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Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water

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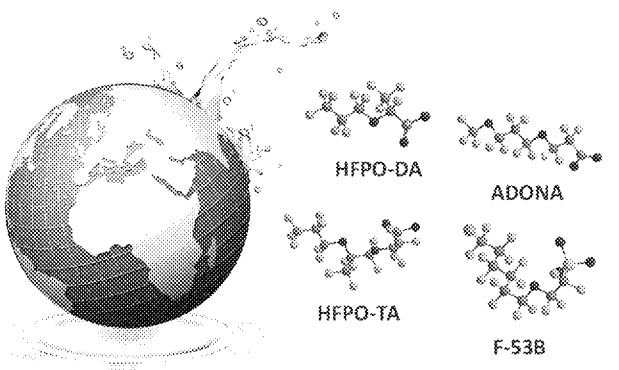
Supporting Information

ABSTRACT: Driven by increasingly stringent restrictions on long-chain per- and polyfluoroalkyl substances (PFASs), novel fluorinated compounds have emerged on the market. Here we report on the occurrences of several perfluoroalkyl ether carboxylic and sulfonic acids (PFECAs and PFESAs), including hexafluoropropylene oxide dimer and trimer acids (HFPO-DA and HFPO-TA), ammonium 4,8-dioxa-3*H*-perfluorononanoate (ADONA), chlorinated polyfluorinated ether sulfonic acid (6:2 Cl-PFESA), and its hydrogen-substituted analogue (6:2 H-PFESA) in surface waters from China (n = 106), the United States (n = 12), the United Kingdom (n = 6), Sweden (n = 10), Germany (n = 14), The Netherlands (n = 6), and Korea (n = 6). Results showed that HFPO-DA, HFPO-TA, and 6:2 Cl-PFESA (median = 0.95, 0.21, and 0.31 ng/L, respectively) were frequently detected in all countries, indicating ubiquitous dispersal and distribution in global surface waters. The presence of 6:2 H-PFESA was widely detected in China (detection rate > 95%) but not in any other country. Only trace levels of ADONA (0.013−1.5 ng/L) were detected in the Rhine River flowing through Germany. The estimated total riverine mass discharges of HFPO-DA, HFPO-TA, and ΣPFESAs reached 2.6, 6.0, and 4.3 ton/year in five of the major river systems in China. Our results indicated that novel PFECAs and PFESAs might become global contaminants, and future investigations are warranted.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are a group of man-made chemicals that have been used for >60 years. According to a recent survey, over 3 000 PFASs are currently used on the global market in a wide range of applications, such as fire-fighting foams, metal plating, fluoropolymer manufacture, photoimaging, and surface repellents.[1] Among them, worldwide attention has been drawn to long-chain PFASs, including perfluoroalkyl carboxylic acids (PFCAs, ≥7 perfluorinated carbons) and perfluoroalkanesulfonic acids (PFSAs, ≥6 perfluorinated carbons), due to their ubiquitous environmental presence, biopersistence, and toxicity to wildlife and humans.[2] Since 2000, numerous regulations have been introduced to decrease and ultimately eliminate the production and use of long-chain PFASs.[3−6] Perfluorooctanesulfonic acid (PFOS) and related substances are listed as Persistent Organic Pollutants under the Stockholm Convention,[5] with perfluorooctanoic acid (PFOA) and perfluorohexanesulfonic acid (PFHxS) currently being evaluated for inclusion.[7,8] The European Commission amended Annex XVII in REACH: Regulation (EC) no. 1907/2006 to regulate PFOA, its salts, and related chemicals in June 2017.

Stricter regulations and increasing public awareness of long-chain PFASs have led to a shift in the production and usage of fluorinated replacements of long-chain PFASs, including short-chain homologues[9] (e.g., perfluorobutanesulfonic acid (PFBS)) and functionalized perfluoropolyethers[10] (e.g., perfluoroether carboxylic and sulfonic acids (PFECAs and PFESAs)). By insertion of ether linkage(s) into their much shorter perfluorinated chains, PFECAs and PFESAs were initially expected to be more degradable.[11] However, some PFECAs

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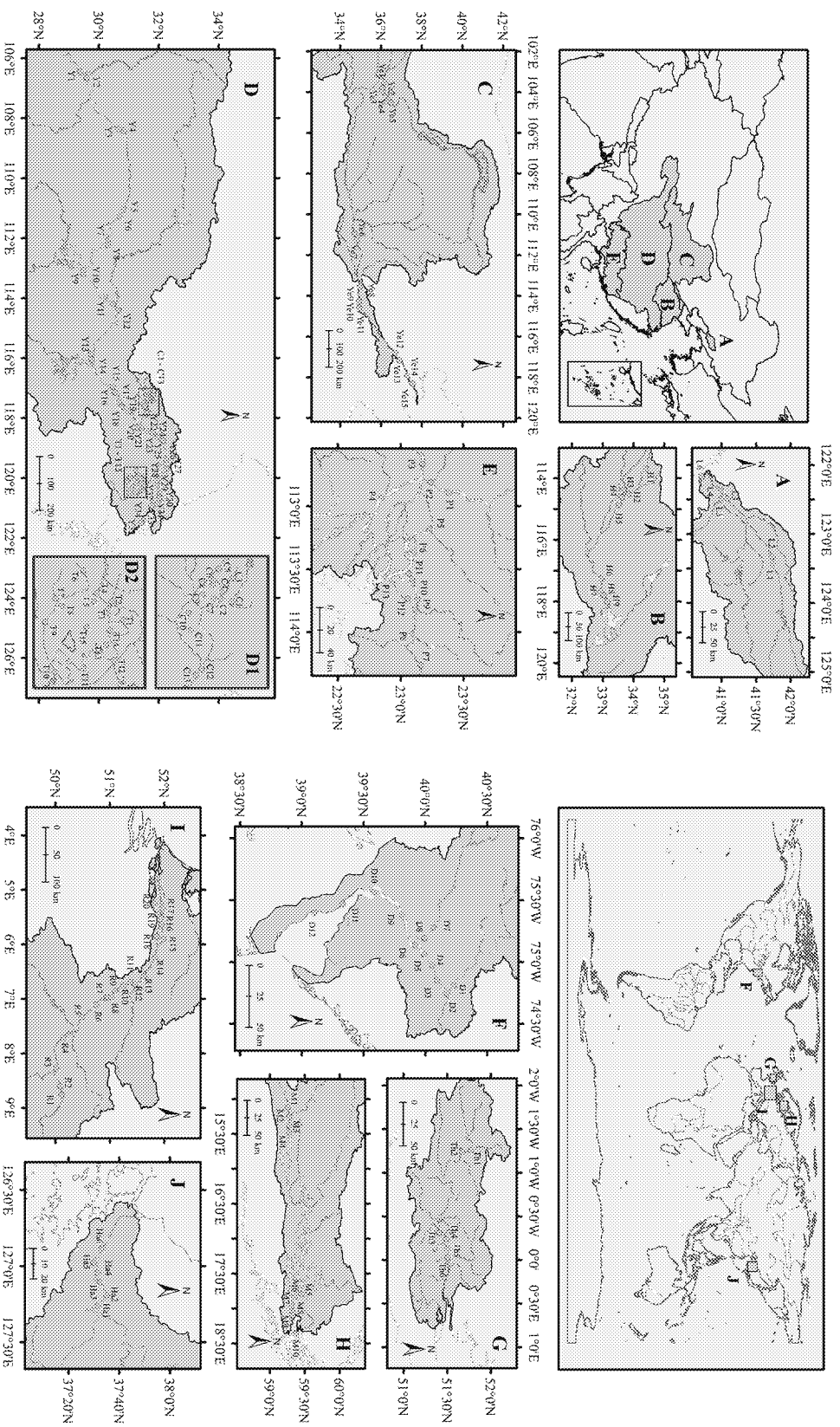

Figure 1. Overview of water sampling sites in China (left, A–E) and other countries (right, F–J). Green spots represent sampling sites and pink areas indicate watersheds for the respective water systems. (A) Liao River, (B) Huai River, (C) Yellow River, (D) Yangtze River, (D1) Chao Lake, (D2) Tai Lake, (E) Pearl River, (F) Delaware River (U.S.A.), (G) Thames River (U.K.), (H) Mälaren Lake (Sweden), (I) Rhine River (Germany, R1–R14; The Netherlands, R15–R20), (J) Han River (Korea).

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and PFESAs are still highly persistent in natural conditions, and their occurrences in abiotic and biotic environments have been reported in recent years.[12−15]

Several PFECAs have been produced to replace legacy PFOA as processing aids in the production of fluoropolymer high-performance materials;[16] however, trace amounts of processing aid can remain in the final product. During the manufacture of fluoropolymers, PFECAs are not fully consumed and thus may enter the environment following inefficient treatment.[17] Ammonium 4,8-dioxa-3*H*-perfluorononanoate (ADONA, $CF_3OC_3F_6OCHFCF_2COOH$) was detected in the environment as early as 2008, with concentrations ranging from 320 to 6 200 ng/L found downstream of the effluent discharge from a fluorochemical plant in the Alz River, Germany.[18] Hexafluoropropylene oxide dimer acid (HFPO-DA, $C_3F_7OCF(CF_3)$-COOH) is another PFECA, and its ammonium salt (trade name GenX by DuPont Chemours) has been used as a PFOA alternative processing aid in fluoropolymer manufacture since 2010.[19] Subsequently, several studies have reported the presence of HFPO-DA in river waters downstream of fluorochemical plants at concentrations of 108 ng/L in Germany,[12] 631 ng/L in United States,[20] 812 ng/L in The Netherlands,[21] and 3 830 ng/L in China.[12] Drinking water has also shown detectable levels of HFPO-DA (0.25−11 ng/L) in municipalities close to a fluorochemical plant in The Netherlands.[21] Similar to HFPO-DA, other homologues with oligomeric hexafluoropropylene oxide may share similar performance in industrial applications. We recently identified hexafluoropropylene oxide trimer acid (HFPO-TA, $(C_3F_7O)_2CF(CF_3)COOH$), another PFECA that can be used as a processing aid in fluoropolymer production, in the effluent of a fluorinated polymer production plant in China.[13] The maximum level of HFPO-TA exceeded 68 500 ng/L in downstream river water (~4.6 tons of discharge per year), suggesting considerable amounts of this novel compound being used in China. In the same study, locally captured common carp showed high exposure levels (median = 1 540 ng/mL in blood) and a higher bioconcentration factor (189) than that of PFOA, increasing concern that HFPO-TA could be as highly persistent and accumulative as long-chain PFCAs.

As alternatives to PFOS, PFESAs have been used as mist suppressants in the Chinese chromium-plating industry.[14] Among PFESAs, 6:2 chlorinated polyfluorinated ether sulfonic acid (6:2 Cl-PFESA, trade name F-53B) has been widely used, with structurally similar homologues, such as 4:2, 8:2, and 10:2 Cl-PFESA ($Cl(CF_2)_xO(CF_2)_2SO_3H$, where x = 4, 8, and 10, respectively), recognized as impurities of the 6:2 form.[13,22] After 30 years of F-53B usage in China, the presence of Cl-PFESAs has been ubiquitously detected in surface water,[23] sewage sludge,[22] wildlife,[15,24] and humans.[25,26] Recently, Cl-PFESAs showed dechlorination into a hydrogen-substituted analogue (i.e., 6:2 Cl-PFESA → 6:2 H-PFESA) under anoxic reductive environments,[27] with 6:2 H-PFESA now reported in river waters (0.56 ng/L) and sediments (0.011 ng/g) collected near two Chinese metal-plating facilities.[27]

The data discussed indicated the existence of these alternatives close to point sources of fluorochemical facilities. Now it is important to know if these novel PFASs, especially HFPO-DA, HFPO-TA, and 6:2 H-PFESA, show ubiquitous occurrence across the global environment. It is also important to investigate if there would be any difference in usage of these PFAS alternatives between China and western countries, as countries in Northern America and Europe had begun the phase out of long-chain PFASs many years earlier than China.[17] In the present investigation, 24 legacy and alternative PFASs were measured in 160 surface water samples collected from major water systems in seven countries, including China (n = 106), the United States (n = 12), the United Kingdom (n = 6), Sweden (n = 10), Germany (n = 14), The Netherlands (n = 6), and Korea (n = 6). The main objectives were (1) to investigate the global occurrence of PFECAs and PFESAs in riverine waters; (2) to explore any differences in the levels and distributions of key fluorinated alternatives between China and other countries; and (3) to estimate the national riverine discharge of novel PFECAs and PFESAs in China.

MATERIALS AND METHODS

Sample Collection. A total of 160 surface water samples were collected between September and December 2016. The sampling sites are presented in Figure 1 and Supporting Information Table S1. The study locations in China included five major rivers, Yangtze River (n = 35), Yellow River (n = 15), Pearl River (n = 13), Huai River (n = 9), and Liao River (n = 6), and two lakes, Chao Lake (n = 13) and Tai Lake (n = 15). Study sites in other countries included Delaware River (n = 12) in the United States, Thames River (n = 6) in the United Kingdom, Rhine River (n = 20) across Germany and The Netherlands, Han River (n = 6) in South Korea, and Mälaren Lake (n = 10) in Sweden. The Yangtze River is the largest (29 100 m^3/s) and longest river (6 300 km) in China, with a catchment area accounting for nearly 20% of the national land area. Tai and Chao lakes are the third and fifth largest freshwater lakes, respectively, in China. Both lakes are located in or adjacent to the Yangtze River Delta, which is the largest economic and industrial zone in China. The Yellow River is the second longest river (5 464 km), flowing through nine provinces in the north of China. The Pearl River (a collective name for the West, North, and East Rivers in Southern China) has a total runoff of 9 860 m^3/s, which ranks second among all rivers in China. The Huai and Liao rivers are the most important waterways in central and northeast China, respectively. Except for the Hai River and Songhua River, the present study included all seven major river systems in China, with total runoff of the included rivers accounting for ~70% of national riverine flow discharge (Table S2). Because it was impossible for us to conduct a nationwide sampling campaign in countries other than China, we selected those major and important water systems of that countries. All the studied rivers and lakes (i.e., River Thames and River Rhine) are important water systems in their corresponding countries; their annual flow rates are provided in Table S2. Our sampling sites were set along the main stream of the studied rivers, without proximity to known point sources of any fluorochemical facilities. The sampling campaigns inside and outside of China were all conducted by the same personnel following the same cleaning and collection procedure. In each sampling site, two grab samples were collected at a depth of 0.5−1 m and were then pooled into a single 0.5 L of composite sample using polypropylene bottles that had been prerinsed with methanol and river water. Two field blanks (prerinsed bottles filled with LC-MS grade water) were conducted during each sampling campaign in China, altogether 14 field blanks for seven sampling campaigns, but not in other countries. After collecting the samples, they were stored in a cooler box with ice pack, and then we brought them back to the laboratory in Beijing with ice pack during the flight from other countries to China. After that,

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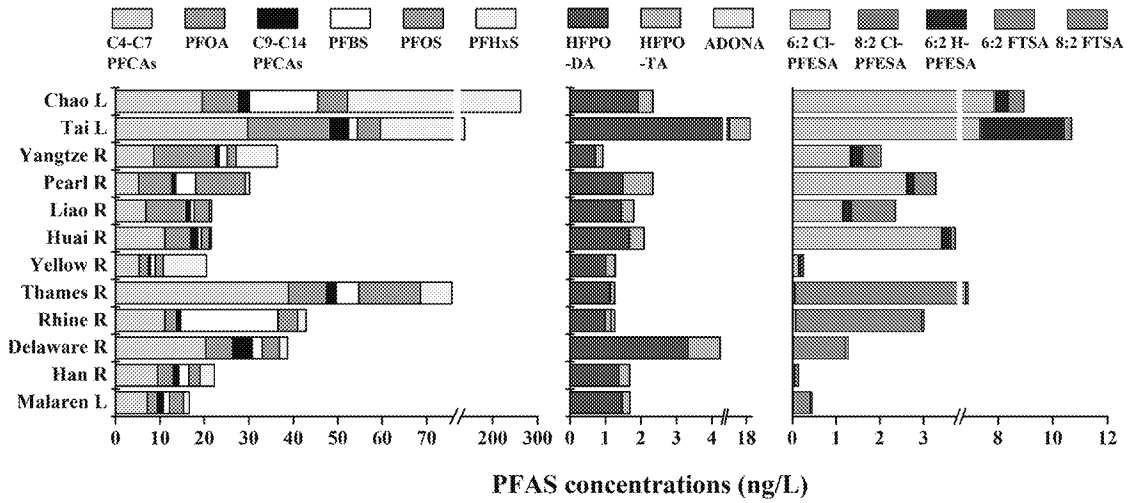

Figure 2. Mean concentrations (ng/L) of legacy PFASs (PFCAs and PFSAs) and fluorinated alternatives (PFECAs, PFESAs, and FTSAs) in the studied rivers and lakes: Chao Lake (n = 13), Tai Lake (n = 15), Yangtze River (n = 35), Pearl River (n = 13), Liao River (n = 6), Huai River (n = 9), Yellow River (n = 15), Thames River (n = 6), Rhine River (n = 20), Delaware River (n = 12), Han River (n = 6), and Mälaren Lake (n = 10).

all samples were stored in fridge at 4 °C and extracted within a week or stored at −20 °C until analysis. All samples (inside and outside of China) were extracted and analyzed using the same methods.

PFAS Analysis. A total of 24 target PFASs, as listed in the Supporting Information, were monitored. Native and mass-labeled standards for C4−C14 PFCAs, PFBS, PFHxS, PFOS, HFPO-DA, ADONA, and fluorotelomer sulfonates (4:2, 6:2, and 8:2 FTSAs) were purchased from Wellington Laboratories, Inc. (Ontario, Canada). Native standards of HFPO-TA, 4:2, 6:2, and 8:2 Cl-PFESAs, and 6:2 H-PFESA were synthesized in our Shanghai laboratory based on previously published methods.[13] The purities of all standards were >98%.

Water samples were extracted by solid-phase extraction (SPE) according to earlier literature.[13] Briefly, a subsample of 200 mL of water (without filtration) was spiked with mass-labeled standards and then extracted by a weak anion-exchange cartridge (strata X-AW, 200 mg/6 mL, Phenomenex, CA, U.S.A.). Target compounds were eluted with basic methanol, evaporated to dryness, and finally reconstituted with 200 μL of pure methanol. Except for HFPO-DA and HFPO-TA, all target PFASs were quantified with an Acquity I-Class UPLC coupled to a Xevo TQ-S mass spectrometer (Waters, Milford, MA, U.S.A.). Analyses of HFPO-DA and HFPO-TA were conducted using an AB Sciex 5500 mass spectrometer (Framingham, MA, U.S.A.), which shows higher sensitivity for HFPO homologues. Chromatographic separation was achieved using an Acquity BEH C18 column (1.7 μm, 2.1 × 75 mm, Waters, Milford, MA, U.S.A.). Further details on instrument parameters are provided in Table S3.

The limits of quantification (LOQs) were evaluated based on (1) the lowest concentration in standards where the measured value showed less than ±20% deviation from the theoretical concentration and (2) the lowest PFAS concentration in river waters resulting in a S/N ratio ≥ 10. In daily operation, one instrumental blank and one 0.1 ng/mL standard were injected in every 10 samples to monitor background contamination and instrumental drift. Extraction blanks (n = 19) were below the LOQs for most target PFASs; therefore, the method detection limit (MDL) values were the LOQs of the compounds when no contamination was found in the extraction blank. However, for PFBS and HFPO-DA, contaminations (means of 0.019 and 0.194 ng/L, respectively) were detected in the extraction blanks. The levels for PFBS and HFPO-DA were therefore reported on a blank-subtracted level, and the MDL values were defined as the means plus 3 times the standard deviation of the extraction blanks (Table S4). No detectable contamination was found in the field blanks, suggesting that no contamination occurred during the sampling campaigns. Average spike recoveries (n = 5, spiking at 0.02, 0.2, and 2 ng of standards) ranged from 77−109% in the pooled river waters (Table S4). No instrumental drift was observed as the standard deviations in all injections were no more than ±10% from theoretical concentrations (0.1 ng/mL).

Estimation of National Riverine Discharge. A MDL/2 value was used for PFAS concentrations below the MDL. Mass ratios of certain PFAS alternatives (e.g., short-chain PFASs, PFECAs, and PFESAs) versus their corresponding predecessors (e.g., PFOA or PFOS) were calculated to explore the extent of PFAS alternative usage among countries. The rivers studied in China accounted for ~70% of national riverine flow discharge to the oceans (Table S2), which allowed us to explore total national riverine discharge of PFECAs and PFESAs in China, which are currently lacking. The annual PFAS discharges were also estimated for River Delaware, River Thames, River Rhine, and River Han. However, it is important to remember that the reported PFAS discharges should not be used for representing the whole national discharge of that country, as only one river from each country was used for the calculation. Annual riverine discharge (ton/year) was calculated by multiplying the measured PFAS concentrations (ng/L) with water flux (m^3/year) for the respective rivers and dividing by 10^{12} to harmonize the units. Measured PFAS concentrations were averaged in selected water samples (Table S2) close to the river mouth. The annual water flux of the respective rivers was derived from hydrological data reported by the Ministry of Water Resources of P. R. China.[28] As the annual water flux in 2016 has not yet been published, the average of annual water flux in 2013−2015 (Table S2) was used. As a continental river, the Huai River enters a lake, rather than an ocean, and therefore its data were excluded in the estimation of national riverine discharge. We further cited the estimated PFAS discharge from Xiaoqing

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River, which is a small river but has Asia's largest polytetrafluoroethylene production plant upstream. On the basis of our earlier report,[13] significant amounts of PFOA and HFPO-TA are released in Xiaoqing River, with discharge estimated by the same method in the present investigation.

RESULTS AND DISCUSSION

PFAS Concentrations. The mean concentrations of legacy and alternative PFASs in surface water are presented in Figure 2. Descriptive data, including detection rates and median, minimum, and maximum levels of PFASs in all water samples, are provided in Tables S5 and S6. The average composition profile and spatial distribution of PFASs in each water system are illustrated in Figure 3 and Figures S2 and S3, respectively.

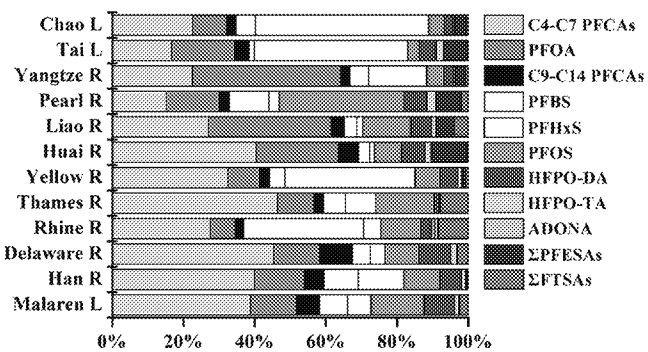

Figure 3. Average contributions of individual PFASs to ΣPFASs in the studied rivers and lakes.

PFCAs and PFSAs. The detection frequencies for C4−C9 PFCAs, PFBS, PFHxS, and PFOS were 100%, but they ranged from 10% to 98% for C10−C14 PFCAs. The mean concentrations for the sum of PFCAs and PFSAs (ΣPFCA + ΣPFSA) ranged from 17 ng/L (Mälaren Lake, Sweden) to 260 ng/L (Chao Lake, China) (Figure 2). In the current investigation, Chao and Tai lakes had the greatest ΣPFCA + ΣPFSA levels in the Chinese water systems, whereas the Thames River had the greatest level among the other studied countries. Most rivers (collected in 2016) in this study showed similar PFCA and PFSA ranges to those reported in previous research (listed in Table S7). For example, the levels of PFOA and PFOS in the Yangtze River in the present investigation (median = 12 and 1.4 ng/L, respectively) were comparable to those reported earlier in the same river and region (e.g., 12 and 0.50 ng/L in 2005;[29] 7.8 and 0.66 ng/L in 2013;[30] 9.2 and 1.1 ng/L in 2013[23]). However, the Chao and Tai freshwater lakes showed obviously higher PFHxS concentrations (median = 56 and 62 ng/L, respectively) than reported previously (0.070 ng/L[31] and 0.75 ng/L[32], respectively, in 2010−2011). On the basis of the composition profiles of PFASs (Figure S2), PFHxS has become the predominant PFAS in Chao Lake, Tai Lake, and the Yellow River, indicating its increased use and emission in China in recent years. We found PFOA to be the dominant PFAS in most samples from the Yangtze and Liao rivers, whereas PFOS was the dominant compound in most Pearl River samples (Figure S2). The distinct patterns observed in the Chinese rivers showed that (1) the contribution of short-chain (C4−C7) PFCAs was greater than that of PFOA in all water samples collected from other countries (Figure S3) and (2) the proportion of PFBS in Chinese surface waters (1.5−11%) was generally lower than those in other countries (5.0−34%). These observations indicate greater replacement of long-chain PFAS by short-chain homologues in western countries, which is further discussed below.

PFECAs. HFPO-DA and HFPO-DA were detected in 96% and 83% of all water samples, respectively (Table S5). Mean levels of HFPO-DA ranged from 0.73 ng/L (Yangtze River) to 14 ng/L (Tai Lake), and mean levels of HFPO-TA ranged from 0.14 ng/L (Thames River) to 5.0 ng/L (Tai Lake). The greatest concentration of ΣHFPO (sum of HFPO-DA and HFPO-TA) was observed in Tai Lake (T14:180 ng/L, T12:50 ng/L, Figure 1D2), suggesting an inflow of HFPO homologues from the northeast into the lake. In the Pearl River, the ΣHFPO levels in sampling sites P3 and P4 (2.9 and 20 ng/L, respectively) were significantly greater than those in other sampling sites (range = 0.33−1.4 ng/L), indicating significant discharge from the western tributary (namely, the West River, Figure 1E) to the Pearl River. Elevated ΣHFPO levels were also observed in the mouth of the Delaware River (sampling sites D9−D11, 8.0−13 ng/L, Figure S3). For all other locations, the concentrations of ΣHFPO ranged from LOQ to 1.4 ng/L, and no observable spatial trends were found. Except for the 15 samples collected in the Rhine River, ADONA was not measurably detected in any other water sample. Along the Rhine River, the peak level of ADONA (1.5 ng/L) was observed in Rheinbrohl, Germany (site R5, Figure S3); after passing through this location, only trace levels (0.013−0.085 ng/L) were detected downstream.

This is the first time PFECAs have been reported in surface waters at the worldwide scale. Our study showed the ubiquitous occurrence of HFPO-DA and HFPO-TA in surface water, not limited to fluorochemical industrial zones. Although only trace levels of ADONA were reported in the current investigation, it is clear that ADONA has been used and emitted into the environment. Among all detected PFASs, a considerable proportion (1.4−8.9%) was HFPO-DA, with HFPO-TA also accounting for 0.18−2.0% in the studied rivers (Figure 3). Unlike our earlier research in Xiaoqing River, in which HFPO-TA was the major component (1 000 times higher than HFPO-DA) in the effluent from a polytetrafluoroethylene-producing plant,[13] the river samples in this investigation showed much lower HFPO-TA than HFPO-DA concentrations. It is possible that HFPO-TA is only used as a minor component or impurity in industrial products containing HFPO-DA (e.g., GenX). This was somewhat supported by our observation that high HFPO-DA sampling sites (e.g., T14, P4 D10−D11) showed elevated HFPO-TA levels as well. Strong positive correlations between HFPO-TA and HFPO-DA were observed in all water samples (Spearman correlation coefficient >0.70, greater than the correlations with other PFASs, Table S8), indicating similar sources and usage patterns for both compounds.

PFESAs. The most frequently detected PFESA homologue was 6:2 Cl-PFESA, which was detected in 100% of samples from China and in 89% of samples from the other countries (Table S6). Most of the studied rivers and lakes in China showed comparable or even greater mean concentrations of 6:2 Cl-PFESA (1.1−7.8 ng/L) than of PFOS (1.8−11 ng/L), except for the Yellow River (mean level = 0.14 ng/L for 6:2 Cl-PFESA, which was 13 times lower than that of PFOS). Only trace levels of 6:2 Cl-PFESA (median = 0.031 ng/L, range = 0.010−0.38 ng/L) were detected in samples from the other countries. Other PFESA homologues, including 6:2 H-PFESA, 8:2 Cl-PFESA, and 4:2 Cl-PFESA, were detected in 95%, 51%, and 32% of samples from China but were not detected in any

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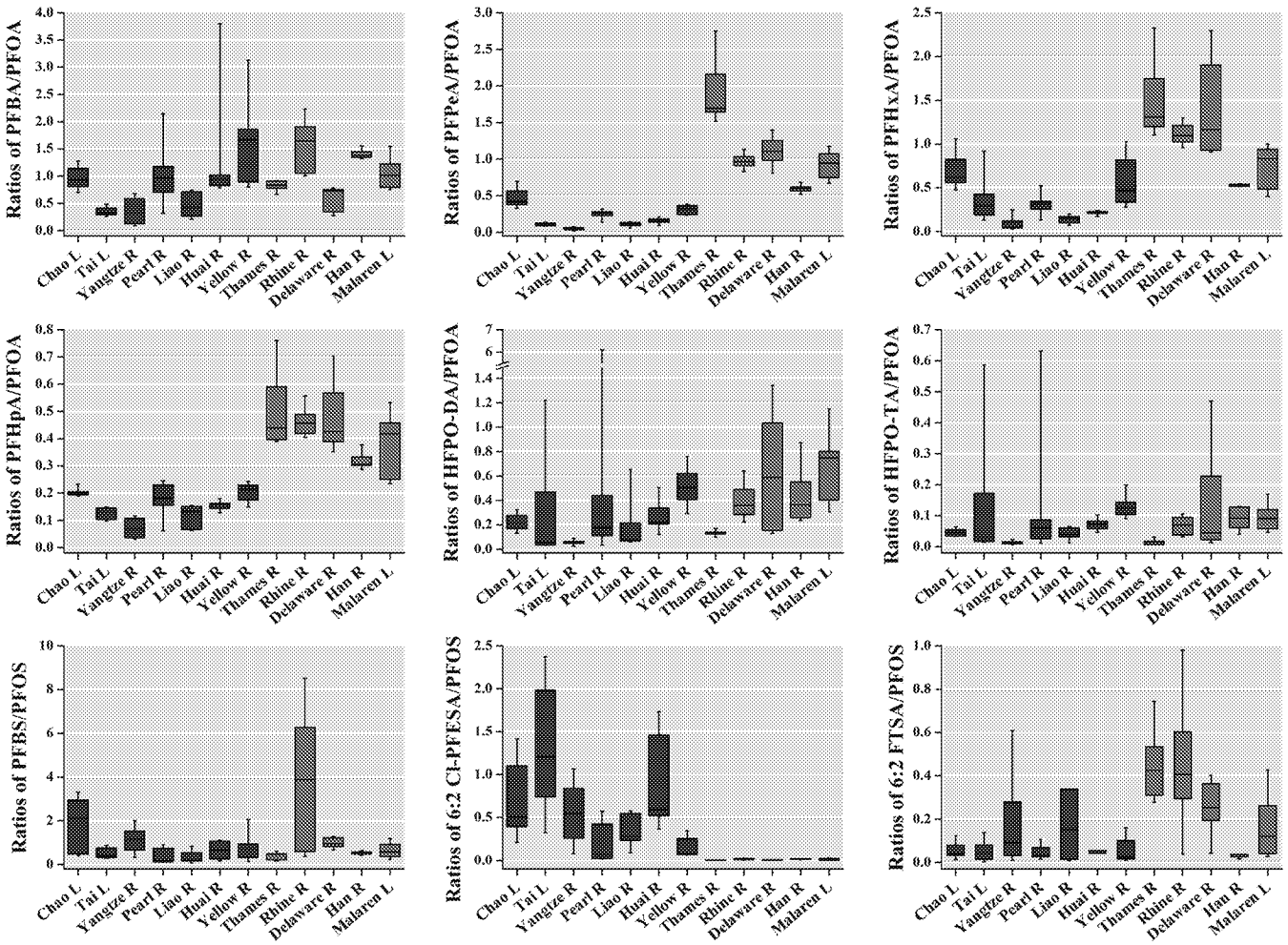

Figure 4. Mass ratios of individual PFAS alternatives (short-chain PFASs, PFECAs, or PFESAs) versus corresponding predecessors (PFOA or PFOS). Boxes display the 25th, 50th, and 75th percentiles, and whiskers represent the 10th and 90th percentiles.

other country. After 6:2 Cl-PFESA, the concentrations of 6:2 H-PFESA ranked second among all PFESA homologues, accounting for ~16% of the ΣPFESA and 0.62% of all analyzed PFASs in the Chinese water samples.

The widespread existence of 6:2 Cl-PFESA has been well-reported in abiotic and biotic environments in China.[15,22−26] Here, the frequent detection of 6:2 Cl-PFESA in rivers from western countries, albeit at trace concentrations, indicates it may have already become a global contaminant. China is currently the only known emission source of F-53B with a history of production and usage of >30 years. Thus, considerable amounts of 6:2 Cl-PFESA (the major component of F-53B) have likely been released from China to other parts of the world. Our results are in accordance with an earlier investigation that detected 6:2 Cl-PFESA in marine mammals living above the Arctic Circle.[33] Worldwide attention and continuous effort should be given to this emerging chemical, especially as very little is known about its toxicity and transformation.

The hydrogen-substituted analogue of 6:2 Cl-PFESA (6:2 H-PFESA) was ubiquitously detected in all Chinese water samples (median = 0.091 ng/L). Reductive dechlorination under anoxic environments has been reported for the transformation of 6:2 Cl-PFESA to 6:2 H-PFESA.[27] The molar ratio of 6:2 H-PFESA to 6:2 Cl-PFESA in commercial F-53B is ~1.1%.[27] In the present investigation, the molar ratios of 6:2 H-PFESA to 6:2 Cl-PFESA were much greater (mean = 27%, range = 1.3−280%). These results suggest that the 6:2 H-PFESA detected in the present study did not originate from F-53B alone and may have also come from the dechlorination of 6:2 Cl-PFESA. It is worth noting that Tai Lake had a higher 6:2 H-PFESA level (mean = 3.0 ng/L) and molar ratio (mean = 72%, range = 13−280%) than that in other rivers or lakes. As a well-known eutrophic lake suffering persistent algal blooms for the past three decades,[34] the dissolved oxygen in Tai Lake may be seriously depleted, leading to a more anoxic environment and thus favoring the transformation of 6:2 H-PFESA.

FTSAs. The 4:2, 6:2, and 8:2 FTSAs were detected in 11%, 95%, and 26% of samples, respectively. Results showed that 6:2 FTSA was dominant, whereas 4:2 and 8:2 FTSAs only accounted for a small fraction (<5.0%) of total FTSA. The greatest ΣFTSA (sum of FTSA homologues) concentration was found in the Thames River (mean = 6.9 ng/L), followed by the Rhine River (2.9 ng/L). No significant differences in ΣFTSA levels were found in samples from the other water systems (range = 0.10−1.3 ng/L). The proportions of ΣFTSA exceeded 8.0% of the total PFAS concentrations in the Thames and Rhine rivers (Figure 3), suggesting that FTSAs are an important class of fluorinated alternatives being used in these regions.

Ratios of Alternatives versus Predecessors. Legacy PFASs, mainly PFOS and PFOA, are being phased out by

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shorter-chain homologues and novel fluorinated alternatives. The ratios of certain alternatives to their corresponding predecessors are presented in Figure 4, which may help determine the extent of PFOS and PFOA replacement by alternatives among different countries. No significant differences in the ratios of PFBA to PFOA were observed among water samples from China and those from other countries (Mann–Whitney U test, $p > 0.05$). However, for short-chain PFCAs (C5–C7), their respective ratios to PFOA were significantly higher in samples from other countries than those in China. These discrepancies may indicate different usage patterns of short-chain PFCAs among countries. Our results suggest that PFBA has likely replaced PFOA in China and other countries, whereas C5–C7 PFCAs are more frequently used in western countries but not in China. In addition, the higher ratios of C5–C7 PFCAs might not only come from the direct use of products containing PFCAs but may also originate from indirect sources. Numerous fluorinated substances such as polyfluoroalkyl phosphate esters (PAPs) and telomer-based products (e.g., 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) and fluorotelomer thioether amido sulfonate (FtTAoS)) are reported to be PFCA precursors[35–37] and can transform into PFPeA, PFHxA, and PFHpA through biota degradation or photolysis. These precursors were not included in the present analysis, which may have hampered our exploration on whether indirect sources of shorter-chain PFCAs dominate in western countries. No observable discrepancy was found in the ratios of HFPO-DA or HFPO-TA versus PFOA. Several sampling sites in Tai Lake, Pearl River, and Delaware River showed relatively high concentrations of HFPOs (as mentioned above), resulting in elevated ratios versus PFOA, but these did not reach statistically significant differences among the water systems. It was expected that the ratios of 6:2 Cl-PFESA to PFOS would be much higher in China compared with that in other countries, as China is the only known emission source of F-53B. Significantly higher ratios of PFBS and 6:2 FTSA versus PFOS (median = 3.9 and 0.41) were observed in samples from the Rhine River compared with other samples. Our results indicated greater PFBS usage in Germany, which is consistent with earlier research showing PFBS to be the dominant PFAS in most samples from the Rhine River.[12] Samples collected from the Thames and Delaware rivers also showed elevated ratios of 6:2 FTSA to PFOS, indicating that 6:2 FTSA may be an important fluorinated replacement introduced following restriction of PFOS. Thus, further monitoring of FTSAs and FTSA-based substances (e.g., 6:2 FTAB) is necessary.

Riverine Discharge of PFASs in China. The estimated total riverine discharge of PFASs and the composition for individual rivers are shown in Figure 5. The PFAS discharges of respective rivers are provided in Table S9. Most PFAS discharge was derived from the Yangtze and Pearl rivers, the largest and second largest rivers in China, respectively. The two rivers contributed almost 70% to the national riverine runoff; their watersheds cover most of the eastern and southern parts of China, which are highly industrialized and urbanized regions. The Yangtze River contributed a considerable proportion (64–98%) of riverine discharge for most individual PFASs, whereas the Pearl River and Xiaoqing River accounted for the largest proportions of HFPO-DA (65%) and HFPO-TA (77%), respectively. Although Xiaoqing River is a very small river, with only 0.071% runoff compared to the Yangtze River, the extensive emissions of PFOA and HFPO-TA from the local

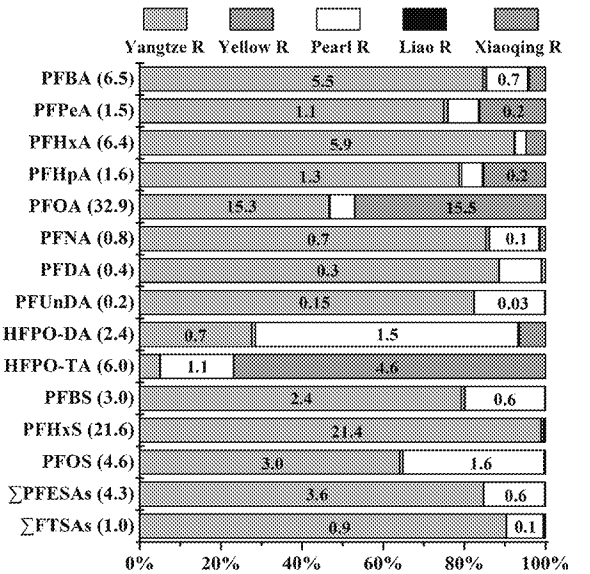

Figure 5. Relative contributions of individual rivers to total annual riverine mass discharge in China. Numbers in brackets next to bars indicate total discharge (ton/year), whereas numbers on bars indicate discharge (ton/year) from respective rivers. The data for Xiaoqing River were cited from our earlier literature,[13] which calculated the PFAS discharge using a water flux of 6.5×10^8 m^3/year.

PTFE-producing plant[13] make it an important contributor to total national riverine discharge in China.

Overall, PFOA had the greatest annual mass discharge at 32.9 ton, followed by PFHxS (21.6 ton), PFBA (6.5 ton), PFHxA (6.4 ton), HFPO-TA (6.0 ton), PFOS (4.6 ton), PFESA (4.3 ton), and PFBS (3.0 ton). The values and order of PFAS discharge were similar to those from previous research,[23] except for a major difference for PFHxS. The national discharge of PFHxS was estimated to be 0.09 ton in 2013 but raised to 21.6 ton, which was second highest in this investigation (in 2016). Increasing PFHxS discharge was observed in several sampling locations; for example, in the downstream of the Yangtze and in the nearby lakes (Tai and Chao lakes), elevated PFHxS concentrations were observed when compared to earlier reports.[31,32] This indicated that related industries in China may have switched to PFHxS in response to PFOS restrictions. While this replacement strategy is currently legitimate, PFHxS also shows similar persistence, bioaccumulation, and toxicity as that of PFOS and has already been listed as a substance of very high concern by the European Chemicals Agency.[38] In addition to PFHxS, special attention should be paid to novel fluorinated alternative substances. The estimated discharge of ΣPFESA has already reached 4.3 ton/year (6:2 Cl- and H-PFESA accounting for 83% and 15%, respectively), which is comparable to the 4.6 ton/year discharge of PFOS. Furthermore, this value is somewhat higher than the F-53B discharge (1.2 ton/year) estimated by Wang et al.,[23] which suggests that greater amounts of F-53B have been used and released in recent years. The ΣPFECA discharge exceeded 8.4 ton (2.4 ton of HFPO-DA and 6.0 ton of HFPO-TA), whereas the ΣFTSA discharge was nearly 1.0 ton. Despite the significant amounts of these emerging substances being released into the environment, little is known about their transport potential, fate, or toxicological effects.

To the best of our knowledge, this is the first time that national riverine discharge has been estimated for HFPO-DA,

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HFPO-TA, and 6:2 H-PFESA. Despite improving our understanding on the status of these emerging PFAS alternatives, our calculations may have underestimated total riverine emissions in China. Although we included five of the major river systems in China, ~30% of national runoff via other rivers was not included. Importantly, certain rivers such as the Xiaoqing River may have a tiny waterflow when compared to major water systems but can receive extensive input from point sources such as fluoropolymer manufacturing or chrome-plating industries, thus exhibiting considerable contributions to total emissions. Temporal variation of river water flux and PFAS concentrations may further contribute to uncertainties in the calculations, as instantaneous concentrations of PFAS were used. In addition, the present study only provided estimates on PFAS discharge in rivers, with other possible routes such as transport via air or dust not taken into account. The PFAS discharges were only estimated for one single river in foreign countries other than China (Table S9). Further comprehensive study on PFAS discharges on these countries is needed.

Environmental Implications. Following restriction of the production and use of long-chain PFASs, modern industry has responded by introducing fluorinated replacements with similar molecular structures, such as PFECAs, PFESAs, and FTSAs. In the present study, these emerging substances were ubiquitously detected in worldwide surface waters. Although their concentrations may not be as great as their predecessors, the sum of these replacements already accounts for 6.7−19% of all analyzed PFASs, effectively explaining a considerable proportion of unknown extractable organic fluorine. Our results indicated that HFPO-DA, HFPO-TA, and 6:2 Cl-PFESA have become global contaminants, but important information regarding their physicochemical properties, emission sources, and annual production remain unknown. The anaerobic transformation product 6:2 H-PFESA was also detected ubiquitously in Chinese water samples. This may be a practical path for the biodegradation of Cl-PFESAs, and continuous effort should be paid to its distribution, fate, behavior, and toxicity. Furthermore, substantial discharges of PFASs (e.g., 2.4 ton for HFPO-DA, 6.0 ton for HFPO-TA, 4.3 ton for PFESAs, and 1.0 ton for FTSAs) from Chinese rivers into the ocean were found. Thus, with such little information available on these emerging alternatives, proper precautions are necessary.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00829.

Additional information on sampling sites, water flux of studied rivers, PFAS analysis, QA/QCs, PFAS concentrations, and other materials (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

(26 pages, 9 tables, 3 figures)

Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids (PFECAs and PFESAs) in Surface Water

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Table S1. Information on the sampling sites

No.	River/lake	City	Country	Longitude (°E)	Latitude (°N)	Date
Y1	Yangtze River	Chongqing,	China	106.46026	29.38641	Dec 05, 2016
Y2	Yangtze River	Chongqing	China	106.65253	29.59354	Dec 05, 2016
Y3	Yangtze River	Chongqing	China	108.36956	30.66676	Dec 05, 2016
Y4	Yangtze River	Chongqing	China	108.42217	30.82951	Dec 05, 2016
Y5	Yangtze River	Yichang	China	111.04778	30.82467	Dec 06, 2016
Y6	Yangtze River	Yichang	China	111.27702	30.69478	Dec 06, 2016
Y7	Yangtze River	Jingzhou	China	112.09484	30.28828	Dec 06, 2016
Y8	Yangtze River	Jingzhou	China	112.23826	30.30172	Dec 06, 2016
Y9	Yangtze River	Yueyang	China	113.06132	29.49340	Dec 06, 2016
Y10	Yangtze River	Yueyang	China	113.19090	29.49211	Dec 06, 2016
Y11	Yangtze River	Wuhan	China	114.21169	30.45975	Dec 06, 2016
Y12	Yangtze River	Wuhan	China	114.40070	30.65140	Dec 06, 2016
Y13	Yangtze River	Jiujiang	China	115.87424	29.74061	Nov 30, 2016
Y14	Yangtze River	Jiujiang	China	116.05326	29.76939	Nov 30, 2016
Y15	Yangtze River	Anqing	China	116.95488	30.45725	Nov 30, 2016
Y16	Yangtze River	Anqing	China	117.14454	30.52010	Nov 30, 2016
Y17	Yangtze River	Chizhou	China	117.46735	30.67928	Nov 30, 2016
Y18	Yangtze River	Chizhou	China	117.63256	30.76853	Nov 30, 2016
Y19	Yangtze River	Tongling	China	117.76813	30.97858	Nov 30, 2016
Y20	Yangtze River	Wuhu	China	118.32315	31.28479	Nov 30, 2016
Y21	Yangtze River	Wuhu	China	118.34375	31.41823	Nov 30, 2016
Y22	Yangtze River	Ma'anshan	China	118.44930	31.65506	Dec 01, 2016
Y23	Yangtze River	Ma'anshan	China	118.47889	31.78917	Dec 01, 2016
Y24	Yangtze River	Nanjing	China	118.63829	31.97092	Dec 01, 2016
Y25	Yangtze River	Nanjing	China	118.76035	32.13637	Dec 01, 2016
Y26	Yangtze River	Zhenjiang	China	119.39188	32.24161	Dec 01, 2016
Y27	Yangtze River	Zhenjiang	China	119.69249	32.26421	Dec 01, 2016
Y28	Yangtze River	Jiangyin	China	120.08844	31.94081	Dec 02, 2016
Y29	Yangtze River	Jiangyin	China	120.26153	31.93414	Dec 02, 2016
Y30	Yangtze River	Zhangjiagang	China	120.51618	32.04066	Dec 02, 2016
Y31	Yangtze River	Zhangjiagang	China	120.66576	32.01862	Dec 02, 2016
Y32	Yangtze River	Changshu	China	120.82580	31.77921	Dec 02, 2016
Y33	Yangtze River	Changshu	China	120.93523	31.76438	Dec 02, 2016
Y34	Yangtze River	Shanghai	China	121.41286	31.46676	Dec 02, 2016
Y35	Yangtze River	Shanghai	China	121.50160	31.40609	Dec 02, 2016
Ye1	Yellow River	Lanzhou	China	103.52943	36.14382	Nov 04, 2016
Ye2	Yellow River	Lanzhou	China	103.81433	36.06483	Nov 04, 2016
Ye3	Yellow River	Lanzhou	China	104.00576	36.06071	Nov 04, 2016
Ye4	Yellow River	Baiyin	China	104.36441	36.38548	Nov 04, 2016

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Table S1. Continued

No.	River/Lake	City	Country	Longitude (°E)	Latitude (°N)	Date
Ye5	Yellow River	Baiyin	China	104.53689	36.47644	Nov 04, 2016
Ye6	Yellow River	Sanmenxia	China	110.95507	34.70638	Oct 21, 2016
Ye7	Yellow River	Sanmenxia	China	111.26929	34.80746	Oct 21, 2016
Ye8	Yellow River	Zhengzhou	China	113.55745	34.95161	Oct 21, 2016
Ye9	Yellow River	Zhengzhou	China	114.23829	34.90528	Oct 21, 2016
Ye10	Yellow River	Kaifeng	China	114.29674	34.90948	Oct 21, 2016
Ye11	Yellow River	Kaifeng	China	114.62466	34.93033	Oct 21, 2016
Ye12	Yellow River	Ji'nan	China	116.81181	36.70799	Oct 22, 2016
Ye13	Yellow River	Ji'nan	China	117.17782	36.90322	Oct 22, 2016
Ye14	Yellow River	Binzhou	China	117.95299	37.29371	Oct 22, 2016
Ye15	Yellow River	Binzhou	China	118.32642	37.55523	Oct 22, 2016
P1	Pearl River (North River)	Foshan	China	112.89490	23.38153	Oct 16, 2016
P2	Pearl River (North River)	Foshan	China	112.81297	23.23697	Oct 16, 2016
P3	Pearl River (West River)	Foshan	China	112.66604	23.17091	Oct 16, 2016
P4	Pearl River (West River)	Foshan	China	112.93380	22.84647	Oct 16, 2016
P5	Pearl River (East River)	Guangzhou	China	113.18039	23.22967	Oct 16, 2016
P6	Pearl River (East River)	Guangzhou	China	113.36006	23.10869	Oct 16, 2016
P7	Pearl River (East River)	Huizhou	China	114.26414	23.15610	Oct 16, 2016
P8	Pearl River (East River)	Dongguan	China	114.01525	23.08577	Oct 16, 2016
P9	Pearl River (East River)	Dongguan	China	113.74657	23.13340	Oct 16, 2016
P10	Pearl River (East River)	Dongguan	China	113.58081	23.08683	Oct 16, 2016
P11	Pearl River (East River)	Dongguan	China	113.53858	23.06297	Oct 16, 2016
P12	Pearl River (East River)	Dongguan	China	113.73621	23.05338	Oct 16, 2016
P13	Pearl River (East River)	Dongguan	China	113.56292	22.87135	Oct 16, 2016
H1	Huai River	Xinzheng	China	113.70176	34.40331	Oct 28, 2016
H2	Huai River	Zhoukou	China	114.52741	33.83447	Oct 28, 2016
H3	Huai River	Zhoukou	China	114.37576	33.68798	Oct 28, 2016
H4	Huai River	Zhoukou	China	114.62291	33.62180	Oct 28, 2016
H5	Huai River	Zhoukou	China	114.86073	33.52924	Oct 28, 2016
H6	Huai River	Bengbu	China	117.25128	32.95897	Oct 20, 2016
H7	Huai River	Bengbu	China	117.67287	32.93963	Oct 20, 2016
H8	Huai River	Bengbu	China	117.80425	33.02978	Nov 06, 2016
H9	Huai River	Bengbu	China	118.00177	33.14334	Nov 06, 2016
L1	Liao River	Shenyang	China	123.43444	41.75028	Sep 27, 2016
L2	Liao River	Shenyang	China	123.32806	41.73389	Sep 27, 2016
L3	Liao River	Anshan	China	122.49037	41.08299	Sep 27, 2016
L4	Liao River	Panjin	China	122.37127	40.98692	Sep 27, 2016
L5	Liao River	Anshan	China	122.50291	40.99352	Sep 27, 2016
L6	Liao River	Yingkou	China	122.16151	40.70410	Sep 27, 2016

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Table S1. Continued

No.	River/Lake	City	Country	Longitude (°E)	Latitude (°N)	Date
C1	Nanfei River (inflow)	Hefei	China	117.42190	31.78212	Oct 19, 2016
C2	Chao Lake	Hefei	China	117.40450	31.70998	Oct 19, 2016
C3	Shiwuli River (inflow)	Hefei	China	117.27316	31.78940	Oct 19, 2016
C4	Chao Lake	Hefei	China	117.36175	31.72126	Oct 19, 2016
C5	Pai River (inflow)	Hefei	China	117.21785	31.69818	Oct 19, 2016
C6	Chao Lake	Hefei	China	117.29138	31.66701	Oct 19, 2016
C7	Chao Lake	Hefei	China	117.40553	31.66608	Oct 30, 2016
C8	Chao Lake	Hefei	China	117.32014	31.66053	Oct 30, 2016
C9	Chao Lake	Hefei	China	117.37779	31.59597	Oct 30, 2016
C10	Chao Lake	Hefei	China	117.49384	31.50629	Oct 30, 2016
C11	Chao Lake	Hefei	China	117.60397	31.52475	Oct 30, 2016
C12	Chao Lake	Chaohu	China	117.85059	31.59094	Oct 19, 2016
C13	Yuxi River (outflow)	Chaohu	China	117.88515	31.55572	Oct 19, 2016
T1	Tai Lake	Wuxi	China	120.13530	31.51181	Dec 03, 2016
T2	Tai Lake	Wuxi	China	120.02985	31.43095	Dec 03, 2016
T3	Tai Lake	Wuxi	China	120.03128	31.39761	Dec 03, 2016
T4	Tai Lake	Wuxi	China	119.93212	31.31135	Dec 03, 2016
T5	Tai Lake	Wuxi	China	119.94500	31.31450	Dec 03, 2016
T6	Tai Lake	Wuxi	China	119.75463	31.22287	Dec 03, 2016
T7	Tai Lake	Huzhou	China	119.98783	31.03520	Dec 03, 2016
T8	Tai Lake	Huzhou	China	119.98952	31.03954	Dec 03, 2016
T9	Tai Lake	Huzhou	China	120.12970	30.94365	Dec 03, 2016
T10	Tai Lake	Suzhou	China	120.49291	31.01114	Dec 03, 2016
T11	Tai Lake	Suzhou	China	120.46710	31.22580	Dec 03, 2016
T12	Tai Lake	Wuxi	China	120.40790	31.44634	Dec 03, 2016
T13	Tai Lake	Wuxi	China	120.29530	31.38655	Dec 16, 2016
T14	Tai Lake	Wuxi	China	120.18773	31.41117	Dec 16, 2016
T15	Tai Lake	Wuxi	China	120.17062	31.24861	Dec 16, 2016
D1	Delaware River	Trenton	U.S.	-74.80753	40.22718	Dec 17, 2016
D2	Delaware River	Trenton	U.S.	-74.74372	40.17455	Dec 17, 2016
D3	Delaware River	Bristol	U.S.	-74.85089	40.09172	Dec 17, 2016
D4	Delaware River	Philadelphia	U.S.	-74.97192	40.05412	Dec 17, 2016
D5	Delaware River	Philadelphia	U.S.	-75.06169	39.98700	Sep 24, 2016
D6	Delaware River	Philadelphia	U.S.	-75.13495	39.91906	Sep 24, 2016
D7	Schuylkill River (tributary)	Philadelphia	U.S.	-75.27715	40.06470	Sep 24, 2016
D8	Schuylkill River (tributary)	Philadelphia	U.S.	-75.19123	39.99248	Sep 24, 2016
D9	Delaware River	Chester	U.S.	-75.37662	39.81417	Dec 17, 2016
D10	Delaware River	Delaware	U.S.	-75.56372	39.57996	Dec 17, 2016
D11	Delaware River	Smyrna	U.S.	-75.46468	39.33054	Dec 17, 2016
D12	Delaware River	Frederica	U.S.	-75.39557	39.10128	Dec 17, 2016

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Table S1. Continued

No.	River/Lake	City	Country	Longitude (°E)	Latitude (°N)	Date
Th1	Thames River	Oxford	U.K.	-1.25625	51.77458	Oct 01, 2016
Th2	Thames River	Oxford	U.K.	-1.23625	51.67292	Oct 01, 2016
Th3	Thames River	London	U.K.	-0.30833	51.40583	Oct 02, 2016
Th4	Thames River	London	U.K.	-0.23721	51.49042	Oct 02, 2016
Th5	Thames River	London	U.K.	-0.11972	51.50361	Oct 02, 2016
Th6	Thames River	London	U.K.	-0.02861	51.50556	Oct 02, 2016
M1	Mälaren Lake	Örebro	Sweden	15.12217	59.26125	Sep 28, 2016
M2	Mälaren Lake	Örebro	Sweden	15.26061	59.27680	Sep 28, 2016
M3	Mälaren Lake	Örebro	Sweden	15.38172	59.27470	Sep 28, 2016
M4	Mälaren Lake	Örebro	Sweden	15.48373	59.27171	Sep 28, 2016
M5	Mälaren Lake	Stockholm	Sweden	17.79691	59.45512	Sep 29, 2016
M6	Mälaren Lake	Stockholm	Sweden	17.83444	59.35722	Sep 29, 2016
M7	Mälaren Lake	Stockholm	Sweden	17.96758	59.31228	Sep 29, 2016
M8	Mälaren Lake	Stockholm	Sweden	18.04218	59.32335	Sep 29, 2016
M9	Mälaren Lake	Stockholm	Sweden	18.10071	59.32511	Sep 29, 2016
M10	Mälaren Lake	Stockholm	Sweden	18.36688	59.37378	Sep 29, 2016
R1	Rhine River	Offenbach	Germany	8.76528	50.10833	Dec 28, 2016
R2	Rhine River	Frankfurt	Germany	8.60278	50.08917	Dec 28, 2016
R3	Rhine River	Wiesbaden	Germany	8.28028	50.00639	Dec 28, 2016
R4	Rhine River	Goarshausen	Germany	7.71917	50.15139	Dec 28, 2016
R5	Rhine River	Rheinbrohl	Germany	7.33333	50.48917	Dec 21, 2016
R6	Rhine River	Bonn	Germany	7.10639	50.74250	Dec 21, 2016
R7	Rhine River	Cologne	Germany	6.96917	50.94444	Dec 21, 2016
R8	Rhine River	Leverkusen	Germany	6.97089	51.02931	Dec 21, 2016
R9	Rhine River	Dormagen	Germany	6.85083	51.08611	Dec 21, 2016
R10	Rhine River	Düsseldorf	Germany	6.75517	51.25117	Dec 21, 2016
R11	Rhine River	Duisburg	Germany	6.69263	51.37488	Dec 21, 2016
R12	Rhine River	Duisburg	Germany	6.72583	51.46083	Dec 21, 2016
R13	Rhine River	Wesel	Germany	6.58639	51.62778	Dec 21, 2016
R14	Rhine River	Emmerich	Germany	6.23681	51.83019	Dec 21, 2016
R15	Rhine River	Arnhem	Netherlands	5.89556	51.98255	Dec 22, 2016
R16	Rhine River	Lienden	Netherlands	5.63253	51.94361	Dec 22, 2016
R17	Rhine River	Duurstede	Netherlands	5.34578	51.96761	Dec 22, 2016
R18	Rhine River	Nijmegen	Netherlands	5.85861	51.85333	Dec 22, 2016
R19	Rhine River	Wamel	Netherlands	5.44603	51.88200	Dec 22, 2016
R20	Rhine River	Zaltbommel	Netherlands	5.24711	51.81542	Dec 22, 2016
Ha1	Han River	Seoul	South Korea	127.26462	37.52594	Nov 17, 2016
Ha2	Han River	Seoul	South Korea	127.19276	37.58245	Nov 17, 2016
Ha3	Han River	Seoul	South Korea	127.10661	37.54097	Nov 17, 2016
Ha4	Han River	Seoul	South Korea	127.04649	37.52348	Nov 17, 2016
Ha5	Han River	Seoul	South Korea	126.98065	37.49865	Nov 17, 2016
Ha6	Han River	Seoul	South Korea	126.89157	37.54896	Nov 17, 2016

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Table S2. Reported annual flow rates for the studied rivers

River[1]	Station[2]	Year	Flow rate (m^3/s)	Mean (m^3/s)	Sampling site[3]
in China					
Yangtze River	Datong	2013	25000	27433	Y26-35
		2014	28300		
		2015	29000		
Yellow River	Lijin	2013	751	512	Ye12-15
		2014	362		
		2015	424		
Pearl River[4]	Makou	2013	6540	7190	P3, P4
(West tributary)		2014	6530		
		2015	8500		
Pearl River	Sanshui	2013	1880	1980	P1, P2
(North tributary)		2014	1850		
		2015	2210		
Pearl River	Boluo	2013	904	690.3	P5-13
(East tributary)		2014	596		
		2015	571		
Liao River	Sanchahe	2013	246.4	144	L3-6
		2014	102.2		
		2015	83.4		
Total flow rate of the studied rivers in China				37950	
Total runoff of rivers within China into oceans[5]				54700	
in other countries					
Delaware River	–	–	371		D5-6, D9-10
Thames River	–	–	65.8		Th3-6
Rhine River	–	–	2900		R10-20
Han River	–	–	670		Ha1-6

[1] The flow rate of the respective rivers in China was derived from the annual hydrological report (in Chinese) by the Ministry of Water Resources of P.R. China; the flow rate of rivers in other countries was derived from the corresponding entries in Wikipedia

[2] The hydrological station where flow rate was determined.

[3] Sampling sites close to the river mouth, average PFAS concentrations in these sites were used to estimate PFAS discharge.

[4] Pearl River consists of three tributaries: West, North, and East Rivers. PFAS discharge from these tributaries was calculated separately and values were combined for the Pearl River.

[5] Wang, T.; Vestergren, R.; Herzke, D.; Yu, J. C.; Cousins, I. T. Levels, isomer profiles, and estimated riverine mass discharges of perfluoroalkyl acids and fluorinated alternatives at the mouths of Chinese rivers. *Environ. Sci. Technol.* **2016**, *50* (21), 11584-11592.

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Table S3. LC-MS/MS instrument parameters for the quantification of target analytes.

Instrument	Acquity UPLC coupled to a Xevo TQ-*S* triple quadrupole mass spectrometer (Waters, Milford, MA, USA) or a API 5500 triple-quadrupole mass spectrometer (AB SCIEX Inc., Framingham, MA, USA)
Analytical column	Acquity BEH C18 column (100 mm × 2.1 mm, 1.7 μm, Waters, MA, USA)
Trap column	C18 column (50 mm × 2.1 mm, 3.0 μm, Waters, MA, USA)
Column temperature	40°C
Injection volume	2 μL
Mobile phase	2 mM ammonium acetate in water (A) and methanol (B)
Gradient	

Time (min)	Flow rate (mL/min)	A (%)	B (%)
0.0	0.30	90	10
1.0	0.30	80	20
4.0	0.30	10	90
6.0	0.30	10	90
6.1	0.30	90	10
9.0	0.30	90	10

Multiple reaction monitoring (MRM) transitions

Compound	Ion transitions	CV/DP (V)	CE (V)	Internal standard
PFBA	213→169	30	11	$^{13}C_4$-PFBA
PFPeA	263→119	10	8	$^{13}C_5$-PFPeA
PFHxA	313→269	14	10	$^{13}C_2$-PFHxA
PFHpA	363→319	30	10	$^{13}C_4$-PFHpA
PFOA	413→369	30	10	$^{13}C_4$-PFOA
PFNA	463→419	28	10	$^{13}C_5$-PFNA
PFDA	513→469	12	10	$^{13}C_2$-PFDA
PFUnA	563→519	30	10	$^{13}C_2$-PFUnA
PFDoA	613→569	2	10	$^{13}C_2$-PFDoA
PFTriA	663→619	10	10	$^{13}C_2$- PFTeDA
PFTeDA	713→669	10	15	$^{13}C_2$- PFTeDA
PFBS	299→80	40	30	$^{13}C_4$-PFOS
PFHxS	399→80	45	33	$^{18}O_2$-PFHxS
PFOS	499→80	30	39	$^{13}C_4$-PFOS
4:2 Cl-PFESA	431→251	30	24	$^{13}C_4$-PFOS
6:2 Cl-PFESA	531→351	30	24	$^{13}C_4$-PFOS
8:2 Cl-PFESA	631→451	30	30	$^{13}C_4$-PFOS

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	6:2 H-PFESA	497→317	30	30	$^{13}C_4$-PFOS
	4:2 FTSA	327→307	2	20	$^{13}C_2$-4:2 FTSA
	6:2 FTSA	427→407	30	24	$^{13}C_2$-6:2 FTSA
	8:2 FTSA	527→507	30	26	$^{13}C_2$-8:2 FTSA
	HFPO-DA	329→169	30	18	$^{13}C_3$-HFPO-DA
	HFPO-TA	495→185	20	12	$^{13}C_5$-PFNA
	ADONA	377→251	14	10	$^{13}C_4$-PFHpA
	CV: cone voltage; DP: declustering potential; CE: collision energy				
Other mass parameters	**Xevo TQ-S, Waters** Capillary voltage, -0.5 kV Source temperature, 150°C Desolvation temperature, 450°C Desolvation gas flow, 850 L/h Cone gas flow, 150 L/h **API 5500, AB Sciex** Ion spray voltage: -4.5 kV Curtain gas: 20 psi Collision gas: Medium Temperature: 500°C Ion source gas 1: 50 psi Ion source gas 2: 45 psi				

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Table S4. Limits of quantification (LOQ), average blank levels, method detection limits (MDL), spike recoveries, and matrix effects in water samples (n = 5)

	LOQ (ng/L)	Blank (ng/L)	MDL (ng/L)	Spike recovery ± SD (%)			Matrix effect ± SD (%)
				0.1 ppb (0.02 ng)	1 ppb (0.2 ng)	10 ppb (20 ng)	
PFBA	0.05	n.d.	0.05	96.7 ± 5.7	104.0 ± 3.1	106.8 ± 3.3	99.4 ± 2.1
PFPeA	0.05	n.d.	0.05	97.5 ± 4.7	103.5 ± 3.3	102.7 ± 2.1	101.2 ± 0.6
PFHxA	0.02	n.d.	0.02	98.3 ± 4.4	104.5 ± 1.6	103.0 ± 2.1	100.2 ± 0.8
PFHpA	0.02	n.d.	0.02	97.2 ± 3.4	104.7 ± 2.7	103.9 ± 2.8	101.1 ± 1.3
PFOA	0.02	n.d.	0.02	97.4 ± 5.9	103.1 ± 3.3	102.9 ± 2.7	98.1 ± 2.0
PFNA	0.02	n.d.	0.02	97.6 ± 4.5	105.7 ± 1.3	103.9 ± 2.2	100.9 ± 2.0
PFDA	0.02	n.d.	0.02	96.1 ± 5.6	105.4 ± 5.0	104.1 ± 3.3	102.3 ± 2.6
PFUnA	0.02	n.d.	0.02	92.7 ± 4.3	106.1 ± 2.4	103.8 ± 3.1	102.3 ± 3.4
PFDoA	0.02	n.d.	0.02	96.1 ± 7.5	99.0 ± 8.5	105.7 ± 2.1	97.1 ± 7.4
PFTriA	0.02	n.d.	0.02	93.8 ± 5.4	93.3 ± 1.6	104.4 ± 3.5	108.8 ± 4.0
PFTeDA	0.02	n.d.	0.02	95.7 ± 6.3	104.5 ± 1.8	109.2 ± 4.4	120.1 ± 3.8
PFBS	0.01	0.02	0.03	96.3 ± 5.1	104.3 ± 3.0	105.6 ± 1.4	99.2 ± 1.3
PFHxS	0.05	n.d.	0.05	97.7 ± 3.4	105.0 ± 3.5	103.7 ± 1.6	98.6 ± 0.9
PFOS	0.02	n.d.	0.02	95.1 ± 3.6	102.3 ± 3.7	102.4 ± 2.6	99.3 ± 1.5
4:2 Cl-PFESA	0.01	n.d.	0.01	93.5 ± 4.8	102.5 ± 3.3	103.1 ± 2.5	99.2 ± 0.9
6:2 Cl-PFESA	0.01	n.d.	0.01	89.0 ± 3.6	104.9 ± 2.5	98.2 ± 1.4	98.0 ± 1.4
8:2 Cl-PFESA	0.01	n.d.	0.01	87.1 ± 5.2	104.9 ± 4.3	99.4 ± 1.9	99.2 ± 1.3
6:2 H-PFESA	0.01	n.d.	0.01	94.6 ± 4.3	98.8 ± 3.5	97.3 ± 2.2	97.4 ± 3.1
4:2 FTSA	0.02	n.d.	0.02	98.4 ± 5.0	100.9 ± 1.2	82.4 ± 0.9	121.6 ± 4.9
6:2 FTSA	0.02	n.d.	0.02	93.0 ± 5.9	103.2 ± 2.7	85.4 ± 0.8	136.0 ± 6.3
8:2 FTSA	0.02	n.d.	0.02	87.6 ± 4.6	93.5 ± 2.8	77.1 ± 0.6	154.2 ± 8.0
HFPO-DA	0.05	0.194	0.38	89.6 ± 5.0	102.4 ± 6.4	102.9 ± 3.4	109.3 ± 0.9
HFPO-TA	0.10	n.d.	0.10	85.1 ± 1.0	100.3 ± 2.2	97.1 ± 1.1	98.6 ± 6.7
ADONA	0.01	n.d.	0.01	98.2 ± 5.7	104.2 ± 1.9	99.6 ± 1.5	105.1 ± 3.3

Pooled river waters were used for QA/QC. LOQ: Lowest concentration spiked in river water samples resulting in S/N ratio above 10.

MDL: Average plus three times the standard deviation of extraction blanks (n = 19). Most PFASs were not detected in blank samples, MDLs were set as their LOQs.

n.d. not detected

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Table S5. Detection rates and mean, median, min, and max concentrations (ng/L) of PFCAs and PFECAs in surface waters from different rivers and lakes

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTriA	PFTeDA	HFPO -DA	HFPO -TA	ADONA
All samples (n = 160)	> LOQ	160	160	160	160	160	160	156	135	79	40	16	153	132	15
	mean	4.71	2.46	4.74	1.32	8.19	0.93	0.43	0.16	0.07	0.04	0.02	2.55	0.79	0.02
	median	4.46	1.42	1.73	1.02	6.17	0.61	0.25	0.07	< LOQ	< LOQ	< LOQ	0.95	0.21	< LOQ
	min	0.84	0.04	0.10	0.02	0.15	0.05	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.18	< LOQ	< LOQ
	max	22.8	19.9	198	5.70	52.8	5.73	5.75	3.06	2.30	1.56	1.34	144	34.8	1.55
Yangtze River (n = 35)	> LOQ	35	35	35	35	35	35	35	28	4	5	1	33	27	0
	mean	4.36	0.72	2.54	0.91	13.5	0.56	0.15	0.07	0.01	0.01	0.01	0.73	0.19	< LOQ
	median	3.92	0.58	1.07	0.76	12.2	0.36	0.07	0.03	< LOQ	< LOQ	< LOQ	0.67	0.14	< LOQ
	min	0.93	0.21	0.33	0.29	3.48	0.15	0.03	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
	max	9.61	3.60	28.2	4.43	36.5	2.75	1.59	0.70	0.07	0.05	0.02	1.54	1.29	< LOQ
Yellow River (n = 15)	> LOQ	15	15	15	15	15	15	11	3	0	0	0	10	10	0
	mean	3.52	0.63	0.80	0.41	2.05	0.39	0.06	0.01	< LOQ	< LOQ	< LOQ	1.01	0.27	< LOQ
	median	4.05	0.85	1.01	0.56	2.45	0.45	0.04	< LOQ	< LOQ	< LOQ	< LOQ	1.30	0.29	< LOQ
	min	1.20	0.04	0.10	0.02	0.15	0.05	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
	max	7.38	1.13	1.57	0.74	4.92	0.76	0.31	0.06	< LOQ	< LOQ	< LOQ	1.74	0.74	< LOQ
Pearl River (n = 13)	> LOQ	13	13	13	13	13	13	13	13	7	4	0	13	11	0
	mean	2.94	0.82	0.93	0.57	7.45	0.44	0.24	0.12	0.02	0.02	< LOQ	1.51	0.83	< LOQ
	median	1.80	0.47	0.58	0.42	1.82	0.35	0.18	0.11	0.02	< LOQ	< LOQ	0.70	0.15	< LOQ
	min	0.88	0.15	0.34	0.07	0.40	0.22	0.06	0.04	< LOQ	< LOQ	< LOQ	0.21	< LOQ	< LOQ
	max	9.40	3.68	2.99	2.11	52.8	1.28	0.87	0.30	0.05	0.08	< LOQ	10.3	9.20	< LOQ

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Table S5 Continued

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTriA	PFTeDA	HFPO-DA	HFPO-TA	ADONA
	n > LOQ	6	6	6	6	6	6	6	5	0	0	0	6	6	0
Liao	mean	3.82	0.95	1.17	0.96	8.95	0.61	0.21	0.05	< LOQ	< LOQ	< LOQ	1.44	0.36	< LOQ
River	median	3.15	0.90	1.07	0.91	9.39	0.56	0.17	0.02	< LOQ	< LOQ	< LOQ	0.88	0.36	< LOQ
(*n* = 6)	min	2.53	0.71	0.91	0.69	5.28	0.48	0.06	< LOQ	< LOQ	< LOQ	< LOQ	0.62	0.13	< LOQ
	max	7.52	1.46	1.73	1.30	12.3	0.90	0.36	0.15	< LOQ	< LOQ	< LOQ	4.51	0.61	< LOQ
	n > LOQ	9	9	9	9	9	9	9	9	2	0	0	9	9	0
Huai	mean	7.90	0.92	1.29	0.91	6.02	1.08	0.24	0.09	0.01	< LOQ	< LOQ	1.66	0.43	< LOQ
River	median	5.37	0.94	1.20	0.87	6.01	1.15	0.23	0.09	< LOQ	< LOQ	< LOQ	1.40	0.43	< LOQ
(*n* = 9)	min	3.91	0.58	0.89	0.72	4.24	0.77	0.13	0.03	< LOQ	< LOQ	< LOQ	0.83	0.28	< LOQ
	max	22.8	1.25	1.97	1.30	9.06	1.35	0.42	0.15	0.03	< LOQ	< LOQ	3.62	0.61	< LOQ
	n > LOQ	13	13	13	13	13	13	13	13	10	4	2	13	13	0
Chao	mean	7.91	4.01	5.95	1.68	8.16	1.39	0.68	0.20	0.08	0.02	0.01	1.92	0.42	< LOQ
Lake	median	6.97	4.01	6.24	1.55	8.17	1.34	0.51	0.16	0.03	< LOQ	< LOQ	1.81	0.39	< LOQ
(*n* = 13)	min	5.17	2.29	3.41	1.36	7.00	1.19	0.28	0.06	< LOQ	< LOQ	< LOQ	0.93	0.20	< LOQ
	max	11.7	6.82	10.8	2.35	10.5	1.65	2.02	0.61	0.54	0.07	0.04	3.32	1.08	< LOQ
	n > LOQ	15	15	15	15	15	15	15	15	14	12	2	15	15	0
Tai	mean	6.52	1.87	19.3	2.19	18.5	2.09	1.25	0.33	0.42	0.05	0.02	14.0	4.99	< LOQ
Lake	median	6.25	1.89	5.66	2.41	17.95	1.67	1.00	0.23	0.06	0.04	< LOQ	0.77	0.38	< LOQ
(*n* = 15)	min	0.88	0.27	0.36	0.37	3.15	0.41	0.19	0.10	< LOQ	< LOQ	< LOQ	0.38	0.12	< LOQ
	max	12.9	2.74	198	3.05	44.5	5.73	5.75	0.94	2.30	0.18	0.13	143.7	34.8	< LOQ

ED_005565_00005099-00021

Table S5 Continued

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTriA	PFTeDA	HFPO -DA	HFPO -TA	ADONA
	n > LOQ	6	6	6	6	6	6	6	6	5	0	0	6	4	0
Thames	mean	6.96	15.7	12.2	4.10	8.51	1.18	0.86	0.07	0.04	< LOQ	< LOQ	1.12	0.14	< LOQ
River	median	6.86	16.1	12.7	4.15	8.46	1.17	0.85	0.07	0.04	< LOQ	< LOQ	1.10	0.16	< LOQ
(*n* = 6)	min	4.62	10.1	7.32	2.58	5.56	0.77	0.52	0.03	< LOQ	< LOQ	< LOQ	0.70	0.05	< LOQ
	max	9.79	19.9	15.0	5.19	11.7	1.71	1.22	0.10	0.05	< LOQ	< LOQ	1.58	0.21	< LOQ
	n > LOQ	20	20	20	20	20	20	20	17	13	4	3	20	14	15
Rhine	mean	4.31	2.58	2.94	1.22	2.63	0.42	0.37	0.06	0.03	0.04	0.01	0.99	0.16	0.09
River	median	4.57	2.63	2.95	1.22	2.71	0.39	0.31	0.05	0.03	< LOQ	< LOQ	0.90	0.15	0.02
(*n* = 20)	min	0.84	0.42	0.83	0.20	0.86	0.09	0.07	< LOQ	< LOQ	< LOQ	< LOQ	0.59	< LOQ	< LOQ
	max	6.17	4.02	4.56	1.99	3.66	0.67	1.02	0.18	0.10	0.27	0.03	1.98	0.31	1.55
	n > LOQ	12	12	12	12	12	12	12	12	11	8	4	12	9	0
Delaware	mean	3.02	6.29	8.39	2.71	5.95	2.51	0.87	0.80	0.12	0.10	0.02	3.32	0.91	< LOQ
River	median	2.32	6.14	7.78	2.02	5.24	2.36	0.83	0.54	0.09	0.03	< LOQ	2.02	0.16	< LOQ
(*n* = 12)	min	1.47	1.72	1.89	0.93	2.12	0.76	0.15	0.10	< LOQ	< LOQ	< LOQ	0.78	< LOQ	< LOQ
	max	6.51	11.0	15.5	5.70	14.9	4.81	1.84	3.06	0.29	0.54	0.07	8.75	4.33	< LOQ
	n > LOQ	10	10	10	10	10	10	10	8	9	3	4	10	8	0
Mälaren	mean	2.35	2.12	1.73	0.86	2.31	0.54	0.30	0.09	0.08	0.17	0.16	1.47	0.20	< LOQ
Lake	median	2.42	2.12	1.71	0.90	2.32	0.54	0.27	0.06	0.04	< LOQ	< LOQ	1.38	0.20	< LOQ
(*n* = 10)	min	1.69	1.00	0.89	0.55	1.07	0.24	0.09	< LOQ	< LOQ	< LOQ	< LOQ	0.88	< LOQ	< LOQ
	max	3.01	3.17	2.92	1.32	3.34	0.76	0.67	0.38	0.47	1.56	1.34	2.68	0.39	< LOQ

ED_005565_00005099-00022

Table S5 Continued

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTriA	PFTeDA	HFPO -DA	HFPO -TA	ADONA
	n > LOQ	6	6	6	6	6	6	6	6	4	0	0	6	6	0
Han	mean	4.72	1.98	1.79	1.07	3.40	0.69	0.44	0.10	0.04	< LOQ	< LOQ	1.38	0.29	< LOQ
River	median	5.03	2.09	1.94	1.11	3.69	0.73	0.46	0.09	0.04	< LOQ	< LOQ	1.16	0.28	< LOQ
(n = 6)	min	2.56	1.14	0.98	0.55	1.84	0.47	0.17	0.07	< LOQ	< LOQ	< LOQ	0.78	0.16	< LOQ
	max	6.31	2.54	2.38	1.45	4.53	0.85	0.81	0.16	0.08	< LOQ	< LOQ	2.49	0.58	< LOQ

ED_005565_00005099-00023

Table S6. Detection rates and mean, median, min, and max concentrations (ng/L) of PFSAs, PFESAs, and FTSAs in surface waters from different rivers and lakes

		PFBS	PFHxS	PFOS	4:2 Cl-PFESA	6:2 Cl-PFESA	8:2 Cl-PFESA	6:2 H-PFESA	4:2 FTSA	6:2 FTSA	8:2 FTSA
All samples (n = 160)	n > LOQ	160	160	160	34	154	54	101	18	152	42
	mean	5.65	28.3	4.39	0.01	2.08	0.02	0.41	0.01	0.97	0.03
	median	2.04	2.19	3.17	< LOQ	0.31	< LOQ	0.04	< LOQ	0.21	< LOQ
	min	0.07	0.09	0.09	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
	max	146	1434	29.7	0.06	52.2	0.42	6.22	0.11	13.9	0.28
Yangtze River (n = 35)	n > LOQ	35	35	35	4	35	18	35	1	33	1
	mean	1.84	9.12	1.83	0.01	1.29	0.03	0.25	0.01	0.41	0.01
	median	2.22	3.11	1.41	< LOQ	0.53	0.01	0.05	< LOQ	0.11	< LOQ
	min	0.22	0.92	0.36	< LOQ	0.12	< LOQ	0.02	< LOQ	< LOQ	< LOQ
	max	4.68	85.77	12.12	0.04	12.94	0.29	4.07	0.05	6.97	0.03
Yellow River (n = 15)	n > LOQ	15	15	15	0	15	0	10	1	12	0
	mean	0.99	9.72	1.84	< LOQ	0.14	< LOQ	0.05	0.01	0.05	< LOQ
	median	0.45	7.88	2.29	< LOQ	0.17	< LOQ	0.06	< LOQ	0.04	< LOQ
	min	0.07	0.09	0.09	< LOQ	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
	max	2.23	25.69	4.40	< LOQ	0.29	< LOQ	0.10	0.03	0.24	< LOQ
Pearl River (n = 13)	n > LOQ	13	13	13	2	13	7	13	0	13	3
	mean	4.49	0.97	11.09	0.01	2.60	0.03	0.15	< LOQ	0.50	0.02
	median	2.47	0.62	8.56	< LOQ	0.61	0.01	0.04	< LOQ	0.48	< LOQ
	min	0.21	0.09	1.38	< LOQ	0.13	< LOQ	0.02	< LOQ	0.09	< LOQ
	max	21.51	4.17	23.57	0.02	11.06	0.12	0.55	< LOQ	1.28	0.05

ED_005565_00005099-00024

Table S6 Continued

		PFBS	PFHxS	PFOS	4:2 Cl-PFESA	6:2 Cl-PFESA	8:2 Cl-PFESA	6:2 H-PFESA	4:2 FTSA	6:2 FTSA	8:2 FTSA
Liao River (n = 6)	n > LOQ	6	6	6	6	6	6	6	2	6	0
	mean	0.94	0.42	3.46	0.03	1.15	0.02	0.19	0.02	0.99	< LOQ
	median	0.64	0.37	3.15	0.03	1.18	0.02	0.19	< LOQ	0.46	< LOQ
	min	0.43	0.23	2.26	0.02	0.24	0.01	0.08	< LOQ	0.02	< LOQ
	max	2.16	0.84	5.66	0.05	2.29	0.04	0.26	0.08	4.03	< LOQ
Huai River (n = 9)	n > LOQ	9	9	9	4	9	3	9	0	7	0
	mean	0.83	0.33	1.85	0.01	3.41	0.01	0.21	< LOQ	0.09	< LOQ
	median	0.74	0.15	1.90	< LOQ	1.02	< LOQ	0.19	< LOQ	0.03	< LOQ
	min	0.52	0.09	0.48	< LOQ	0.36	< LOQ	0.04	< LOQ	< LOQ	< LOQ
	max	1.59	1.52	3.72	0.04	21.38	0.04	0.67	< LOQ	0.41	< LOQ
Chao Lake (n = 13)	n > LOQ	13	13	13	6	13	10	13	1	13	4
	mean	15.4	210	6.68	0.01	7.84	0.06	0.46	0.01	0.57	0.03
	median	6.49	55.9	3.45	< LOQ	1.62	0.03	0.46	< LOQ	0.13	< LOQ
	min	1.50	0.23	1.96	< LOQ	0.69	< LOQ	0.13	< LOQ	0.05	< LOQ
	max	81.5	1434	29.7	0.04	52.2	0.42	0.83	0.03	2.01	0.07
Tai Lake (n = 15)	n > LOQ	15	15	15	12	15	10	15	0	14	0
	mean	2.02	78.3	5.13	0.03	7.33	0.06	3.04	< LOQ	0.24	< LOQ
	median	2.15	61.7	5.40	0.02	6.59	0.02	3.24	< LOQ	0.12	< LOQ
	min	0.17	0.11	0.22	0.01	0.21	0.01	0.03	< LOQ	0.01	< LOQ
	max	4.85	292	15.2	0.06	27.6	0.25	6.22	< LOQ	0.85	< LOQ

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Table S6 Continued

		PFBS	PFHxS	PFOS	4:2 Cl-PFESA	6:2 Cl-PFESA	8:2 Cl-PFESA	6:2 H-PFESA	4:2 FTSA	6:2 FTSA	8:2 FTSA
	n > LOQ	6	6	6	0	6	0	0	5	6	6
Thames	mean	5.06	7.14	13.8	< LOQ	0.05	< LOQ	< LOQ	0.04	6.75	0.09
River	median	5.27	6.42	12.9	< LOQ	0.05	< LOQ	< LOQ	0.03	5.07	0.07
(*n* = 6)	min	3.26	4.96	8.12	< LOQ	0.01	< LOQ	< LOQ	< LOQ	2.25	0.06
	max	6.75	11.3	18.8	< LOQ	0.08	< LOQ	< LOQ	0.11	13.9	0.19
	n > LOQ	20	20	20	0	20	0	0	2	20	15
Rhine	mean	21.9	1.98	4.40	< LOQ	0.08	< LOQ	< LOQ	0.01	2.87	0.05
River	median	20.1	2.03	4.28	< LOQ	0.04	< LOQ	< LOQ	< LOQ	2.08	0.04
(*n* = 20)	min	0.46	0.12	0.23	< LOQ	0.02	< LOQ	< LOQ	< LOQ	0.04	< LOQ
	max	146	3.90	8.56	< LOQ	0.38	< LOQ	< LOQ	0.06	11.3	0.18
	n > LOQ	12	12	12	0	8	0	0	6	12	10
Delaware	mean	2.19	1.68	3.98	< LOQ	0.02	< LOQ	< LOQ	0.02	1.18	0.07
River	median	1.92	1.72	3.50	< LOQ	0.01	< LOQ	< LOQ	0.02	0.96	0.05
(*n* = 12)	min	0.52	0.65	0.97	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.04	< LOQ
	max	4.20	2.63	6.92	< LOQ	0.08	< LOQ	< LOQ	0.03	2.79	0.28
	n > LOQ	10	10	10	0	8	0	0	0	10	3
Mälaren	mean	1.43	1.30	3.15	< LOQ	0.02	< LOQ	< LOQ	< LOQ	0.37	0.05
Lake	median	1.53	0.97	2.07	< LOQ	0.02	< LOQ	< LOQ	< LOQ	0.34	< LOQ
(*n* = 10)	min	0.75	0.56	0.99	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.04	< LOQ
	max	1.92	2.79	8.23	< LOQ	0.05	< LOQ	< LOQ	< LOQ	1.05	0.19

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Table S6 Continued

		PFBS	PFHxS	PFOS	4:2 Cl-PFESA	6:2 Cl-PFESA	8:2 Cl-PFESA	6:2 H-PFESA	4:2 FTSA	6:2 FTSA	8:2 FTSA
	n > LOQ	6	6	6	0	6	0	0	0	6	0
Han	mean	2.27	3.18	2.50	< LOQ	0.04	< LOQ	< LOQ	< LOQ	0.08	< LOQ
River	median	2.42	3.54	2.78	< LOQ	0.04	< LOQ	< LOQ	< LOQ	0.08	< LOQ
(*n* = 6)	min	1.34	1.39	1.08	< LOQ	0.02	< LOQ	< LOQ	< LOQ	0.03	< LOQ
	max	3.17	4.68	3.86	< LOQ	0.06	< LOQ	< LOQ	< LOQ	0.13	< LOQ

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Table S7 Comparison of PFCA and PFSA levels (ng/L) in Chinese rivers from previous studies.

	Year	Level	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFBS	PFHxS	PFOS	Ref
Yangtze R	2016	mean	4.36	0.72	2.54	0.91	13.5	0.56	0.15	0.07	1.84	9.12	1.83	This study
		median	3.92	0.58	1.07	0.76	12.2	0.36	0.07	0.03	2.22	3.11	1.41	
		range	0.93–9.61	0.21–3.6	0.33–28.2	0.29–4.43	3.48–36.5	0.15–2.75	0.03–1.59	ND–0.7	0.22–4.68	0.92–85.8	0.36–12.1	
Yangtze R	2005	mean	—	—	0.72	1.13	51.7	1.06	0.39	0.32	0.77	0.04	2.70	[1]
		median	—	—	0.22	0.29	12.3	0.15	0.04	0.04	0.97	ND	0.50	
		range	—	—	ND–5.3	ND–9.2	2–260	ND–10.0	ND–3.8	ND–3.0	ND–2.1	ND–0.4	0.01–14.0	
Yangtze R	2013	mean	1.67	0.57	2.13	0.32	8.44	0.11	0.02	ND	4.56	0.31	0.79	[2]
		median	1.45	0.54	0.58	0.12	7.78	0.07	ND	ND	3.69	0.06	0.66	
		range	0.45–8.38	ND–2.51	0.11–22.7	ND–2.59	1.02–15.8	ND–0.86	ND–0.33	ND	0.09–32	ND–3.27	ND–3.93	
Yangtze R	2013	mean	2.88	1.4	1.34	0.94	12.36	0.72	0.76	—	2	ND	3.04	[3]
		median	3.1	1.2	1.1	0.8	9.2	0.4	0.4	—	ND	ND	1.1	
		range	2.1–3.3	1.1–1.9	1–2.4	0.7–1.5	7.4–27.8	0.4–2.0	0.3–2.3	—	ND–3.5	ND	1.0–10.7	
Yangtze R	2003	mean	—	—	—	—	16.5	—	—	—	—	—	6.9	[4]
		median	—	—	—	—	5.4	—	—	—	—	—	4.7	
		range	—	—	—	—	0.2–297.5	—	—	—	—	—	0.1–25.5	
Yellow R	2016	mean	3.52	0.63	0.8	0.41	2.05	0.39	0.06	0.01	0.99	9.72	1.84	This study
		median	4.05	0.85	1.01	0.56	2.45	0.45	0.04	ND	0.45	7.88	2.29	
		range	1.2–7.38	0.04–1.13	0.1–1.57	0.02–0.74	0.15–4.92	0.05–0.76	ND–0.31	ND–0.06	0.07–2.23	0.09–25.69	0.09–4.4	
Yellow R	2011	mean	4.21	0.72	0.74	0.56	2.74	0.67	0.17	ND	1.02	0.25	2.45	[5]
		median	3.78	0.75	0.68	0.56	2.73	0.64	ND	ND	0.81	0.22	2.18	
		range	2.89–6.41	0.52–0.92	0.49–1.08	0.31–0.88	0.96–4.15	0.17–1.04	ND–0.20	ND	0.72–1.86	0.15–0.37	0.95–5.37	
Yellow R	2013	mean	5.38	2.22	1.12	1.33	3.15	0.75	0.28	—	ND	ND	1.33	[3]
		median	5.35	2.25	1.2	1.4	3.0	0.75	0.25	—	ND	ND	1.3	
		range	4.9–5.9	1.0–3.4	1.1–1.2	1.0–1.5	2.7–3.9	0.5–1.0	0.2–0.4	—	ND	ND	0.9–1.8	

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Table S7 Continued

	Year	Level	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFBS	PFHxS	PFOS	Ref
Pearl R	2016	mean	2.94	0.82	0.93	0.57	7.45	0.44	0.24	0.12	4.49	0.97	11.09	This study
		median	1.80	0.47	0.58	0.42	1.82	0.35	0.18	0.11	2.47	0.62	8.56	
		range	0.88–9.4	0.15–3.68	0.34–2.99	0.07–2.11	0.4–52.8	0.22–1.28	0.06–0.87	0.04–0.30	0.21–21.51	0.09–4.17	1.38–23.57	
Pearl R	2005	mean	—	—	0.73	1.35	4.15	0.88	0.35	0.28	0.61	ND	23.05	[1]
		median	—	—	0.51	0.93	2.80	0.46	0.32	0.17	0.03	ND	8.75	
		range	—	—	ND–2.2	ND–4.1	0.14–13	ND–3.1	ND–0.67	ND–0.67	ND–3.4	ND	0.9–99	
Pearl R	2013	mean	2.5	1.3	1.37	1.37	3.13	0.77	0.4	—	ND	ND	2.2	[3]
		median	2.6	1.5	1.6	1.6	3.2	0.9	0.4	—	ND	ND	2.5	
		range	1.3–3.6	0.8–1.6	0.8.1.7	0.8–1.7	1.3–4.9	0.5–0.9	0.3–0.5	—	ND	ND	0.9–3.2	
Liao R	2016	mean	3.82	0.95	1.17	0.96	8.95	0.61	0.21	0.05	0.94	0.42	3.46	This study
		median	3.15	0.9	1.07	0.91	9.39	0.56	0.17	0.02	0.64	0.37	3.15	
		range	2.53–7.52	0.71–1.46	0.91–1.73	0.69–1.30	5.28–12.3	0.48–0.9	0.06–0.36	ND–0.15	0.43–2.16	0.23–0.84	2.26–5.66	
Liao R	2012	mean	—	—	3.77	11	12	0.51	0.13	0.087	134	0.73	2.27	[6]
		median	—	—	2.19	3.97	8.38	0.47	0.05	0.027	80	0.6	1.78	
		range	—	—	0.53–18.4	1.17–94.8	0.67–61.6	0.08–1.64	0.01–1.38	0.01–0.74	14.4–758	0.02–5.51	0.09–9.5	
Chao L	2016	mean	7.91	4.01	5.95	1.68	8.16	1.39	0.68	0.2	15.4	210	6.68	This study
		median	6.97	4.01	6.24	1.55	8.17	1.34	0.51	0.16	6.49	55.9	3.45	
		range	5.17–11.7	2.29–6.82	3.41–10.8	1.36–2.35	7–10.5	1.19–1.65	0.28–2.02	0.06–0.61	1.5–81.5	0.23–1434	1.96–29.7	
Chao L	2011-2012	mean	2.04	0.82	1.23	0.77	8.62	0.46	0.08	0.01	0.36	0.07	0.08	[7]
		range	0.31–6.77	0.03–8.12	0.19–15.9	0.14–1.47	1.32–23.5	0.05–1.74	0.02–0.70	ND–0.12	0.03–6.14	0.01–0.96	ND–0.82	
Tai L	2013	mean	6.52	1.87	19.3	2.19	18.5	2.09	1.25	0.33	2.02	78.3	5.13	This study
		median	6.25	1.89	5.66	2.41	17.95	1.67	1.00	0.23	2.15	61.7	5.40	

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Table S7 Continued

	Year		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFBS	PFHxS	PFOS	Ref
		mean	—	—	20.2	2.41	24.7	1.18	0.59	0.17	3.18	0.75	9.78	
Tai L	2012	median	—	—	17.8	2.4	25.9	1.17	0.55	0.13	3.35	0.79	11.3	[6]
		range	—	—	2.72–45.7	1.46–3.36	8.07–34.4	0.68–1.54	0.31–0.88	0.09–0.37	0.47–5.83	0.11–1.19	2.3–18.30	
		mean	0.86	2.75	11.3	3.17	28.2	3.04	1.8	0.63	—	1.41	3.54	
Tai L	2010	median	0.41	2.82	11	3.25	25.9	3.63	1.94	ND	—	0.72	2.52	[8]
		range	ND–4.06	ND–6.08	ND–22.2	1.28–4.53	2.15–73.9	0.55–5.04	ND–2.93	ND–3.27	—	ND–6.92	ND–10.50	

"ND", not detected; "—", not analyzed.

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Table S8 Spearman's rank correlation coefficients between individual PFAS levels in surface waters (n = 160)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	HFPO -DA	HFPO -TA	PFBS	PFHxS	PFOS	6:2 Cl-PFESA	6:2 H-PFESA	6:2 FTSA
PFBA	1.000															
PFPeA	0.490	1.000														
PFHxA	0.628	0.906	1.000													
PFHpA	0.653	0.853	0.941	1.000												
PFOA	0.439	0.076	0.320	0.443	1.000											
PFNA	0.429	0.618	0.670	0.707	0.461	1.000										
PFDA	0.493	0.813	0.827	0.819	0.250	0.750	1.000									
PFUnA	0.312	0.531	0.603	0.602	0.296	0.742	0.823	1.000								
HFPO-DA	0.224	0.432	0.357	0.262	-0.092	0.445	0.315	0.267	1.000							
HFPO-TA	0.483	0.298	0.379	0.381	0.254	0.546	0.396	0.403	0.705	1.000						
PFBS	0.548	0.613	0.632	0.585	0.187	0.191	0.510	0.297	0.040	0.064	1.000					
PFHxS	0.420	0.287	0.420	0.423	0.437	0.377	0.288	0.185	0.013	0.191	0.418	1.000				
PFOS	0.358	0.597	0.582	0.531	0.075	0.358	0.670	0.458	0.146	0.149	0.634	0.247	1.000			
6:2 Cl-PFESA	0.404	-0.189	0.036	0.112	0.643	0.290	0.116	0.257	-0.068	0.364	0.049	0.268	0.111	1.000		
6:2 H-PFESA	0.449	-0.138	0.096	0.160	0.642	0.366	0.125	0.266	-0.002	0.489	0.042	0.352	0.079	0.922	1.000	
6:2 FTSA	0.115	0.562	0.511	0.430	0.003	0.237	0.511	0.317	0.142	-0.097	0.439	0.088	0.615	-0.141	-0.258	1.000

PFAS analytes with detection rates less than 50% were excluded from analysis.

Extremely significant correlations ($p < 0.001$) are presented in blue, significant correlations ($0.05 < p < 0.001$) are presented in green, and correlations that did not reach statistical significance ($p > 0.05$) are shown in yellow.

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Table S9 Estimated riverine mass discharge (kg/y) of selected PFASs for individual rivers

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	HFPO -DA	HFPO -TA	PFBS	PFHxS	PFOS	6:2 Cl-PFESA	6:2 FTSA	ADONA
Yangtze R	5500	1100	5900	1300	15300	710	330	150	660	300	2400	21400	3000	2900	880	n.d.
Yellow R	58	15	17	11	61	7.8	0.63	0.21	22	8.2	28	160	38	2.7	0.54	n.d.
Pearl R	660	110	170	84	2000	100	38	32	1500	1100	600	82	1600	620	87	n.d.
Liao R	20	4.5	5.8	4.9	35	2.6	0.58	0.067	7.9	1.8	4.5	2.1	15	4.8	5.8	n.d.
Xiaoqing R	270	240	300	250	15500	11	3.4	0.39	150	4600	0.73	0.24	2.8	4.4	n.a.	n.d.
Delaware R	47	110	130	50	120	50	19	20	38	15	42	25	67	0.36	21	n.d.
Thames R	16	32	24	8.2	20	2.8	2.1	0.18	2.6	0.38	12	13	24	0.13	8.6	n.d.
Rhine R	480	263	316	127	275	45	35	5.7	99	16	2300	200	420	7.4	220	1.7
Han R	100	42	38	23	72	15	9.3	2.1	29	6.2	48	67	53	0.80	1.7	n.d.

n.d., not detected;

n.a., not analyzed

The data for Xiaoqing River were cited from our earlier literature [1], which calculated the PFAS discharge using a water flux of 6.5×10^8 m^3/y for Xiaoqing River.

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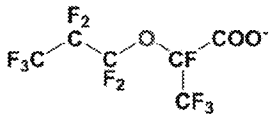
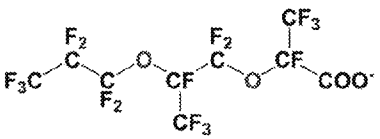
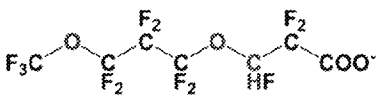
PFECAs



HFPO-DA

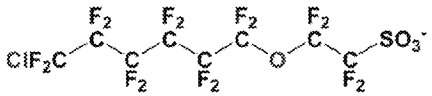


HFPO-TA



ADONA

PFESAs



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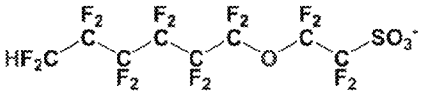

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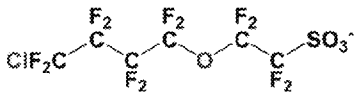

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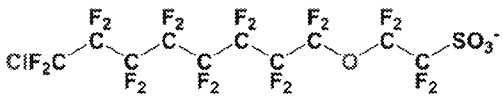
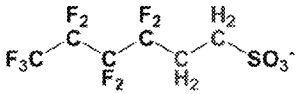


8:2 Cl-PFESA

FTSAs



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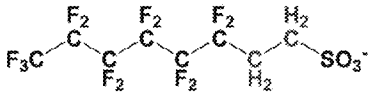

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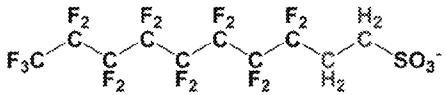

8:2 FTSA

Figure S1 Molecular structures of novel fluorinated alternatives in this study

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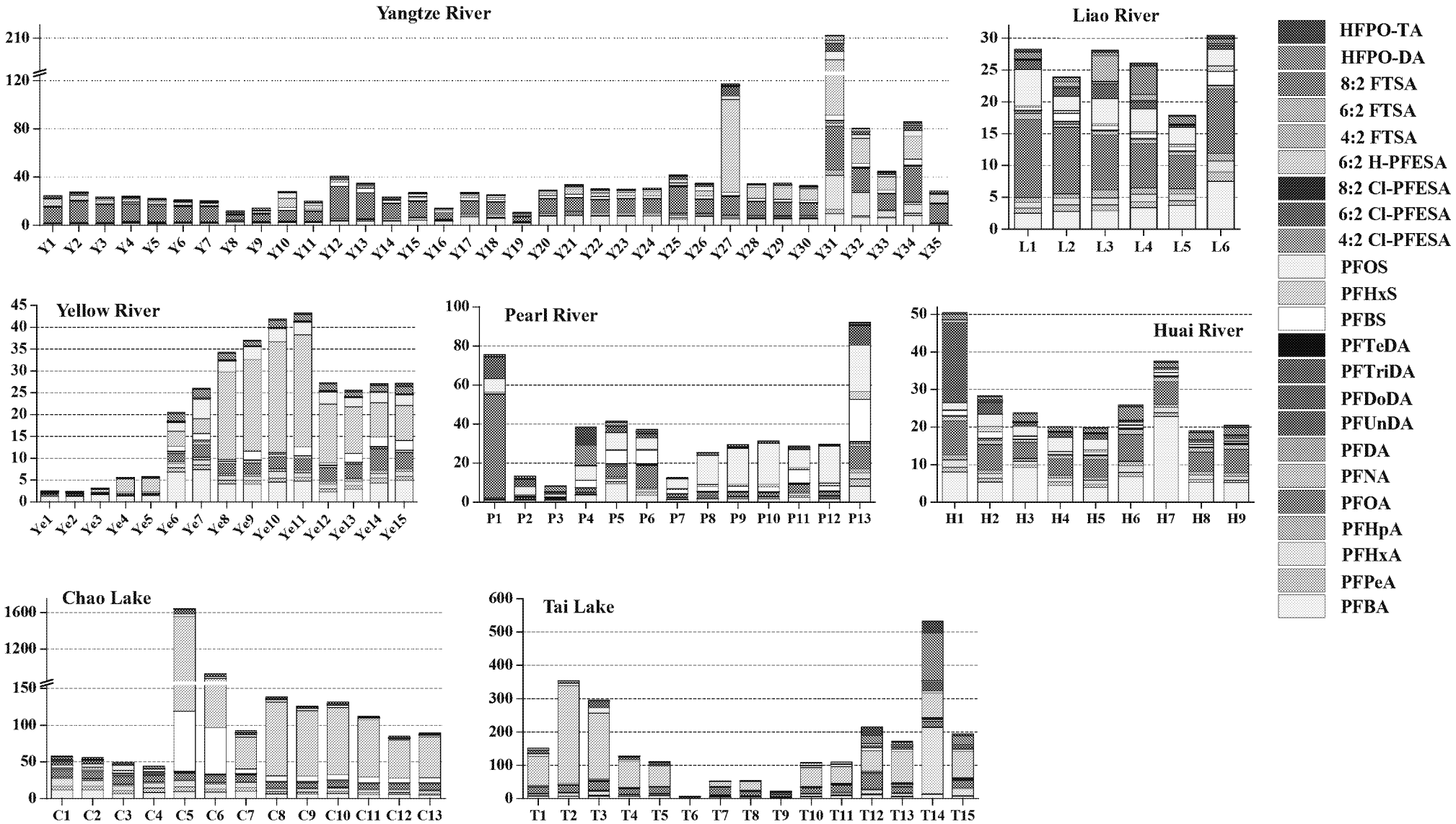

Figure S2 PFAS concentrations (ng/L) in surface waters from Chinese rivers and lakes

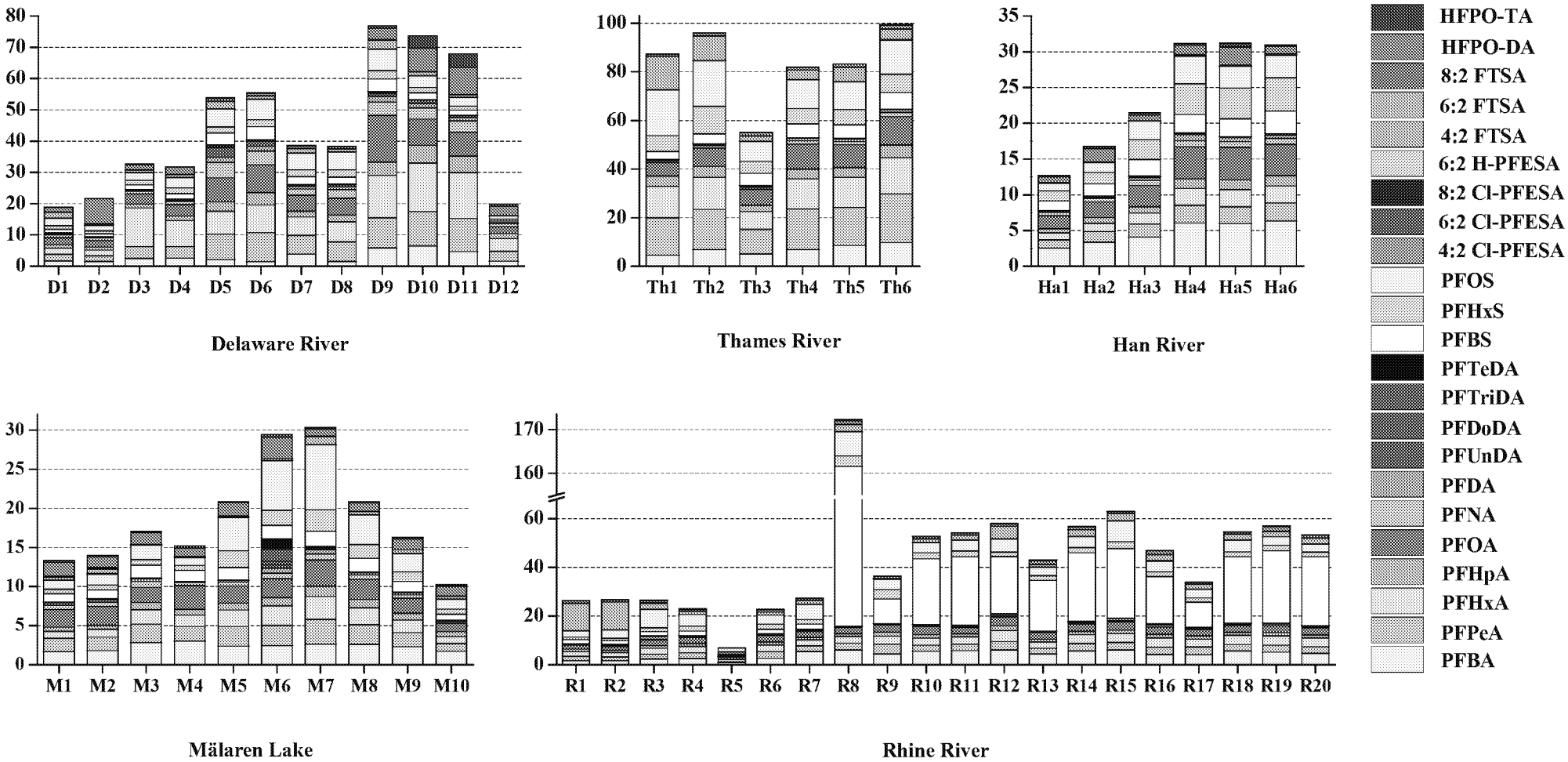

Figure S3 PFAS concentrations (ng/L) in surface waters from rivers and lakes in other countries