFASs extensively used in impregnated paper, carpet, textiles, leather, furniture, paints, cleaning detergents, and cosmetics, and people's daily life are full of these consumer goods (Xie et al., 2013). PFASs can be transmitted to the waste water treatment plants (WWTPs) that are identified as another emission source (Filipovic and Berger, 2014). WWTPs are generally facing the fact that the technology they use cannot eliminate PFASs in the waste water and may even increase the concentration of PFASs in recycled water it discharges into the surrounding environment (Thompson et al., 2011).

Actually, since PFOS and its related compounds have been listed into the Annex B of the Stockholm Convention in 2009 (Wang et al., 2009), the output of PFASs has sharply declined. Although the major historic global manufacturer of PFASs was ordered to halt production in 2002 and China became the largest producer in the world, the quantity of fluorine industries and output that was about 200 t of PFASs every year in China was still small (Xie et al., 2013). This means that there are no fluorine industries in the vast majority of regions. However, the concentration of PFASs in rivers, lakes or any waters that are far away from fluorine industries can be still high due to the impact of WWTPs. The exploration of PFASs that focuses on WWTPs has gradually been in a hot research (Alder and van der Voet, 2015; Lindim and Cousins, 2015; Ruan et al., 2015; Lindim et al., 2016).

The water source of urban river is usually consisted of recycle water discharged from WWTPs (Becker et al., 2008). As a consequence, the concentrations of PFASs in urban rivers are relatively higher than natural ones (Pan et al., 2014; Xia et al., 2015). Aquatic creatures living in urban rivers which are polluted by PFASs are suffering the ecological risk. Moreover, due to the bioaccumulation of PFASs, this risk can be transferred into human beings through food chains or food webs (Martin et al., 2004; Lescord et al., 2015). Previous studies usually focused on animals (Houde et al., 2008; Zhao et al., 2013) or built food chains or food webs (Houde et al., 2008) to evaluate the eco-environmental risk of PFASs in that area. However, in some urban rivers, the water quality is too poor to build a food chain or food web. It will even be difficult to find some animals, such as fish, river shrimp and crab. So aquatic plants could be a better choice to analyze the potential ecological risk of PFASs.

In present study, the Qing River which is a significant urban river of Beijing was selected as the study area. Some world famous buildings such as the Summer Palace, Old Summer Palace, Tsinghua University and Olympic Park are located surrounding this river. The main source of the Qing River was recycling water from the WWTPs along the river. This urban river belongs to the Haihe basin and serves as landscape water. People who relax or exercise there may have the opportunity to contact with the water. The Qing River joins with the Wenyu River in the downstream and finally flows into the Bohai Sea. Moreover, the riverbanks of the Qing River in the upstream are partly hardened, the others are original ones (Fig. 1). It is meaningful for us to figure out the contamination status of PFASs in the Qing River.

This study provided detail information about the concentration of PFASs in waters, sediments, aquatic plants and scientific evidences for bioaccumulation in aquatic plants. According to the results of bioaccumulation function of aquatic plants in the Qing River, *hornwort*, one widespread species of the aquatic plants, was chosen to do indoor cultivation, and its bioaccumulation factors (BAFs) were further analyzed. The objectives of this study were 1) to analyze the concentration of PFASs in environmental media, such as water and sediment; 2) to figure out the concentration, bioaccumulation and ecological risks of PFASs towards aquatic plants in recycle water from WWTPs; 3) to evaluate possibility for *hornwort* to be a remediation plant for PFOS. Finally, this study might give a reference for similar urban rivers, and explore a way to eliminate the pollution of PFASs.

2. Materials and methods

2.1. Standards and reagents

12 PFASs in all samples were analyzed, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorobutane sulfonate (PFBS), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorooctane sulfonate (PFOS), perfluoroundecanoate acid (PFUdA), and perfluorododecanoic acid (PFDoA) and 9 mass-labeled PFAAs, containing $^{13}C_4$PFBA, $^{13}C_4$PFHxA, $^{13}C_4$PFOA,$^{13}C_4$PFNA, $^{13}C_4$PFDA, $^{13}C_4$PFUdA, $^{13}C_2$PFDoA, $^{18}O_2$PFHxS and $^{13}C_4$PFOS were purchased from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada). More detail descriptions on standards and reagents were available in Supporting Information.

2.2. Sample collection

13 sampling sites were uniformly arranged along the Qing River (Fig. 1). Water samples ($n = 52$), sediment samples ($n = 13$), and aquatic plant samples ($n = 36$) including 6 species (*reed, calamus, scirpus tabernaemontani, stuckenia pectinata, hydrilla and hornwort*) were all collected away from the bank over 2 m in the river in order to avoid influence from the river bank. Water samples were collected in the first week of the first month in each quarter from 2013 to 2014 to discover the seasonal variations. Sediment samples were collected in autumn for the reason that at that time aquatic plants began to fade. Considering the growth situation of plants, aquatic plant samples were collected twice in spring and autumn, respectively.

Water samples were collected in polypropylene (PP) bottles and before collecting, all the bottles were rinsed 3 times by water in the river to minimize system contamination. Samples of sediment and aquatic plant were stored in PP plastic automatic sealing bags. All the samples were kept in an icebox during transport. Sediment samples were grinded after freeze-drying to get through the 2 mm nylon sieve, then stored in double-deck polypropylene plastic bags. Aquatic plant samples were washed out by using the tap water and then flushed 3 times by using Milli-Q water. The samples of submerged plants (*stuckenia pectinata, hydrilla and hornwort*) were kept completely, while emergent ones (*reed, calamus and scirpus*