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Riverine Discharge of Perfluorinated Carboxylates from the European Continent

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The discharge of C_6−C_9 perfluorinated carboxylates (PFCAs) from major European rivers was studied and employed to assess European emissions of these compounds. Water samples were collected close to the mouths of 14 major rivers including the Rhine, Danube, Elbe, Oder, Seine, Loire, and Po. PFCA concentrations were determined using LC-MS/MS and used together with the mean annual water flow to estimate the riverine discharge of the PFCAs. The highest concentration measured was 200 ng/L for perfluorooctanoate (PFOA) in the Po River. The Po accounted for two-thirds of the total PFOA discharge of all the rivers studied, suggesting a major industrial source of PFOA in the Po watershed. All other nonremote rivers showed PFOA concentrations in the lower ng/L range, which indicates that widely distributed sources are also significant contributors to PFOA emissions in Europe. The total discharge of PFOA from the European rivers was estimated to be 14 tonnes/year, which is in reasonable agreement with reported emissions estimates. However, the total riverine discharge of perfluorohexanoate (PFHxA) of 2.8 tonnes/year estimated in this study was three times greater than the reported global emissions estimate, suggesting that there are significant, as yet unidentified sources of this compound.

Introduction

Perfluorinated chemicals (PFCs) have been found in water, wildlife, and humans throughout the world (*1*−*3*). Perfluorinated carboxylates (PFCAs), in particular perfluorooctanoate (PFOA), are among the PFCs with the highest levels in humans (*4*−*6*). PFCAs are also highly persistent in the environment, and time trend studies have shown that their levels have increased markedly over the last 30 years in Norwegian bird eggs and Canadian Arctic seal liver (*7*−*8*). Furthermore, a wide range of toxicological effects of PFOA has been observed (*9*), among them developmental toxicity in rodents (*10*). This has spurred interest in identifying the sources of PFCAs in the environment.

The sources of PFCAs were explored in a recent review by Prevedouros et al. (*11*). These authors concluded that PFOA and perfluorononanoate (PFNA) accounted for >90% of PFCA emissions in 2000, and that fluoropolymer manufacturing has historically been and continues to be the dominant source of total PFCA release to the environment. All other sources, apart from the manufacture of ammonium perfluorooctanoate (APFO), were found to be very small in comparison.

On the other hand, other researchers have proposed that indirect sources may be important contributors to PFCA levels in the environment. Transformation of volatile atmospheric precursors has been suggested to play a significant role, particularly in remote regions such as the Arctic (8, *12*). Such precursors have been shown to be present in consumer products (*13*) and to occur in Arctic air (*14*). The direct release of PFCAs present as residuals in consumer products or as a consequence of degradation of fluoropolymers has also been proposed (*13*, *15*−*16*). Given the multitude of PFCs in use, other, as yet unidentified sources, are also conceivable. To date, there are insufficient environmental data to be able to establish the relative importance of these different sources.

In their review, Prevedouros et al. (*11*) also discussed the physical chemical properties and environmental behavior of PFCAs. They concluded that these chemicals are primarily emitted to water, that they accumulate in surface waters, that water is the major reservoir of PFCAs in the environment, and that water is a major medium for their transport. It has been shown that PFOA is not significantly retained by geosolids; it is transferred virtually unhindered with infiltrating water from the soil surface through the unsaturated zone to the aquifer (*17*). Emissions to land are rapidly transferred to surface water or shallow groundwater (*18*). Environmental transformation of PFCAs is—if it occurs—extremely slow (*11*). In summary, most emissions of PFCAs with a carbon chain length <9 will rapidly enter the hydrosphere, where they will be transported with the water virtually unimpeded toward the oceans. A consequence of this environmental behavior is that the total emissions of PFCAs into a watershed will—on a time scale of the watershed's hydraulic retention time—roughly equal the riverine discharge of PFCAs.

Based on this assessment, we undertook to study PFCA emissions in Europe by sampling river water. Water samples were collected close to the mouths of major European rivers and analyzed for PFCAs. The riverine discharge was calculated and used to compare the emissions in different regions and to obtain an initial estimate of total PFCA emissions on the continent.

Materials and Methods

Sampling. Water samples were collected from 14 major European rivers. The rivers sampled and the approximate sampling sites are shown in Figure 1, while the coordinates of the sampling site and the date of sampling are given in Table S1 in the Supporting Information.

The samples were collected either by members of the EU funded PERFORCE project or by qualified scientific personal contacted by project members. All samplers were provided with empty sample bottles, two sample bottles filled with laboratory water (Milli-Q) as transport and field blanks, a sampling protocol, and detailed instructions on where and how to collect, store, and ship the samples, as well as how to complete the sampling protocol (see Supporting Information, SI). Included were instructions not to use any sampling equipment containing PTFE or Viton rings, and not to wear any clothing containing fluoropolymers (Gore-Tex or similar) or that had been treated with stain or water repellants.

Sampling was carried out during the autumn of 2005 (for the Baltic rivers as well as the Elbe and Danube) or the winter of 2006. The Po and the Rhine were resampled in late summer 2006. Periods of unusually high or low river flow were avoided. The samples were collected as close to the river mouth as

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FIGURE 1. Map showing the water sampling sites and the rivers sampled.

was practical to capture the PFCA load from as large a drainage basin as possible. At the same time, sampling of estuarine water was avoided to preclude dilution of the river water with saline water. The samples were not collected immediately downstream of potential sources, as far as these could be identified.

The water was taken from the subsurface but well above the river bottom. Polypropylene or polyethylene bottles (500 mL) were filled to the top, sealed, stored in a refrigerator, and sent by courier to Stockholm University where they were stored at 4 °C. Field blanks were collected by filling the laboratory water from the field blank bottle into the sampling device, letting it stand for 5 min, and then transferring this water back to the field blank bottle. As far as could be determined, all samplers followed the sampling instructions carefully. However, not all field and travel blanks were returned.

Sample Preparation and Analysis. Standards of perfluorohexanoic acid (PFHxA, >97%), perfluoroheptanoic acid (PFHpA, 99%), perfluorooctanoic acid (PFOA, 98%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, >97%) and perfluoroundecanoic acid (PFUnA, 95%) were purchased through Sigma-Aldrich (Sweden). 7H-perfluoroheptanoic acid (7H-PFHpA, 98%) was obtained from ABCR (Germany). Perfluoro-*n*-[1,2,3,4-$^{13}C_4$]-octanoic acid ([$^{13}C_4$]-PFOA, >99%) was obtained from Wellington Laboratories (Canada) and ammonium perfluorooctane-[$^{18}O_2$]-sulfonate ([$^{18}O_2$]-PFOS, >99%) was kindly provided by the 3M company.

Methanol Multisolvent (HPLC Grade, 99.98%) was obtained from Scharlau (Spain). Formic acid p.a. (>98%) and ammonium acetate p.a. (>98%) were purchased from Merck (Germany). Water was obtained from a Milli-Q (Millipore AB, Sweden) purification unit.

A method originally developed for the analysis of PFCAs and perfluoroalkyl sulfonates (PFSs) was employed. The recovery of the PFSs was erratic, which indicated that for this group of compounds the method was not robust enough to cope with the wide range of matrix properties in the river waters sampled. Hence, only the results for the PFCAs are reported here. The salinity was measured in all samples for which an estuarine influence was possible.

The method employed was based on the method reported by Berger and Kallenborn (*19*). An aliquot of ~250 mL was taken from the water sample and 1.25 mL of 0.5 vol % aqueous formic acid was added, followed by 40 mg NH_4OAc (~2 mM) and 10 ng of the surrogate standards ([$^{18}O_2$]-PFOS and [$^{13}C_4$]-PFOA; 100 μL of 0.1 ng/μL solution in methanol). Particle rich waters were filtered over a piece of cleaned, silane treated glass wool prior to solid-phase extraction (SPE). SPE was conducted using an Oasis HLB Plus SPE cartridge (0.25 g, Waters Corp., Milford, MA), which had been prepared by rinsing with at least 20 mL of methanol and then conditioning with 1 mL of Milli-Q water. The water was extracted on the SPE cartridge at ~2 drops/s. The SPE cartridge was rinsed with 2 mL of methanol/water (40/60) (discarded), and the PFCAs were then eluted with 8 mL of methanol at ~2 drops/sec. The eluate was concentrated to ~0.25 mL under a gentle stream of nitrogen (N48, Air Liquide, Malmö, Sweden) and 2 ng of the volumetric standard 7H-PFHpA (20 μL of a 0.1 ng/μL solution in methanol) as well as 250 μL of 4 mM NH_4OAc in water were added. Prior to analysis, samples were transferred into a 2 mL PP syringe (BD Dicardit II, PVC free, Becton Dickinson S.A., Spain) and passed through a syringe filter (GHP Acrodisc Minispike, 0.45 μm, 13 mm, PP, Waters Corp.) to remove precipitation.

The samples were analyzed using high-performance liquid chromatography combined with negative ion electrospray tandem mass spectrometry (HPLC-ESI$^-$-MS/MS). An aliquot of 50 μL of extract was injected onto a C_{18}-precolumn (Chrom Tech, 10 × 2 mm, 5 μm HyPurity) followed by a C_{18}-column (Thermo Hypersil-Keystone, 50 × 2.1 mm, 5 μm HyPurity). The flow rate was 0.2 mL/min delivered by a Waters Alliance pump (2695 Separation Module, Waters Corp.). The mobile phase was 10 mM ammonium acetate in both methanol (A) and water (B). The following binary gradient was applied: for 1 min 40% A, 1–6 min linear gradient to 95% A, 6–18 min 95% A, then returning to 40% A. Total run time was 27 min, including time for conditioning of the column. The C_6 through C_{11} PFCAs (PFHxA, PFHpA, PFOA, PFNA, PFDA, and PFUnA, respectively) were measured using a Micromass Quattro II mass spectrometer (Altrincham, UK) in the selected reaction monitoring (SRM-MS/MS) mode with argon as collision gas. The following optimized parameters were applied: source temperature: 120 °C, argon pressure: 6.1×10^{-4} mbar, drying and nebulizer nitrogen gas flows: 350 and 25 L/h, respectively. Monitored transitions as well as collision energy and sample cone voltages are summarized in Table S2 in the SI.

The performance of this method had been documented by assessing the recovery of tap water spiked with PFCAs at 3 different levels. The recoveries ranged from 63 to 105% (*ref 19*, see Table S3 in the SI).

Quality Assurance and Quality Control. In addition to laboratory blanks, transport blanks, field blanks, and surrogate standard recoveries, two further studies were undertaken to ensure the quality of the data produced.

In the first study, the effect of sample storage on PFCA recovery was explored. This was deemed particularly important since others have reported considerable losses of PFCAs and PFSs during storage of water samples (*20*). High-density polyethylene (500 mL), polypropylene (250 mL), and glass (200 mL volumetric flask) were filled with 200 mL of Milli-Q-water, spiked with 1 ng of each PFCA, sealed with their respective caps and stored at room temperature in the laboratory for 36 days. The water in the bottles was then extracted and analyzed for PFCAs and PFSs. The bottles were subsequently rinsed exhaustively with 8 mL of methanol, which was then concentrated and analyzed separately.

The second study was a laboratory intercomparison exercise. Two European laboratories that are active in PFC research and that have considerable experience in the analysis of PFCs in water were invited to participate. Four water samples from the river sampling program were sent to each laboratory and the laboratories were asked to analyze them for PFCAs using their in-house methods. The samples were analyzed concurrently in our laboratory.

Results

The C_6–C_9 PFCAs were detected in most of the samples. PFDA and PFUnA lay close to the method detection limit (MDL), and their levels are not reported here. The recovery of the labeled PFOA internal standard ranged from 33 to 98%, whereas it was >50% in 80% of the samples.

The results of the sample storage study are summarized in Table S4 in the SI. The recovery of the spiked PFCAs (C_6–C_9) in the Milli-Q water was 95% ± 17%. The amount of PFCAs in the methanol rinses was comparable to blank values for all container materials and no quantifiable quantities were found. This indicates that PFCA losses during sample storage were not a major concern in this study.

The laboratory blanks contained traces of PFHxA and PFOA. The method detection limit (MDL) was set to 3 times the laboratory blank (PFHxA and PFOA) or 3 times the peak to peak noise in the blanks (for the other chain lengths). The transport blanks and field blanks were below the MDL for PFNA (i.e., less than three times the noise), above the laboratory blank but below the MDL for PFOA, while they were above the MDL for PFHxA and PFHpA in several transport and field blanks (see Table S5 in the SI). The PFHxA and PFHpA blanks above the MDL varied little (relative standard deviation of 18 and 23%, respectively). The source of the blanks was traced back to an unexpected contamination of the laboratory Milli-Q water sent in the transport and field bottles. No evidence of sample contamination during transport or sampling was found.

For seven of the rivers, several samples were taken on the same day close to each other (e.g., on a transect across the river, or from opposite banks). Although these were not true parallel samples, one would expect similar concentrations if the PFCA sources to the river were well upstream of the sampling points. In most cases similar concentrations were obtained (see Table S6 in the SI); the coefficient of variation (CV) was <25% in 78% of the cases. The average CV was lowest for PFOA (12%), which reflects the use of a stable PFOA isotope as a surrogate standard in the analytical method. The average CV was highest for PFHxA (24%), which was attributed to variation in its retention on the SPE cartridge. This CV could likely be reduced by including a stable PFHxA isotope as a surrogate standard. Overall, the good agreement lends confidence to the quality of the sampling and analytical methods. It also indicates that most of the sampling locations were not impacted by local contamination, i.e., they were representative for the river water in that river segment.

The laboratory intercomparison yielded good results (see Table S7 in the SI). The difference between the ITM and JRC results was <25% in most cases. NILU measured consistently higher than the other labs, but by less than a factor of 2 for most analytes. The method repeatability was also very good for all of the laboratories. One sample was analyzed twice, and the difference in the parallel determination was <10% in most cases. The largest discrepancies both within and between labs were for PFHxA, which likely reflects the difficulties in consistently extracting this analyte mentioned above.

The PFCA concentrations are summarized in Table 1, whereby mean values are given for each river (the original data are given in Table S6 in the SI). A salinity correction was applied to the few brackish samples, assuming no PFCAs in the diluting seawater. Values below the MDL are designated "<".

PFHxA and PFOA had the highest level of contamination. The concentrations ranged over a factor of >30, with low levels in the three Scandinavian river samples, somewhat higher levels in Eastern European rivers, and even higher levels in Western European rivers. With the exception of the

TABLE 1. Mean Concentrations of PFCAs in European River Water (ng/L)

	PFHxA	PFHpA	PFOA	PFNA
Dalälven	<0.94[a]	0.36	<0.97	<0.14
Vindelälven	<0.58	0.20	<0.65	0.22
Kalix Älv	<0.58	0.26	<0.85	<0.14
Elbe	15.4	2.7	7.6	0.27
Oder	2.2	0.73	3.8	0.73
Vistula	2.3	0.48	3.0	0.36
Po	19	6.6	200	1.46
Danube	3.0	0.95	16.4	0.27
Daugava	<1.4	0.86	<2.2	0.36
Seine	13.3	3.7	8.9	1.26
Loire	3.4	0.90	3.4	0.43
Thames	32	4.1	23	0.79
Rhine (February 2006)	18.2	1.8	11.6	0.55
Rhine (August 2006)	3.3	3.3	12.3	1.50
Guadalquivir	6.2	1.58	4.6	1.02

[a] "<" denotes values below the MDL

Po river, the PFOA concentrations (<0.65−23 ng/L) were mostly in the range observed in urban surface waters in Minnesota and Japan (*21*−*22*), but lower than reported for the lower Great Lakes and surface waters in New York State (*23*−*24*). In Europe, PFOA concentrations reported for the Rhine, namely 8 ng/L close to the German/Dutch border (*18*), and 16−57 ng/L in the Rhine, Scheldt, and Meuse within The Netherlands (*25*), were in reasonable agreement with the concentrations in Rhine water sampled at the German/Dutch border in this study (11.6, 12.1, and 12.5 ng/L). Skutlarek et al. (*18*) also reported a concentration for PFHxA in the Rhine that is in good agreement with the second sample in this study (3 versus 3.3 ng/L).

Discussion

Simcik and Dorweiler (*21*) suggested that the ratio of PFHpA: PFOA concentrations can be used as an indicator of the source of PFCAs in water, with ratios <1 indicative of urban sources, and ratios markedly >1 indicative of atmospheric deposition. The ratios determined in this study (0.03−0.4) suggest that there was no evidence of an atmospheric source of PFCAs in the European rivers. However, the ratios were also lower than those reported by Simcik and Dorweiler for urban areas in Minnesota (0.53−0.9). This indicates that there are differences in urban source signatures for these chemicals, and hence the criterion developed from the Minnesota data likely cannot be applied to European rivers.

The highest PFCA concentration measured was 200 ng/L for PFOA in the Po. After a sample from November 2005 that was analyzed with a different method indicated high levels of PFOA in the Po, a sample from this river was included in the laboratory intercomparison exercise. All three participating laboratories confirmed the high level in this sample. It was more than an order of magnitude higher than the PFOA concentrations in the other rivers. The concentrations of the other PFCAs were also high in the Po, but with the exception of PFHpA they lay in the range of the other rivers. Loos and co-workers collected samples from the same location in June and October 2006 and measured PFOA at 60 and 158 ng/L, respectively, confirming the high concentrations (Robert Loos, personal communication). These results suggest that there is a very strong source of PFOA somewhere in the Po River watershed.

In a recent review of PFOA sources it was reported that fluoropolymer manufacturing and APFO production were responsible for >95% of global PFOA/APFO emissions during 2004−2006 (*11*). The high concentrations of PFOA in the Po are consistent with this conclusion. There are fluoropolymer manufacturing facilities in the Po watershed (*26*).

TABLE 2. Total Estimated Flux of PFCAs in the Rivers Studied (tonnes/year)

	PFHxA	PFHpA	PFOA	PFNA
flux	2.8	0.86	14.3	0.26

However, the results also indicate a widespread, low level contamination of European rivers. With the exception of the Po, the remote Scandinavian rivers, and the Daugava, all of the rivers studied contained PFOA at between 3 and 23 ng/L. Fluoropolymer manufacturing facilities are located in only three of the river watersheds studied (Po, Danube and Vistula) (*26*), while APFO is presumably also manufactured in the Rhine watershed, as several major suppliers of perfluoroalkyl substances are located there (*27*). Thus, other, diffusely distributed sources appear to be making a contribution to PFOA emissions in Europe. Industries that use/process APFO (e.g., fluoropolymer dispersion processors (*11*)) or fluoropolymers (e.g., the textile industry (*25*, *27*)) can be sources of PFCAs. Wastewater treatment plant effluents in Europe and the United States contain PFCAs in the ng/L range, even when there is little or no industrial effluent being treated (*25*, *28*−*31*), and thus they are likely important diffusely distributed sources to the rivers in this study. It has been hypothesized that PFCAs are formed in wastewater treatment plants from precursor chemicals, although to date no consistent picture has emerged on which, if any, of the PFCAs are being formed on a widespread basis (*29*−*32*). Textiles containing fluoropolymers and fluorinated surface protection products have also been found to contain PFCAs (*13*, *29*), which may enter the wastewater treatment plant following washing of the textiles. Release of PFCA contamination from fluoropolymers in consumer goods is another conceivable source of the PFCAs in wastewater treatment plant effluents.

To gain more insight into the relationship between environmental levels and emissions, the annual riverine discharge of the PFCAs was estimated. The average PFCA concentration was multiplied by the mean annual river discharge for the period 1990−2004 (see Table S1 in the SI). Recall that sampling was done during periods of normal water flow to avoid concentration/dilution of the PFCAs due to drought/flood conditions. However, the limitations of calculating an annual load based on one sampling time point should be recognized. For instance, while the PFOA concentrations in the Rhine at the two different time points in this study were similar, the concentrations of the other PFCAs varied considerably. Thus the annual riverine discharges of PFCAs must be regarded as rough approximations, but they nevertheless provide interesting insights into PFCA sources in Europe.

The total riverine discharge of each chemical, obtained by adding the discharges of all of the studied rivers, is given in Table 2. These can be compared with the global emissions estimates for PFCAs given by Prevedouros et al. (*11*). They estimated global PFOA emissions of ∼75 tonnes/year for the year 2005. While they give no information on the spatial distribution of these emissions, one might expect that Europe could account for ∼20 tonnes/year. The drainage basin of the rivers sampled in this study accounted for ∼35% of the European continent (excluding Iceland, Russia, the Ukraine, and the Belarus) (see Figure S1 in the SI). Although it included a greater proportion of the more industrialized areas, the sampling program did not account for sources in estuaries or on the coast (e.g., Hamburg, London, and The Netherlands were not captured in the sampling of the Elbe, Thames, and Rhine, respectively). Thus, the PFOA flux of 14.3 tonnes/year from this study would appear to be in reasonable agreement but perhaps somewhat higher than the emissions estimates of Prevedouros et al. (*11*).

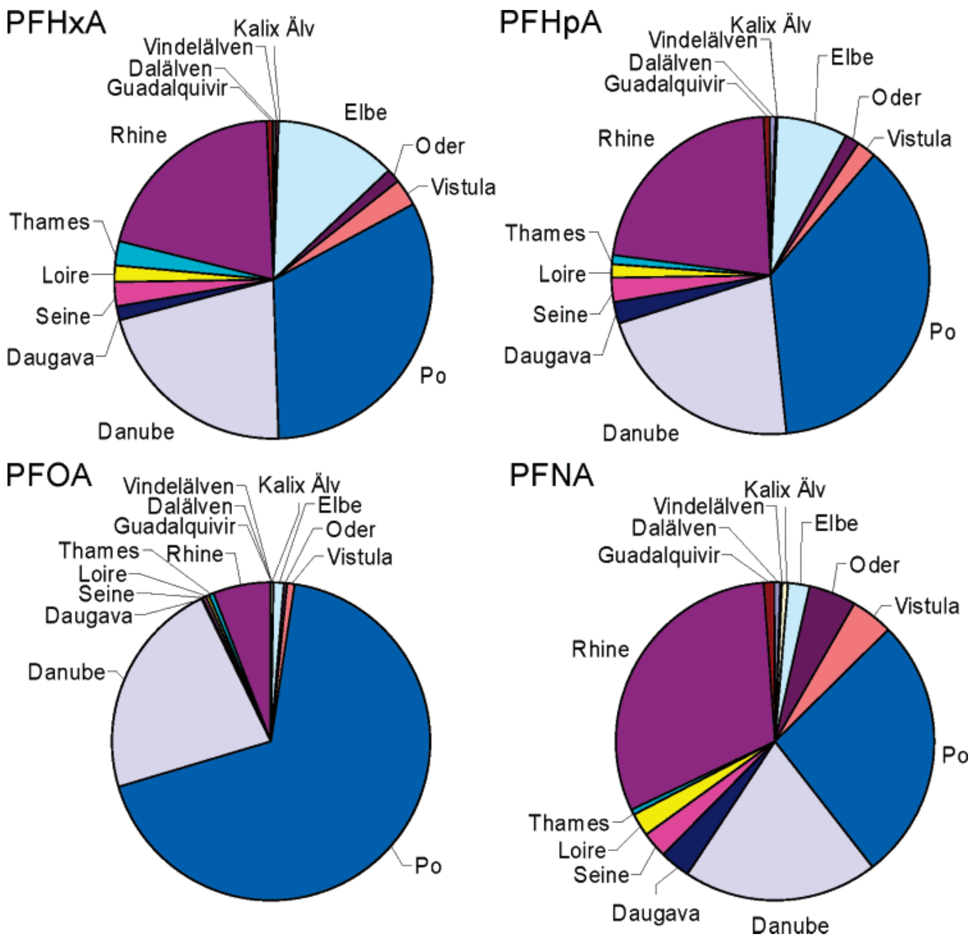

FIGURE 2. Distribution of the PFCA fluxes among the different rivers sampled.

The distribution of the riverine discharge of PFOA between the different watersheds yields further insight (see Figure 2). The Po contributes approximately two-thirds of the total discharge, which, as noted above, is likely due to fluoropolymer/APFO production facilities. Two of the other rivers with known fluoropolymer/APFO production facitilities, the Rhine and the Danube, contribute the large majority of the remainder. However, the fact that the PFOA concentration in these rivers was not markedly elevated compared to the rivers with no fluoropolymer/APFO production facilities (see above) suggests that other, widely distributed sources were making a major contribution. The large contribution of the Rhine and the Danube to the PFOA discharge is a reflection of the large water discharge of these rivers.

Turning to PFHxA, the agreement between the emissions estimates and the measured riverine discharge was poor. Prevedouros et al. (*11*) estimated total global emissions of PFHxA of 1 tonne/year for the year 2000, while the riverine flux from this study was 2.8 tonnes/year. The emissions of PFHxA were estimated to be 0.5% of the emissions of PFOA, while the riverine flux was approximately 20%. The disagreement between the emissions estimates and the observations is further emphasized by the fact that the concentrations of PFHxA were greater than the concentrations of PFOA in several of the rivers studied (see Table 1). Since there is very little retention of PFOA in soils (see above), it is unlikely that this discrepancy can be explained by a strong retention of PFOA in the watershed. Rather, it suggests that the sources of PFHxA were underestimated or that there are other sources that were not accounted for in the work of Prevedouros et al. (*11*).

The distribution of the total PFHxA, PFHpA, and PFNA discharge among the rivers showed many similarities (see Figure 2). For all three the largest contribution was made by the Po, which may be associated with the fluorinated chemical industry located there. This was followed by the Danube and the Rhine. These are watersheds with large populations, which suggests that the sources of the PFCAs may be related to population. However, another watershed with a large population, the Seine, made a relatively small contribution. One clear difference between the different chain lengths is the large contribution of the Elbe for PFHxA and, to a lesser extent PFHpA, compared with PFOA and PFNA (see Figure 2). This suggests that there may be a specific source of PFHxA and PFHpA in the Elbe watershed. The limited number of data does not allow further comment on the sources of the PFCAs, but their ubiquitous occurrence and similar distribution among the rivers suggests that many of their sources are diffuse and that the distribution of these diffuse sources is similar for the different chain lengths.

In conclusion, this work indicates that a large portion of the PFOA emissions in Europe could be eliminated by controlling the industrial source(s) in the Po watershed. However, extensive further reduction of PFOA emissions and the emissions of the other PFCAs studied will require further research to identify the nature of diffuse sources of these chemicals.

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Supporting Information Available

Additional information about the location of the sampling sites, the sampling protocol, the watersheds covered by the sampling program, the instrumental methods, the results of the QA/QC measures, and tabulated PFCA concentrations in river water is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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