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Relationship Between Industrial Discharges and Contamination of Raw Water Resources by Perfluorinated Compounds. Part I: Case Study of a Fluoropolymer Manufacturing Plant

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Abstract Perfluorinated compounds (PFCs) have been recognized as global environmental pollutants. They are used in various applications and high levels have been found in water bodies located near highly industrialized sites. In the present study, 10 PFCs were quantitatively determined in water samples collected in the vicinity of a fluoropolymer manufacturing plant and in drinking water resources located downstream. The release of PFHxA and PFNA to the receiving river was estimated at 10 and 4.5 tons/year, respectively. PFHxA (0.058–0.156 μg/L), PFNA (0.013–0.035 μg/L) and PFOA (0.007–0.025 μg/L) were predominant and prevalent in all the studied drinking water resources, confirming with the composition profile the impact of the industrial park release.

Keywords Drinking water · Contamination · Perfluorinated compounds · Industrial activities

Perfluorinated compounds (PFCs) are a large chemical class of several hundred substances. They are characterized by a carbon chain of varying length, in which all or most of the carbon–hydrogen bonds are replaced by carbon–fluorine bonds. They have been in usage for more than half a century and are used in various applications, such as fire-fighting foams, acid mist suppressants for metal plating and electronic etching baths, water and grease repellants for fabrics, carpets, leather, and paper (Lin et al. 2009; Renner 2001). Due to their ubiquity in ecosystems and their persistence and possible impacts on human health, they have recently become a target of scientific investigation. The two most widely known groups of PFCs are perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs). The former are fully fluorinated carboxylic acids and are named according to the length of the carbon chain, with the main examples of PFCAs being PFOA (perfluorooctanoic acid: $CF_3–(CF_2)_6–COOH$) and PFNA (perfluorononanoic acid: $CF_3–(CF_2)_7–COOH$). The latter are fully fluorinated carbon chain length sulfonates and are also named according to the length of the carbon chain, with the main example of PFASs being PFOS (perfluorooctane sulfonate: $CF_3–(CF_2)_7–SO_3^-$). PFCAs and PFASs may be indirectly released into the environment as chemical impurities formed during the manufacture of PFCs or degradation from fluorotelomer- or PFAS-based substances (Ellis et al. 2004; Lee et al. 2010; Liu et al. 2010; Myers and Mabury 2010; Washington et al. 2009). They may also be directly released during manufacture, application, use, and disposal (Lin et al. 2009; Ruan et al. 2010; Schultz et al. 2004; Skutlarek et al. 2006; Yoo et al. 2010).

Fluoropolymer manufacture is the single largest known source of PFNA and PFOA emissions in the environment (Prevedouros et al. 2006). These two PFCAs are used as processing aids in polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) manufacture, respectively. For this reason, the media has sometimes mistakenly reported that Teflon (a brand name of PTFE)-coated kitchen utensils are an important human exposure pathway for PFOA. PFOA only acts to solubilize fluorotelomers to facilitate their aqueous polymerization. Because PFOA is not incorporated into the polymer structure, it is discharged into waste streams from fluoropolymer manufactures. Moreover, PFOA residuals are almost totally removed from finished consumer articles by the various heat treatments during the coating process (Prevedouros et al. 2006).

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The goal of our field study was to estimate the contribution of effluents from a fluoropolymer manufacturing plant to the water resources located downstream from the effluent discharge point. The fluoropolymer manufacturing plant is located in an industrial park of about 400,000 m^2. Since 1902, this industrial park has been used to produce a large amount of chemical substances (sulfuric acid, hydrofluoric acid, fluorine-based compounds), but is now in decline. In regard to PFCs, three distinct production periods can be defined. From 1960 to 1987, polytetrafluoroethylene (PTFE) was produced. From 1981 to 1996, fluorinated copolymers were synthesized; these copolymers are used to improve the grease- and water-resistance of paper, carton, and textiles. PVDF production is believed to have started in 1981.

In this study, we targeted 10 PFCs, identified as good indicators of this fluoropolymer production: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS).

Materials and Methods

In June 2010, water samples were collected at 11 sampling sites, including waters from the fluoropolymer manufacturing plant (6 sampling sites) and two drinking water treatment plants (DWTP) (5 sampling sites). For the fluoropolymer manufacturing plant, selected sampling points included four monitoring wells (hereafter referred as P01, P13, P14, and P15), the end-stage effluent of the industrial wastewater treatment plant (WWTP) and the effluent of a basin that drains all the run-off waters from the industrial site (hereafter referred as WW and ROW, respectively). The industrial WWTP only uses a pH neutralization process before discharging the effluent into the receiving river (average river flow: 1,000 m^3/s). This WWTP receives wastewater generated by the PVDF manufacturing plant and another industrial facility that uses relatively high levels of PFHxA to synthesize perfluorinated polymers. The effluent samples (WW and ROW) were 24 h flow-proportional composite samples, whereas all other samples were extemporaneously collected. The groundwater flows approximately from monitoring well P14 to P01. P15 is the monitoring well nearest to the PVDF production area. In accordance with good sampling practices, the volume of each monitoring well was renewed twice before collecting the sample. Figure 1 is a map of the industrial site, and includes the two current sources of potential PFC contamination: the fluoropolymer manufacturing plant and the perfluorinated polymers manufacturing plant.

Raw water resources were also collected from two DWTPs. These DWTPs were located on both sides of a river, 15 km downstream from the fluoropolymer manufacturing plant. This river receives wastewater from many domestic and industrial activities, as it flows through a densely populated region. Raw water of the first DWTP (named DWA) is supplied by four alluvial wells (hereafter referred as DWA-1, DWA-2, DWA-3, and DWA-4). The DWTP uses simple chlorination to treat the water. About 5,000 people consume the drinking water produced by this plant. Raw water of the second DWTP (named DWB) is supplied by one alluvial well (hereafter referred as DWB-1). This DWTP also uses simple chlorination to treat the water. About 8,000 people consume the drinking water produced by this plant. The accurate location of the study area has been deliberately anonymized.

Samples were collected by members of our laboratory. New 1 L high-density polyethylene bottles were used to collect water samples. All water samples were stored at 5°C in the dark until extraction. To minimize the possibility of inadvertently introducing PFCs into samples, fluoropolymer materials were avoided throughout the experiment.

Details on the analytical method used and quality controls are described elsewhere (Boiteux et al. 2012). Briefly, 10 PFCs were analyzed. Non-filtered water samples of 500 mL were used for extractions. The analytes were concentrated from water using Oasis Wax (6 ml, 150 mg) solid-phase extraction cartridges. The eluted fraction was concentrated to 200 µL under nitrogen flow. Separation of analytes was accomplished by high-performance liquid chromatography (Acquity, Waters) by injecting 5 µL of each extract onto a 50 × 2.1 mm (1.7 µm) Acquity UPLC BEH C18 column (Waters). A binary mobile phase consisting of 2 mM ammonium acetate in water:methanol (9:1 v/v) (A) and 100 % methanol (B) was used. The gradient started at 30 % methanol. At a flow rate of 0.65 mL/min, the gradient increased to 100 % methanol at 5.1 min, and was maintained for 1 min. The column temperature was maintained at 50°C. Identification and concentrations were determined by using a tandem mass spectrometer (Xevo TQ-MS, Waters) operating in negative electrospray ionization mode and using multiple reaction monitoring (MRM). The limit of quantification (LOQ) of the method was determined to be 4 ng/L for each analyte.

Results and Discussion

The results obtained in the industrial park are presented in Table 1. All the investigated monitoring wells at the

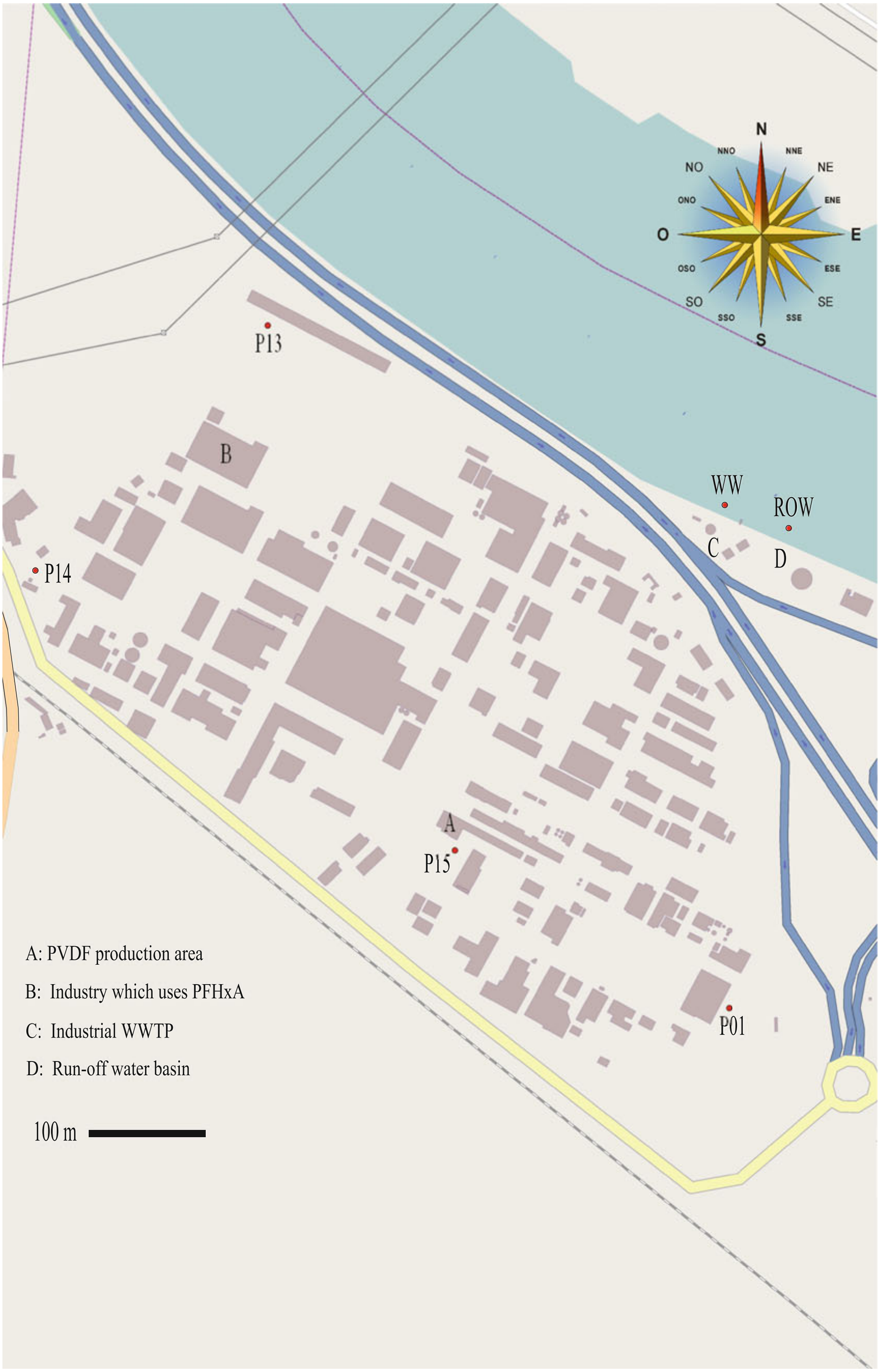

Fig. 1 A map showing sampling locations within the industrial site

Table 1 PFC concentrations in μg/L and PFHxA/PFNA ratios obtained at the fluoropolymer manufacturing plant

Location	P13	P14	P15	P01	ROW	WW
PFBA	0.009	0.020	0.273	0.183	<2.5	n. q.
PFPeA	0.015	0.047	0.364	0.168	<2.5	n. q.
PFBS	n. q.	n. q.	n. q.	0.280	<2.5	n. q.
PFHxA	0.248	0.154	20.6	6.83	17.2	1,136
PFHpA	0.018	0.037	0.285	0.105	<2.5	n. q.
PFHxS	0.068	0.008	n. q.	n. q.	<2.5	n. q.
PFOA	0.727	0.092	19.5	1.06	2.77	9.77
PFNA	n. q.	0.021	0.342	0.724	7.84	525
PFOS	0.188	0.011	0.068	<0.004	<2.5	n. q.
PFDA	n. q.	0.012	n. q.	0.064	<2.5	n. q.
Total PFCs	1.27	0.40	41.4	9.41	27.8	1,670
PFHxA/PFNA	not calculable	7.3	60.4	9.4	2.2	2.2

n. q. Not quantifiable due to dilution or matrix effects

industrial sites contained at least seven of the PFCs analyzed in this study, and the total PFC concentrations ranged from 0.4 μg/L (P14) to 41.4 μg/L (P15). Among the 10 PFCs analyzed, 5 (PFBA, PFPeA, PFHxA, PFHpA and PFOA) were detected in every water sample. PFOS was also a prevalent PFC, but present at relatively lower concentrations. In contrast, water samples from the monitoring wells were generally free of PFDA and PFBS. However, due to the high concentrations of some PFCs and to minimize matrix effects, the samples were highly diluted. The LOQs were therefore increased. The monitoring well located near the PVDF production area (P15) was the most contaminated of the four investigated monitoring wells. PFHxA (20.6 μg/L) and PFOA (19.5 μg/L) were the predominant species. Surprisingly, PFNA was quantified at relatively low levels (<1 μg/L) compared to the other PFCs detected in the same water sample. In this industrial site, PFNA has been used for PVDF production since 1981, but it was not the main PFC found in groundwater. These data suggest that the PFCs detected in groundwater represent previous manufacturing activities (PTFE and fluorinated copolymer production). The groundwater contamination by short-chain PFCs (PFBA, PFHxA, PFHpA, and PFPeA) may be due to the degradation of fluorotelomers used for the production fluorinated copolymers and subsequent infiltration of the breakdown products into the soil (Liu et al. 2007, 2010). It has been reported that the degradation of fluorotelomer compounds generates chemicals with higher environmental mobilities (Higgins and Luthy 2007; Washington et al. 2010). Groundwater contamination by PFOA may be due to the use of PFOA as a processing aid for PTFE, which was formerly produced in this plant. The current PVDF activity appears to be better confined in regard to groundwater contamination.

The total PFC concentration in the run-off water (ROW) basin (27.8 μg/L) was comparable that in the P15 monitoring well. Due to the necessary sample dilutions, only three PFCs were quantified. Interestingly, the PFC composition profile (PFHxA > PFNA > PFOA) in the run-off water basin was different from those observed in the

Table 2 PFC concentrations in μg/L and PFHxA/PFNA ratios obtained from each drinking water treatment plant (DWA and DWB)

DWTP	DWA					DWB	
Location	DWA-1	DWA-2	DWA-3	DWA-4	Treated water	DWB-1	Treated water
PFBA	0.015	0.013	0.013	0.005	0.008	0.005	0.006
PFPeA	0.023	0.027	0.013	<0.004	0.009	0.006	0.006
PFBS	0.004	0.004	<0.004	<0.004	<0.004	<0.004	<0.004
PFHxA	0.081	0.146	0.077	0.089	0.092	0.058	0.053
PFHpA	0.018	0.020	0.010	<0.004	0.007	0.008	0.009
PFHxS	0.011	0.008	0.004	<0.004	0.004	0.005	0.006
PFOA	0.022	0.025	0.018	0.007	0.013	0.018	0.019
PFNA	0.013	0.035	0.030	0.033	0.038	0.021	0.019
PFOS	0.006	0.009	0.006	0.006	0.008	0.011	0.012
PFDA	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Total PFCs	0.193	0.287	0.171	0.140	0.179	0.132	0.130
PFHxA/PFNA	6.4	4.1	2.6	2.7	2.4	2.8	2.8

monitoring wells. Whereas the PFHxA/PFNA ratios ranged from 7 to 60 in the monitoring wells, this ratio dropped to 2.2 in the run-off water basin. PVDF production is probably responsible for this relatively higher level of PFNA. The highest total PFC concentration was found in the wastewater effluent (WW) (1 670 µg/L). Only three PFCs were quantified due to the necessary sample dilutions. The composition profile and PFHxA/PFNA ratios were similar to those observed in the run-off water basin.

The run-off basin water and the industrial WWTP surveyed here generate approximately 6,500 and 24,500 m^3 of waste effluent each day. This corresponds to the release of nearly 10 and 4.5 tons/year of PFHxA and PFNA, respectively, to the receiving river. In the case of PFNA, our results are within the range of previously reported emission values into water from a European fluoropolymer production plant (Prevedouros et al. 2006). Other PFC compounds, such as fluorotelomer sulfonates ($CF_3–(CF_2)_n–(CH_2)_p–SO_3^-$), are used in high quantities (several tons per year) in the studied plant, and may also be present in the effluents. However, our analytical method was not able to measure them. In the environment, these compounds may degrade into short-chain PFCs, via chemical or biological processes.

In addition to effluents from the fluoropolymer manufacturing plant, wastewater discharges from municipal WWTPs and other industries using organic fluorochemicals (for semiconductors and electronic and optoelectronic devices) may influence the concentrations (Lin et al. 2009) and composition profiles of PFCs in raw water resources located downstream.

In the raw water resources (see Table 2), the sum of all the determined PFCs was always greater than 0.1 µg/L and ranged from 0.13 (DWB-1) to 0.29 µg/L (DWA-2). PFNA, PFOA, PFHxA, PFBA, and PFOS were found in all of the samples, while PFPeA, PFHpA, and PFHxS were found in the majority of the samples (4/5). PFBS was less frequently detected (2/5), while PFDA was found in none. Concentrations of PFHxA ranged from 0.058 to 0.145 µg/L, whereas the highest concentrations of the other PFCs were not greater than 0.035 ng/L (PFNA in DWA-2). Comparing the results from the industrial effluents (WW or ROW) with raw water resources (DWA-3, DWA-4 and DWB-1) showed similar profile patterns (PFHxA > PFNA > PFOA). Moreover, the PFHxA/PFNA ratios ranged from 2.6 (DWA-3) to 2.8 (DWB-1), values that are similar to those found in the industrial WWTP and run-off water basin effluents (2.2). In DWA-1 and DWA-2, the composition profiles were PFHxA > PFNA > PFPeA, but PFOA concentrations (0.022 and 0.025 µg/L) were approximately identical to those observed for PFPeA (0.023 and 0.027 µg/L). The PFHxA/PFNA ratios ranged from 4.1 (DWA-2) to 6.4 (DWA-1). The differences found among the raw water resources suggest that some wells are more affected by PFC contamination than others. Compared to other wells, the PFC levels were higher in DWA-1 and DWA-2. These two wells may be less confined and the potential mobility of short-chain PFCs may be enhanced by the characteristics of the local sediment. The slight differences observed with the effluents (WW or ROW) may also be explained by the sorption and subsequent degradation of PFCA precursors in the alluvial aquifer sediment. Further investigation will be required to determine the reasons behind these differences.

We compared the data obtained from these two DWTPs with those obtained from a national screening study on 10 PFCs in raw and treated water in France (Boiteux et al. 2012). Of the 331 raw water samples uniformly distributed across France and analyzed in this previous work, only four samples show the profile pattern PFHxA > PFNA > PFOA. These four sampling points were located downstream from the fluoropolymer production plant investigated in the present study. Moreover, 9 of the 10 analyzed PFCs were quantified in DWA-1 and DWA-2, whereas at most, only 8 PFCs were quantified per sample in the national screening study. Finally, among the 110 treated water samples analyzed during the national screening study, the sum of the 10 PFCs was greater than 100 ng/L at one sampling point (156 ng/L). In the present work, the total PFC level was greater than 100 ng/L at the two DWTPs, and higher than 156 ng/L at DWA (179 ng/L). These data suggest that this industrial park is partly responsible for this composition profile, and the relatively higher levels of PFCs found in raw water resources located downstream. The fluoropolymer manufacturing plant can be considered as the major source of PFNA along the river.

For a national interlaboratory study, raw water from the DWA-2 production well was again sampled three times in November 2010. The results were in good agreement with the first sample in the present study, confirming the level and the persistence of PFC contamination.

Our results suggest that the effluents of this fluoropolymer manufacturing plant are a main source of PFCs in the aqueous environment and illustrate the overall impact of this industry on downstream water resources. At Little Hocking, OH (USA), a fluoropolymer (PTFE) production facility was found to be the source of tap water contamination (Emmett et al. 2006). To the best of our knowledge, our study is the second time that the contribution of fluoropolymer activities to drinking water contamination has been clearly established.

Extensive sample collection is needed in this river drainage basin to pinpoint other sources of inputs and to improve knowledge on contamination levels of other water resources located along this river.

The removal rate of PFCs in the DWTPs was calculated based on the differences in concentrations between raw and treated water samples. For DWA, which is supplied by a well field, the raw water concentration was calculated as the mean of the concentration at all four wells, because each well had the same flow. The removal rate ranged from 1% to 10 % according to the treatment plant (DWB and DWA, respectively). We conclude that chlorination does not efficiently remove PFCs. In the present study, the PFC levels were 40-55 times lower than those found in the Little Hocking Water system (PFOA range 1.5–7.2 μg/L) (Emmett et al. 2006).

In conclusion, this study indicates that the sources of PFHxA are generally underestimated or that all sources have not been taken into account in publications dealing with the PFC emissions into the aquatic environment. A large portion of PFC emissions could be eliminated by controlling the industrial source that was investigated in the present study. PFC levels in drinking water reported in this paper are significantly below the existing regulations on PFCs in countries such as United States and Germany. Therefore, adverse health effects are not expected from exposure to PFCs as a result of water consumption from the studied drinking water sources. A more powerful analytical method is needed to identify the occurrence of fluorotelomers and to quantify the amounts potentially released into the environment.

Investigation will continue in our laboratory in an attempt to determine the occurrence of PFCs in all the water resources located downstream from the two industrial facilities. These water resources provide drinking water to a population estimated at about 500,000 consumers. Moreover, finished water samples are to be investigated to examine the efficiency of water treatment techniques. Also planned is the study of the fate of PFCs in the aquatic environment, i.e. the partition of perfluoroalkyl compounds among different aquatic compartments (sediment, water, suspended particulate matter and biota).

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