Identification, Tissue Distribution, and Bioaccumulation Potential of Cyclic Perfluorinated Sulfonic Acids Isomers in an Airport Impacted Ecosystem

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Supporting Information

ABSTRACT: The use of cyclic perfluoroalkyl acids as anticorrosive agents in hydraulic fluids remains a poorly characterized source of organofluorine compounds to the environment. Here, we investigated the presence of perfluoroethylenecyclohexanesulfonate (PFECHS) isomers in environmental samples for the first time using a combination of high resolution and tandem mass spectrometry. Five distinct peaks attributed to different isomers of PFECHS and perfluoropropylcyclopentanesulfonate (PFPCPeS) were identified in environmental samples. The sum of PFECHS and PFPCPeS isomers displayed logarithmically decreasing spatial trends in water (1.04−324 ng/L) and sediment samples (<MLQ−2.23 ng/g dw) with increasing distance from Beijing international airport. PFECHS and PFPCPeS displayed the highest accumulation in liver, kidney, blood and bladder and average whole body bioaccumulation factors (log BAFwhole-body) were estimated to be 2.7 and 1.9 respectively. Isomer-specific differences in the tissue/blood distribution ratios and BAFwhole-body indicate that ring structure and position of the sulfonic acid group affect the bioaccumulation potential of cyclic perfluorinated acids. Based on the high mobility and moderate bioaccumulation potential of cyclic perfluorinated acids it is suggested that contamination of aquifers used for drinking water around airports may be a hitherto overlooked problem for this novel class of contaminants.

INTRODUCTION

Per- and polyfluorinated alkyl substances (PFASs) have been widely used in industrial processes and consumer products over the past 60 years due to their unique surface activity and chemical stability.1−3 Although fluorochemistry brings many societal and economic benefits, there’s been a growing concern about the environmental and human health risks of PFASs since Giesy and Kannan first reported on the global occurrence of perfluorooctanesulfonic acid (PFOS) in wildlife.4 Numerous studies have dedicated to understand the environmental fate, bioaccumulation and toxicity of long-chain perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFSAs) for which regulatory actions have also been taken.5−9 However, recent inventories suggest that there are more than 3000 PFAS structures in commerce.10,11 Measurements of total organic fluorine in biotic and abiotic environmental samples from different parts of the world further suggest a significant fraction of hitherto unidentified PFASs.12 An increasing research focus is therefore being directed to identification and hazard characterization of a wider array of PFASs in order to allow a more effective management of this diverse group of chemicals.12,13,14 Elevated levels of PFASs in water, soil, and sediment samples around airports were identified already in the late 1990s15 and PFAS groundwater contamination has more recently been recognized as one of the major legacy contamination problems for this group of substances.16−19 The primary source of the contamination around airports is the uncontrolled historical use of PFASs (such as PFOS and 6:2 fluorotelomer sulfonate) in...
aqueous film forming foams (AFFFs) during fire-fighting training and accidents.\textsuperscript{20–22} Yet, there are additional sources of PFASs at airports and in aviation industry that have not received much attention. As first reported by Howard and Muir\textsuperscript{23} perfluoroethylcyclohexanesulfonate (PFECHS) is used as an important erosion inhibitor dissolved in aircraft hydraulic fluid with an estimated production between 4.5 and 220 tonnes in 1994 and 1998.\textsuperscript{23–26} Measurements of PFECHS from the Great Lakes,\textsuperscript{24} downstream of Ontario airport,\textsuperscript{25} the St. Lawrence River\textsuperscript{27} and Canadian High Arctic\textsuperscript{28} demonstrate that the water concentrations of PFECHS close to airports in several cases were higher than those of PFOS. Furthermore, whole body bioaccumulation factors (BAFs) in lake trout indicate that PFECHS may exceed regulatory thresholds for bioaccumulative substances.\textsuperscript{24} However, the occurrence, fate, and bioaccumulation of cyclic PFASs in the environment remain poorly understood.

One reason for the scarcity of data on PFECHS is that the technical products synthesized by electro chemical fluorination typically contain a suite of homologous and isomeric impurities which may hamper accurate identification and quantification.\textsuperscript{23–26} Previous studies on PFASs have shown that the structure of the perfluoroalkyl moiety can significantly alter the uptake, distribution, and elimination in biota.\textsuperscript{25,26} Improved analytical approaches for isomer-specific quantification of cyclic PFASs are therefore needed for accurate measurements and a better understanding of bioaccumulation mechanisms for cyclic PFASs.

In the present study we set out to study the occurrence, tissue distribution and bioaccumulation potential of cyclic perfluorinated sulfonic acids near the suspected point source Beijing International Airport. Particular emphasis was placed on identification and quantification of PFECHS isomers which were hypothesized to be present in technical products. Field-based distribution coefficients and bioaccumulation factors were subsequently compared to measurements of linear and branched PFASs in the same sample sets.

### MATERIALS AND METHODS

#### Study Area and Sampling

The study was carried out in the surrounding area of Beijing International Airport, the largest airport in Asia. Surface water, sediment, and fish samples were collected from one of the two main drainage systems of the airport in April 2014. Figure 1 depicts the sampling area located in the southwest corner of Beijing International Airport. The pond (S1–S6) collects rainwater runoff from the parking apron, a small fire-fighting training area as well as the reclaimed water from the wastewater treatment plant serving the airport. The pond discharges into the adjacent Xiaozhong River (S7–S12) which subsequently drains it into the Jian River (S13–S16). Reference sampling was performed at the upstream of the airport in the Xiaozhong River (U1, U2) and Wenyu River (R1, R2) on the west of the airport.

Paired water and sediment samples were collected at every site, except for S5 and S6, where the sediment samples were not available due to the cement hardening of the riverbed. Surface water samples (0–0.5 m) were collected from S1–S16, U1–U2 and R1-R2 using 500 mL polypropylene (PP) bottles precleaned with methanol and Milli-Q water. Water samples were kept at 4 °C in a fridge prior to analysis of PFASs. Every sediment sample consisted of a composite of five grab samples collected with a stainless steel shovel. The samples were homogenized, freeze-dried under vacuum and stored at −20 °C until extraction.

Cruccian carp (Carassius carassius) was selected as a representative species to investigate bioaccumulation of the targeted PFASs. A total of 28 crucian carps were caught by seine net in the pond between sampling point S1 and S6. Their lengths and weights were recorded, and then immediately transported to the laboratory. Eight fish were selected (length: 10.0–14.7 cm; weight: 16.8–65.1 g) to investigate the tissue distribution, whereas the remaining twenty fish (length: 5.7–7.9 cm; weight: 1.4–4.7 g) were prepared as whole body homogenates. Blood samples were drawn immediately from these fish anesthetized with MS-222.\textsuperscript{31} They were subsequently...
dissected, skin was removed, and muscle, brain, liver, kidney, heart, bladder, gonad, and spleen were excised by scalpels and forceps (precleaned with methanol and Milli-Q water). Fish muscle samples were freeze-dried under vacuum and ground to fine powder. The remaining fish tissues and whole body samples were homogenized and frozen at −20 °C prior to analysis. All fish were euthanized with an ice/water mixture in accordance with the euthanasia guidelines.32

**Chemicals.** A total of 16 PFASs were analyzed in the different matrices, including perfluorobutanoic acid (PFBA), perfluorpentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutanesulfonic acid (PFBS), perfluorotributanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS), the chlorinated polyfluoroalkyl ether sulfonic acid (F-53B) and PFECHS. Nonlabeled calibration standards and isotopically labeled polyfluorododecanoic acid (PFDoDA), perfluoroundecanoic acid (PFUnDA), perfluorooctane sulfonic acid (F-53B) and PFECHS. Nonlabeled calibration standards and isotopically labeled internal standards were obtained from Wellington Laboratories (Ontario, Canada). The authentic F-53B standard was purified from the commercial F-53B product purchased from Shanghai Synica Co., Ltd. The native PFECHS standard was purchased from Chiron AS (Trondheim, Norway). Table S1 lists the abbreviations and mass transitions of the standards.

**Sample Preparation and Analysis.** Sample extraction and cleanup were performed according to a previously validated methodology for linear and branched PFASs,33,34 which is also described in the Supporting Information (SI). Briefly, water samples were extracted by solid phase extraction (SPE) with prefiltration as previously described by Shi et al.33 A 400 mL water sample was spiked with 2 ng of $^{13}$C$_4$PFOS, $^{13}$C$_4$PFOA, $^{13}$C$_4$PFBA, and $^{13}$C$_4$PFDoDA as internal standards. Sediment samples were sieved through a 50-mesh (0.3 mm) stainless steel sieve. Subsequently, they were extracted by a methanol-based extraction method.33 Muscle samples were processed using an alkaline digestion method,34 whereas homogenates of whole fish and other tissue samples were extracted with the ion-pairing liquid extraction method using tetra-n-butyl ammonium hydrogen sulfate (TBA) and methyl tert-butyl ether (MTBE).34

Instrumental analysis was accomplished using a high performance liquid chromatography (Ultimate 3000 HPLC, Thermo Fisher Scientific Co.) equipped with an electrospray ionization tandem mass spectrometer (ESI-MS/MS, API 4500, Applied Biosystems/MDS SCIEX, USA) operated in negative mode. Two different chromatographic systems were tested for effective separation of cyclic PFASs using (i) an Acclaim 120 C18 Column (5 μm, 4.6 mm × 150 mm, ThermoFisher Scientific Co.) and (ii) an ACQUITY HSS PFP Column (1.8 μm, 100 Å, 5 cm × 2.1 mm, Waters Co.), respectively. The details of separation and instrument parameters are further described in the SI.

In addition to the quantification, performed by HPLC-MS/MS, we used accurate molecular mass and characteristic structure fragment ions as two critical parameters to elucidate the structure of unknown impurities of PFECHS technical mixtures.35,36 For this purpose, ultrahigh resolution Orbitrap mass spectrometer (Orbitrap Fusion, Thermo Fisher Scientific, Waltham, MA) was employed. A range of ±5 ppm between theoretical and measured m/z was the criteria for compound confirmation (e.g., unknown isomers) by HPLC-Orbitrap MS.35 The HPLC conditions and the composition of mobile phases for PFASs analysis were identical to those used for ESI-MS/MS (see details in SI).

**Quality Assurance and Quality Control (QA/QC).** As a standard procedure, procedural blanks, matrix spike-recovery tests and duplicate analysis of five samples for each matrix were performed. Procedural blanks were conducted to check the possible laboratory contamination and interferences and were consistently below instrumental detection limits. For spike-recovery experiments (n = 5), 2 ng of the 16 targeted PFASs were added to surface water, sediment collected in a Beijing park, tissue homogenates and blood of fish collected from a Beijing market, which were treated using the same procedures as for real samples (Table S2 and S3). PFAS concentrations in samples were quantified based on the internal standard method with response factors determined from a 7 point calibration curve. For cyclic PFASs the concentration of individual isomers were not specified in the standard. Hence, we assumed the same response factors for all isomers and determined the concentrations in standard solution. The method limit of quantification (MLQ) was defined as the lowest concentration of each compound resulting in a signal-to-noise ratio (S/N) ≥ 10 (Table S2 and S4). More details about the quality assurance and quality control are provided in the SI.

**Data Analysis.** The distribution coefficient ($K_{df}$, L/kg) was used to describe the distribution of PFASs between water and sediment.

$$K_{df} = \frac{C_{sed} \times 10^3}{C_{water}}$$

(1)

where $C_{sed}$ is the concentration of the PFAS in sediment (ng/g dw), $C_{water}$ is the concentration of the PFAS in water (ng/L). Since the sorption of PFASs in sediments can be affected by the organic carbon fraction ($f_{oc}$), correlations between $K_{df}$ and $f_{oc}$ were specifically investigated.37,38

The bioaccumulation factor (BAF$_{whole-body}$) L/kg was calculated to estimate the propensity of the fish to accumulate PFASs from the water using both whole body homogenate concentrations (eq 2) and single tissue concentrations (eq 2 and 3) respectively.

$$BAF_{whole-body} = \frac{C_{whole-body} \times 10^3}{C_{water}}$$

(2)

where $C_{whole-body}$ is the concentration of the PFAS in fish whole body homogenates (ng/g ww), $C_{water}$ is the mean concentration (ng/L) of the PFAS in the pond (S1–S6). For calculation of BAF$_{whole-body}$ from individual tissues $C_{whole-body}$ was defined according to eq 3.

$$C_{whole-body} = \sum_{n=1}^{i} C_{tissue,n} \times f_{tissue,n}$$

(3)

where $C_{tissue}$ is the concentration of the PFAS in fish tissues (ng/g ww) and $f_{tissue}$ is the mass fraction of individual tissues (unlabeled) (Table S5). Since blood and muscle weights were not measured during dissection, their body fractions were estimated to 0.045 and 0.5 respectively according to literature values in other fish species.39,40

Spearman’s rank correlation analysis and Mann–Whitney U test were performed with IBM PASW Statistics 20.0 (SPSS Inc., 1993–2007). All of the tests were two-tailed, and p < 0.05 was considered as statistically significant. The concentrations of
PFASs were treated as zero when they were below MLQ in samples.

■ RESULTS AND DISCUSSION

Identification and Quantification of PFECHS Isomers.

It has previously been reported that PFECHS technical products contain several impurities including perfluoromethylcyclohexanesulfonate (PFMeCHS) and perfluorocyclohexanesulfonate.24 The synthesis of PFECHS using electrochemical fluorination may, however, lead to additional rearrangements of the perfluorocarbon moiety including isomers with eight carbons. Under typical reversed phase HPLC/MS-MS conditions using a C18 column the PFECHS standard displays a shoulder at 3.85 min prior to the main peak at 3.99 min. Although the two peaks have the same accurate mass for the parent ion ($m/z = 460.93448$ and $460.93454$, respectively), some of the product ions, $[C_3F_7]^{-}$, $[C_4F_7]^{-}$, $[C_5F_9]^{-}$ and $[C_5F_9SO_3]^{-}$ at 3.85 min and $[C_2F_5]^{-}$ and $[C_8F_{15}]^{-}$ at 3.99 min, were distinctly different (Figure S1). Using a PFP stationary phase, the PFECHS standard solution provided by Chiron was separated into five peaks. As shown in Figure 2, the peaks at 9.30, 9.53, 9.72, 9.85, and 10.06 min gave the same accurate mass for the parent ion ($m/z = 460.93225$, 460.93228, 460.93247, 460.93231 and 460.93195, respectively) and had the same major product ion ($[FSO_3]^{-}$). However, the minor product ions, $[C_3F_7]^{-}$, $[C_4F_7]^{-}$, $[C_5F_9]^{-}$ and $[C_5F_9SO_3]^{-}$ at the first peak was different from the latter four peaks $[C_2F_5]^{-}$ and $[C_8F_{15}]^{-}$. The characteristic product ions suggested that the first peak (eluting at 9.30 min) was caused by the five-ring isomeric impurity perfluoropropylcyclopentanesulfonate (PFPCPeS) whereas the latter four peaks at 9.53, 9.72, 9.85, and 10.06 min respectively were PFECHS isomers with $-SO_3^-$ and $-CF_2CF_3$ in different positions on the six-ring (Figure 2). However, since there are no individual standards of the four different six-ring isomers it was not possible to positively distinguish these structures from each other.

Although a previous publication on PFECHS24 reported mass spectra containing the $[C_3F_7]^{-}$ fragment for PFECHS, the results presented here demonstrate that this product ion belongs to one or several structural isomers with a cyclopentane structure that should be quantified separately. Consequently, the characteristic product ions $[C_2F_5]^{-}$ and $[C_8F_{15}]^{-}$ were monitored for confirmation of PFECHS in the MS/MS method used for quantification. Accurate mass measurements of PFPCPeS and PFECHS in all environmental samples were within a mass window of 5 ppm of the theoretical mass ($\Delta m \pm 5$ ppm) confirming the presence of PFPCPeS and PFECHS in these samples. Since the structural isomers of PFECHS were not baseline separated and could not be positively identified they were quantified as a sum of isomers ($\sum$PFECHS). Similar to PFECHS, PFPCPeS may also be present as three different isomers with $-SO_3^-$ and $-CF_2CF_2CF_3$ substitution in different
positions of the five-ring (Figure 2). The reasons for why we only observed one peak for this compound may be that only one five-ring isomer was generated in significant amounts during the synthetic process or that the three possible isomers are not separated on the stationary phase. Thus, we also report PFPCPeS as the sum of isomers (\(\sum\)PFPCPeS). Figure S2–S5 illustrate typical chromatograms and MS2 full scan spectrum of PFPCPeS and PFECHS in water, sediment, fish muscle and tissue samples, respectively. Peaks that could tentatively be assigned to PFMeCHS (411.0/98.9) were also identified in some environmental samples (Figure S6). However, since PFMeCHS was not present in the standard solution we could not positively identify and quantify this compound in environmental samples.

Employing the quantification method by HPLC-MS/MS using a PFP stationary phase mean matrix spike recovery (n = 5) of PFASs (including PFECHS and PFPCPeS) ranged from 85.4 to 109.9%, 76.8 to 112.4%, 76.5 to 108.4%, and 65.5 to 127.3% for water, sediment, fish muscle and different tissue samples, respectively (Table S2 and S3). Duplicate samples showed excellent reproducibility with an RSD of lower than 20% for each compound. Quantified concentrations of \(\sum\)PFECHS and \(\sum\)PFPCPeS in different fish tissue samples using a C18 and PFP stationary phases respectively displayed excellent agreement (Table S6, Figure S7–S8). Overall, the different quality assurance tests demonstrate that the presented instrumental techniques provide accurate and robust quantitative data for several PFECHS and PFPCPeS isomers. However, purified native and mass-labeled standards of individual isomers would certainly improve the identification and quantification of cyclic PFASs present in PFECHS technical mixtures.

**Water–Sediment Distribution and Spatial Trends.**
PFECHS was detected in all surface water samples downstream of Beijing International airport (\(\sum\)PFECHS ranging 1.04–195 ng/L), whereas PFPCPeS was only detected in water samples S1–S6 at slightly lower concentrations (\(\sum\)PFPCPeS ranging 13.7–129 ng/L). No detectable levels of PFECHS or PFPCPeS were observed in upstream samples (U1, U2) or at the reference sites (R1, R2) supporting previous findings that the contamination of cyclic PFASs are primarily related to airport emissions.24,25 Twelve linear and branched per- and polyfluoroalkyl acids, including the PFOS replacement F-53B, were detected with variable frequency in surface water and sediment samples (Table S7 and S8). The highest surface water concentrations were observed for PFBS (2.90–51.3 ng/L), PFNA (0.19–47.0 ng/L), PFHxS (0.66–45.0 ng/L), PFOA (4.03–24.0 ng/L), PFBA (10.6–41.5 ng/L) and \(\sum\)PFOS (sum of br-PFOS and lin-PFOS; 0.33–13.2 ng/L). In contrast to surface water samples, long-chain PFASs (PFOS, F-53B, PFDA, PFUnDA, and PFDoDA) were most abundant in sediment samples due to the increasing hydrophobicity with perfluoralkyl chain-length.37 Interestingly, PFECHS and PFPCPeS displayed a relatively low detection frequency in sediments (43 and 14% respectively) despite that they have eight perfluorinated carbon atoms and would fall into the category of long-chain PFASs according to the classification system of Buck et al.41 Field-based sediment-water distribution ratios (Table S9) indicated that the affinity for PFECHS and PFPCPeS was on average 12 and 90 times lower than lin-PFOS. The lower
hydrophobicity for cyclic compared to linear PFASs is supported by their shorter retention time on a reversed-phase C18 HPLC column which has also been reported previously.\textsuperscript{24} Using a PFPeA stationary phase, PFCHS (t = 9.53−10.06 min) and PFPCPeS (9.30 min) eluted between lin-PFOS (12.04 min) and PFHxS (8.90 min) indicating that the cyclic perfluoralkyl carbon structure and two less fluorine atoms compared to PFOS have a significant effect on the hydrophobicity. Unfortunately, the low detection frequency in sediment samples and lack of significant correlations between $K_a$ and $f_{oc}$ (Spearman’s $p > 0.139$; $p > 0.632$) did not allow the sorption of PFCHS and PFPCPeS to be characterized in more detail. Controlled batch experiments\textsuperscript{37} in combination with in silico modeling\textsuperscript{10} would be valuable to gain further understanding of the mechanisms of sediment water partitioning for cyclic PFASs.

Figure 3 shows the spatial distribution of cyclic (PFPCPeS and PFCHS), linear and branched PFASs (PFOS and PFNA) in surface water and sediment from S1 to S16. Concentrations of $\sum$PFPCPeS (<MLQ−129 ng/L) and $\sum$PFCHS (1.04−195 ng/L) declined logarithmically with increasing distance to Beijing airport along the water flow (Figure 3). Spearman’s rank correlation analysis of the concentration data in surface water samples also displayed a highly significant correlation between PFPCPeS and PFCHS (Spearman’s $p = 0.860$; $p < 0.01$) (Table S10). The distinct spatial trends and strong correlations between PFCHS and PFPCPeS support the original hypothesis that runoff water from the airport was the dominant source of the two cyclic PFASs to the surrounding environment. Interestingly, $\sum$PFOS, PFNA and PFHxS also displayed logarithmically decreasing spatial trends and statistically significant correlations with the cyclic PFASs (Spearman’s $p > 0.582$, $p < 0.05$) (Table S10 and Figure S9). The similar spatial trends and correlations between PFOS, PFHxS, and PFNA with the cyclic PFASs may indicate that runoff water from Beijing airport reflects the integrated PFASs emissions from both leakage and spills of hydraulic fluids and releases of AFFFs for fire-training purposes. An alternative explanation for the observed correlations between PFCHS, PFPCPeS, PFHxS, PFOS, and PFNA could be that cyclic PFASs were present as impurities in POSF-based AFFF foams. However, considering that the water concentrations of $\sum$PFCHS were approximately an order of magnitude higher than $\sum$PFOS it seems more likely that distinct emissions from hydraulic fluids were the primary source of cyclic PFASs. The lack of decreasing trends with distance to the airport for some PFASs (e.g. PFBA, PFPeA, and PFBS) indicates that other emission sources and transport pathways, such as domestic wastewater discharges and atmospheric deposition,\textsuperscript{42,43} are more important for these compounds in this particular river system. In addition, the lower adsorption to sediment may also have contributed to a more widespread contamination of short-chain PFASs.

The concentrations of $\sum$PFCHS in the runoff water from Beijing airport were substantially higher than previously reported in the scientific literature.\textsuperscript{24,25,28} For instance the levels of $\sum$PFCHS (195 ng/L) at sampling site S1 were 1 order of magnitude greater than previously reported at a release point of wastewater (20.0 ng/L) from the John C. Munro International Airport, Hamilton, Ontario, Canada.\textsuperscript{25} The mean concentrations of PFCHS (0.16−5.6 ng/L and 4.3 ng/L, respectively) in water samples collected from the Great Lakes and Meretta Lake of Cornwallis Island were also significantly lower than those observed in the present study.\textsuperscript{24,28} The substantially higher concentrations of cyclic PFASs in this study likely reflect the proximity and magnitude of emissions sources at Beijing International Airport (one of the largest airports globally). However, it should be noted that PFASs detected in the pond may only represent a small fraction of the total water-soluble chemicals from the 1480 hectare airport area since a large amount of the waterborne chemicals may be transported vertically through the soil and reach groundwater aquifers.\textsuperscript{44,45} Thus, runoff water samples were not suitable for estimating total emissions of PFASs from the airport. Further studies to characterize the emissions of PFCHS are strongly encouraged.

Tissue Distribution and Bioaccumulation Factors. The measured concentrations of targeted PFASs in whole fish homogenates are shown in Table S11. The detection frequency was 100% for all analytes except C5, C6, and C7 PFCAs which were detected in 52.4, 47.6, and 95.2% of the samples, respectively. PFCHS was detected in 100% of the individual tissue samples with sum isomer concentrations ranging between 1.91 and 125 ng/g ww (Table S12). PFPCPeS
displayed a slightly lower detection frequency in kidney (87.5%), heart (37.5%), brain (75.0%) and muscle (75.0%) and overall lower concentrations (<MLQ−11.8 ng/g ww) among the routinely monitored PFASs, lin-PFOS (29.5−572 ng/g ww) consistently found in the highest concentrations followed by PFDoDA (8.2−316 ng/g ww), PFUnDA (3.6−125 ng/g ww), and PFDA (3.7−107 ng/g ww) whereas PFBA, PFPeA, PFHxA, PFHpA, and PFBS were only infrequently detected. The concentrations of ∑PFECHS in Crucian carp samples were 1−3 orders of magnitude higher than those previously reported from lake trout in the Great Lakes and char in Canadian High Arctic. 24,28 The higher PFCHS concentrations in the present study can to some extent be explained by the higher emissions sources from Beijing International airport, but species-specific differences in bioaccumulation potential may also influence the comparison.

Figure 4 displays tissue/blood ratios for PFCHS, PFPCPeS, br-PFOS, lin-PFOS, and F-53B. A similar trend in tissue/blood ratios (liver > kidney > bladder > muscle) was observed, suggesting that these compounds share similar mechanisms for uptake and distribution in the body. However, the median liver/blood ratios for PFCHS (2.09) and PFPCPeS (1.61) were significantly higher compared to br-PFOS (1.09), lin-PFOS (0.97), and F-53B (0.92), respectively (Mann−Whitney U-test; p < 0.05). Slightly higher median tissue/blood ratios for PFCHS compared to lin-PFOS were also observed in kidney, bladder, heart and brain, however these differences were not statistically significant (Mann−Whitney U-test; p > 0.130).

Field-based BAFs were calculated using both (i) whole fish homogenates and (ii) individual tissue concentrations combined with body fractions from post mortem examinations (Table S13). Although median BAFs based on whole body homogenates consistently resulted in higher values (0.3−0.7 log units) the difference between the two methods to calculate did not reach statistical significance (Mann−Whitney U-test, p > 0.078). The lack of statistically significant differences between the different calculation methods indicates that the contribution of other tissues (e.g., intestine and skin 36,47) than those analyzed here to BAFs may be of lower importance compared to interindividual variability in physiology and exposure. However, the comparison of BAF calculations based on whole body homogenates and individual tissues respectively should be interpreted with caution as the selection of smaller fish for whole body homogenate measurements may have introduced bias to the calculations.

Figure 5 displays the mean log BAF values of different PFASs with eight perfluorinated carbons for the whole body homogenates in Crucian carp. Overall, the trend of mean Log BAFs for F-53B (4.6) ≈ lin-PFOS (4.6) > br-PFOS (3.8) > PFCHS (2.7) > PFPCPeS (1.9) appeared to follow the hydrophobicity (discussed above) with the lowest BAFs observed for cyclic PFASs. Previous studies have showed that the bioaccumulation potential of PFASs in piscivorous food webs is correlated to the perfluoroalkyl chain-length and hence the hydrophobicity. 38 Although the mechanisms behind this apparent trend are not fully understood, the possibility for gill-breathing organisms to eliminate water-soluble chemicals has been suggested as a key process for determining the BAFs of PFASs. 49,50 The lower BAFs of cyclic PFASs observed here may, therefore, partly be attributed to their lower hydrophobicity and more efficient elimination via gill ventilation. 24,36,51 However, sterical effects of the perfluorocarbon moiety may also influence specific protein binding mechanisms. For instance, a careful examination of the PFCHS chromatograms indicates an isomer-specific enrichment in fish tissues which is not easily explained by hydrophobicity alone. Figure S2−S5 display a clear shift in the isomer profile between standard solution, water and sediment samples (isomer B displays the highest response) and fish samples (isomer C displays the highest response) indicating that isomer C is more strongly enriched in biota. Spike-recovery tests confirmed that the isomer profile in fish was not due to matrix-effects and all fish tissue samples displayed fairly consistent isomer profiles (Figure S11). Previous studies on branched and linear isomers of PFOS have shown that interactions with serum albumin are stronger enrichment in serum albumin binding affinities are reflected in BAFs. 45 Analogously, it may be hypothesized that the cyclic perfluorocarbon chain results in a weaker interaction with serum albumin for PFCHS and PFPCPeS compared to PFOS which may explain an increased distribution to other tissues than blood and a more rapid elimination. However, additional studies combining in vitro and in silico studies are needed to better understand how different structures of the perfluoroalkyl moiety (linear, branched and cyclic) affect the interaction with different protein classes.
Moreover, it is possible that the BAFs derived from field studies are influenced by precursors (typically N-substituted perfluoroalkyl sulfonamides) that are metabolized to perfluoroalkyl acids as stable end products. This process, often referred to as indirect exposure, has been shown to result in an overestimation of field-based BAF values for PFOS, but it is not known if this may also be relevant for PFECHS which have also been produced by electrochemical fluorination. Based on the examination of Orbitrap data we could not find support for the presence of suspected PFECHS precursors in the environmental samples from Beijing airport, but more research using for example the total oxidizable precursor assay would be needed to resolve this question.

Implications for Environmental Risk Assessment of Cyclic PFASs. This study provides support to previous findings that contamination of PFECHS and related cyclic PFASs is primarily restricted to the proximity of airports. The approximately ten times higher concentrations of \( \sum \) PFCHS and \( \sum \) PFPCPeS compared to PFOS in airport runoff water, however, suggest that local exposures to cyclic PFASs could significantly contribute to the total sum of organic fluorine compounds in airport impacted ecosystems. Considering the recent attention that has been given to drinking water contamination around airports, it is important to note that cyclic PFASs are not routinely monitored and thus not included in the risk assessment. Based on the substantially lower sorption affinity for soil and sediment of cyclic compared to linear and branched PFASs they will be transported more efficiently to groundwater and potentially lead to human exposure via drinking water. Although the mean BAF values in Crucian carp did not exceed common regulatory criteria for bioaccumulative substances, it has been previously shown that elimination half-lives in humans for perfluoroalkyl acids are not always correlated to bioaccumulation factors in fish due to differences in elimination mechanisms. For instance, PFOA and PFHxS have been found to have long elimination half-lives in humans (3.5 and 7.2 years respectively) despite that they have low BAFs in the fish. Considering the current efforts to investigate PFAS contamination around airports we believe that inclusion of cyclic PFASs in the list of analytes is needed to better characterize human exposure to PFASs and help to close the mass-balance of organofluorine compounds.

**ACKNOWLEDGMENTS**

We acknowledge financial support from the National Natural Science Foundation of China (No. 21537004, 21377145, 21321004) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14010201). We are also grateful for the valuable input from Simon Roberts (Colorado School of Mines), Krista Barzen-Hanson (Oregon State University) and three anonymous reviewers.

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