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Riverine inputs and source tracing of perfluoroalkyl substances (PFASs) in Taihu Lake, China

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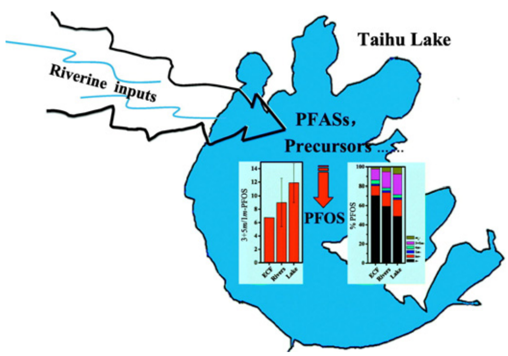
HIGHLIGHTS

- PFHxS was the predominant PFAS compound in Taihu Lake and flow-in river waters.
- The ratio of 3 + 5*m*-/1*m*-PFOS was used as an index to distinguish the degradation of precursors.
- Degradation of precursors made an important contribution to PFOS in Taihu Lake.
- PFHxS mainly originated from the products containing it as active ingredient.
- The riverine flux of PFASs into the Lake was estimated to be 1255 kg/year.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence, riverine inputs and sources of perfluoroalkyl substances (PFASs) in Taihu Lake, one of the largest lakes in China, were investigated by measuring PFASs including the isomers of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA) and perfluorohexanesulfonate (PFHxS) in the Lake and its main flow-in rivers. It was found that PFHxS, instead of PFOS or PFOA, was predominant both in the Lake and rivers (45.9–351 ng/L), reflecting increasing demand of PFHxS in recent years. The riverine flux of PFASs into the Lake was estimated to be 1255 kg/year. The percentage of linear (*n*-) PFOS and the ratio of 3 + 5*m*-/1*m*-PFOS were combined to indicate indirect source due to biodegradation of PFOS-precursors. The percentage order of *n*-PFOS was: the Lake (48.7%) < the flow-in rivers (59.2%) < ECF product (70.3%). While the ratio of 3 + 5*m*-/1*m*-PFOS was in reverse order: the Lake (11.9) > the rivers (8.99) > ECF (electrochemical fluorination) product (6.76). These suggested that degradation of PFOS-precursors made distinct contribution to PFOS load in the waters, particularly in the Lake. The Lake and river waters had a consistent proportion of *n*-PFHxS (89.0%), which was slightly lower than the ECF product (96.0%), indicating it was mainly due to the release from production and application of PFHxS as an active ingredient.

1. Introduction

Perfluoroalkyl substances (PFASs), including perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs), are a group of man-made fluorinated chemicals manufactured since 1950s. Due to their unique properties (e.g. high thermal and chemical stabilities as well as excellent

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surface activity), they have found wide applications in industrial and consumer products (Buck et al., 2012). Currently, PFASs are ubiquitous in the environment, especially in aquatic environment, and they are reported to be persistent, bioaccumulative and may magnify in food webs (Ahrens, 2011; Fang et al., 2014; Lindim et al., 2015). Large lakes and ocean are considered as the main sink and transport media of PFASs in the environment due to the important contribution of riverine inputs (Boulanger et al., 2005; Kim and Kannan, 2007; Lindim et al., 2015; Lindim et al., 2016; Liu et al., 2015; Moller et al., 2010; Muir and Lohmann, 2013; Niisoe et al., 2015; Orata et al., 2009; Scott et al., 2010; Yeung et al., 2009). Taihu Lake is the third-largest freshwater lake, with a surface area of 2338 km^2, in eastern China. The watershed of Taihu Lake is one of the most urbanized and industrialized regions in China, and it serves as an important fresh water resource and ecosystem for surrounding populations. Our group and other research groups have made investigations on the occurrence of PFASs in water, sediment and organisms in Taihu Lake in the last ten years (Chen et al., 2015b; Fang et al., 2014; Guo et al., 2015; Pan et al., 2014; Qiu et al., 2010; Yang et al., 2011; Yu et al., 2013). The results indicated that PFAS contamination was common in Taihu Lake and relatively high levels of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) were found in the Lake. However, the riverine input of PFASs into the Lake is still not unclear.

More than 200 rivers at different scales are connected with Taihu Lake. Among them, about 22 primary flow-in rivers (Fig. 1 and Table S1) contribute the most water discharge and >80% of chemical oxygen demand (COD), nitrogen (N) and phosphorus (P) to Taihu Lake (Sun et al., 2009). These rivers flow through many industrial cities, such as Wuxi, Chanzhou, Yixing, where there are large amount of PFAS-related plants, including PFAS manufacturing, textile treatment, firefighting foams, paper making, plastic and electronics, and so on (Chen et al., 2015b; Yang et al., 2011). In order to implement effective environmental protection of the Lake, Taihu Lake as well as the areas within 5-km of the lakeside were set as the priority protection region in 2012 (Xu et al., 2012). Disclosing the riverine input of PFASs to the Lake would provide vital information for the environmental management of local government.

It was reported that some short-chain PFASs ($C \le 6$), which are supposed to be less toxic than the long-chain homologues, are increasingly demanded in the market due to the regulations on PFOS, PFOA and related compounds (Lu et al., 2015; Wang et al., 2016). This shift in production and application could be imaged by the contamination profiles and trends of PFASs in the environment (Guo et al., 2015; Lu et al., 2015; Wang et al., 2016; Yu et al., 2013; Zhou et al., 2013). Thus, continuous PFAS monitoring in Taihu Lake is needed to investigate the change of pollution profiles and trends.

There are two main manufacturing methods for PFASs, namely electrochemical fluorination (ECF) and telomerization. The ECF method usually produces a mixture of linear (*n*-) and branched (*br*-) isomers, while telomerization produces only pure isomer products. PFOS-related chemicals (i.e. PFOS and its precursors) are produced solely by the ECF method and typically consisted of ~30% *br*-isomers (Benskin et al., 2010a). Different from PFOS, PFOA was historically produced by ECF (~20% branched), while the production of PFOA and its precursors such as fluorotelomer alcohol (FTOH)-based chemicals are usually 100% linear geometry (Benskin et al., 2010b). The precursors of PFOS and other perfluoroalkyl acids in the environment may undergo isomer-specific degradation and finally produce PFOS, which is considered as an indirect source of PFOS in the environment (Chen et al., 2015a; Peng et al., 2014). Isomer profiling of PFASs, especially using the fingerprints of branched isomers, may be able to give important clues for source apportionment in the waters (Benskin et al., 2010a; Chen et al., 2015b).

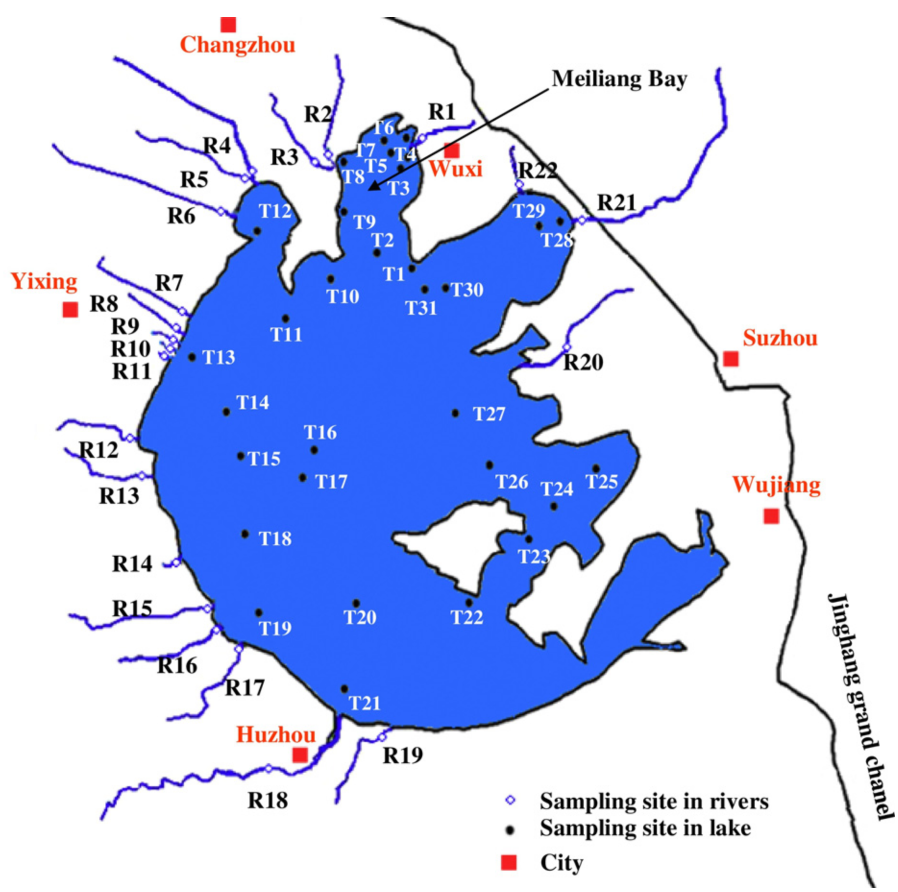

Fig. 1. Sampling sites in Taihu Lake and flow-in rivers.