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Determination of polyfluoroalkyl compounds in water and suspended particulate matter in the River Elbe and North Sea, Germany

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Abstract The distribution of polyfluoroalkyl compounds (PFCs) in the dissolved and particulate phase and their discharge from the river Elbe into the North Sea were studied. The PFCs quantified included C_4-C_8 perfluorinated sulfonates (PFSAs), 6:2 fluorotelomer sulfonate (6:2 FTS), C_6 and C_8 perfluorinated sulfinates (PFSiAs), C_4-C_{12} perfluorinated carboxylic acids (PFCAs), perfluoro-3,7-dimethyl-octanoic acid (3,7m_2-PFOA), perfluorooctane sulfonamide (FOSA), and n-ethyl perfluroctane sulfonamidoethanol (EtFOSE). PFCs were mostly distributed in the dissolved phase, where perfluorooctanoic acid (PFOA) dominated with 2.9–12.5 ng/L. In the suspended particulate matter FOSA and perfluorooctane sulfonate (PFOS) showed the highest concentrations (4.0 ng/L and 2.3 ng/L, respectively). The total flux of ∑PFCs from the river Elbe was estimated to be 802 kg/year for the dissolved phase and 152 kg/year for the particulate phase. This indicates that the river Elbe acts as a source for PFCs into the North Sea. However, the concentrations of perfluorobutane sulfonate (PFBS) and perfluorobutanoic acid (PFBA) in the North Sea were higher than that in the river Elbe, thus an alternative source must exist for these compounds.

Keywords polyfluoroalkyl compounds (PFCs), perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), surface water, water-particulate partitioning

1 Introduction

Polyfluoroalkyl compounds (PFCs) are man-made chemicals which are found ubiquitously in water [1,2], soil [3], wildlife [4,5], and humans [6,7]. They are persistent against the typical environmental degradation processes [8]. The longer-chained PFCs are known to be bioaccumulative [9] and toxic effects in biota. For example, neuroendocrine effects [10] and peroxisome proliferation have been shown to occur [11,12]. Emissions of perfluorinated carboxylic acids (PFCAs) from direct and indirect sources are estimated to be approximately 3200–7300 t [13]. Although 3M, the major producer of perfluorooctyl sulfonyl fluoride (POSF, which is a major precursor for several PFCs) voluntarily phased out the production in 2002, it is still in use by other manufacturers [14]. The former POSF-based products are now substituted by perfluorobutyl sulfonyl fluoride (PBSF)-based products [13].

The perfluorinated sulfonamides are neutral compounds and are consequently not as water-soluble as the acids and also more volatile. It has been suggested that they are transformed to perfluorinated sulfonates (PFSAs) and PFCAs in the atmosphere [15,16], whilst fluorotelomer alcohols (FTOHs) are degraded to PFCAs [17]. Since the perfluorinated acids have high water solubilities and low pK_a values, they are dissociated at environmentally relevant pH values. They can be found mostly in water or bound to particles, sediments, and soils. The solid-water distribution coefficient (K_d), which is the ratio of the concentration of a compound in the solid phase (C_s) to the concentration in the water phase (C_w) in equilibrium, is higher for the perfluorooctyl sulfonamide acetic acids and perfluoroundecanoic acid (PFUnDA) than for perfluorooctanesulfonate (PFOS) [3].

Additionally, to the authors' knowledge, there is no peer-reviewed publication relating to particle-bound PFC concentration in surface waters in literatures. The object of this study, therefore, was to investigate the riverine transport of particle-bound PFCs in comparison to dissolved PFCs, which is important for understanding the fluxes, distribution, and the exchange among sea water, particles, and sediments in the marine environment. In addition, the flux of PFCs from the river Elbe into the North Sea was estimated for the dissolved and particulate phase. Surface water samples were taken in the river Elbe and extending out towards the North Sea. After filtration the dissolved and particulate phase were extracted separately and both were analysed simultaneously for the 40 target compounds of PFCAs, PFSAs, perfluorinated sulfinates (PFSiAs), fluorinated telomer acids (FTCAs), unsaturated fluorinated telomer acids (FTCUAs), perfluorinated sulfonamides, and sulfonamido ethanols. A concentration gradient from the river Elbe to the offshore water was shown, and the potential sources and sinks of PFCs were identified.

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2 Materials and methods

2.1 Sampling

Surface water samples were taken at 24 locations from the river Elbe and the North Sea (Germany) in August 2006 (Fig. 1). Details of the sampling and the physicochemical parameters of the water samples are presented in Table S1 in the Supporting Information (SI). One to two litre of water samples were obtained via a metal ship inlet system at 1-m water depth into brown glass bottles. At sampling station 7, 12, and 20, duplicate samples were collected for quality control. A depth profile was taken at sampling station 23 at 0.5, 1.0, 2.0, 2.5, and 2.8-m water depth for the estimation of the flux from the river Elbe into the North Sea. In addition, 1 L of Millipore water bottles were kept on the boat as field blanks. The samples were filtered using glass fibre filters (GFF, GC/C, Whatman, ø 47 mm) in a clean lab (class 10000) on the same or following day. The dissolved phase samples were stored at 4°C, while the GFF were sealed in test-tubes and stored at −20°C in a freezer until the sample extraction. Good aqueous sample and standard stability were shown from Risha et al. [18] at room temperature for PFCAs with chain lengths lower than C_{13}. Furthermore, good recoveries were also observed for aqueous samples after 36 d of storage time in polypropylene, high-density polyethylene (HDPE), and glass bottles [2].

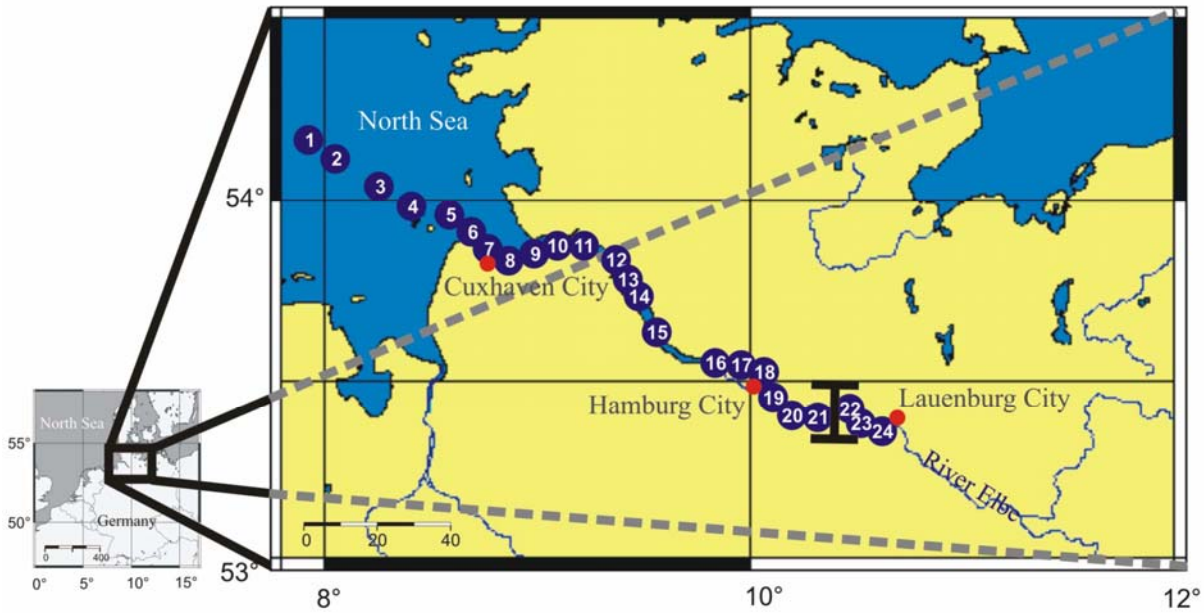

Fig. 1 Map showing the sampling locations in the river Elbe and the North Sea (a dam is located between sampling stations 21 and 22)

2.2 Sample extraction

The native and mass-labelled standards including their acronyms, formula, supplier, and purity are presented in Table 1. Methanol (SupraSolv), acetonitrile (LiChrosolv), ammonium hydroxide (25% for analysis), formic acid (98 – 100% suprapur), and ammonium acetate were purchased from Merck (Darmstadt, Germany).

Table 1 Analytes, acronyms, formula, supplier, purity, precursor, and product ions for the MS/MS detection

analyte	acronym	formula	supplier (purity)	precursor/ product ion [m/z]
perfluorobutane sulfonate	PFBS	$C_4F_9SO_2O^-$	Fluka (97%)	298.877/ 79.8
perfluoropentane sulfonate	PFPS	$C_5F_{11}SO_2O^-$	n.a.	348.939/ 79.8
perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_2O^-$	Fluka (98%)	398.894/ 79.8
perfluoroheptane sulfonate	PFHpS	$C_7F_{15}SO_2O^-$	Well. Lab.[a] (>98%)	449.034/ 79.3
perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_2O^-$	Well. Lab.[a] (>98%)	498.971/ 79.7
perfluorononane sulfonate	PFNS	$C_9F_{19}SO_2O^-$	n.a.	548.926/ 79.8
perfluorodecane sulfonate	PFDS	$C_{10}F_{21}SO_2O^-$	Well. Lab.[a] (>98%)	598.896/ 79.5
6:2 fluorotelomer sulfonate	6:2 FTS	$C_6F_{13}C_2H_4SO_3^-$	ABCR (98%)	426.925/ 406.7
perfluoro-1-hexane sulfinate	PFHxSi	$C_6F_{13}SO_2^-$	Well. Lab.[a] (>98%)	382.865/ 319.0
perfluoro-1-octane sulfinate	PFOSi	$C_8F_{17}SO_2^-$	Well. Lab.[a] (>98%)	482.824/ 418.9
perfluoro-1-decane sulfinate	PFDSi	$C_{10}F_{21}SO_2^-$	Well. Lab.[a] (>98%)	582.934/ 518.9
perfluorobutanoic acid	PFBA	C_3F_7COOH	ABCR (99%)	212.900/ 168.7
perfluoropentanoic acid	PFPA	C_4F_9COOH	Alfa Aesar (98%)	262.825/ 218.9
perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$	Fluka (97%)	312.934/ 268.8
perfluoroheptanoic acid	PFHpA	$C_6F_{13}COOH$	Lanc. Syn.[b] (98%)	362.950/ 318.9
perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$	Lanc. Syn.[b] (95%)	412.987/ 368.9
perfluorononanoic acid	PFNA	$C_8F_{17}COOH$	Lanc. Syn.[b] (97%)	462.908/ 418.9
perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$	Lanc. Syn.[b] (97%)	512.876/ 469.0
perfluoroundecanoic acid	PFUnDA	$C_{10}F_{21}COOH$	ABCR (96%)	562.865/ 519.0
perfluorododecanoic acid	PFDoDA	$C_{11}F_{23}COOH$	Alfa Aesar (96%)	612.991/ 568.9
perfluorotridecanoic acid	PFTriDA	$C_{12}F_{25}COOH$	Well. Lab.[a] (>98%)	663.094/ 618.9
perfluorotetradecanoic acid	PFTeDA	$C_{13}F_{27}COOH$	Alfa Aesar (96%)	713.036/ 669.0
perfluorotridecanoic acid	PFPDA	$C_{14}F_{29}COOH$	n.a.	762.980/ 718.9
perfluorohexadecanoic acid	PFHxDA	$C_{15}F_{31}COOH$	Alfa Aesar (95%)	812.840/ 769.1
perfluoroheptadecanoic acid	PFHpDA	$C_{16}F_{33}COOH$	n.a.	862.980/ 818.9
perfluorooctadecanoic acid	PFOcDA	$C_{17}F_{35}COOH$	Alfa Aesar (97%)	912.870/ 869.0
perfluoro-3,7-dimethyl-octanoic acid	3,7m$_2$-PFOA	$C_9F_{19}COOH$	Alfa Aesar (97%)	512.885/ 468.9
N-methylperfluorobutane sulfonamide	MeFBSA	$C_4F_9SO_2NH(CH_3)$	3M (n.a.)	311.914/ 218.8
perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	ABCR (97%)	497.896/ 77.9
N-methyl perfluorooctane sulfonamide	MeFOSA	$C_8F_{17}SO_2NH(CH_3)$	3M (n.a.)	511.849/ 168.9
N-ethyl perfluorooctane sulfonamide	EtFOSA	$C_8F_{17}SO_2NH(C_2H_5)$	ABCR (95%)	526.008/ 169.0
N-methylperfluorobutane sulfonamidoethanol	MeFBSE	$C_4F_9SO_2N(CH_3)C_2H_4OH$	3M (n.a.)	416.047/ 59.0
N-methyl perfluorooctane sulfonamidoethanol	MeFOSE	$C_8F_{17}SO_2N(CH_3)C_2H_4OH$	3M (n.a.)	616.004/ 58.9
N-ethyl perfluorooctane sulfonamidoethanol	EtFOSE	$C_8F_{17}SO_2N(C_2H_5)C_2H_4OH$	3M (n.a.)	630.109/ 58.8
2-perfluorohexyl ethanoic acid	FHEA	$C_6F_{13}CH_2COOH$	Well. Lab.[a] (>98%)	376.945/ 292.8
2-perfluorooctyl ethanoic acid	FOEA	$C_8F_{17}CH_2COOH$	Well. Lab.[a] (>98%)	476.909/ 392.9
2-perfluorodecyl ethanoic acid	FDEA	$C_{10}F_{21}CH_2COOH$	Well. Lab.[a] (>98%)	577.011/ 493.0
2H-perfluoro-2-octenoic acid	FHUEA	$C_6F_{12}CHCOOH$	Well. Lab.[a] (>98%)	356.885/ 293.0
2H-perfluoro-2-decenoic acid	FOUEA	$C_8F_{16}CHCOOH$	Well. Lab.[a] (>98%)	456.803/ 292.8
2H-perfluoro-2-dodecenoic acid	FDUEA	$C_{10}F_{20}CHCOOH$	Well. Lab.[a] (>98%)	556.937/ 493.1
perfluoro-1-hexane[$^{18}O_2$]sulfonate	[$^{18}O_2$]-PFHxS	$C_6F_{13}S[^{18}O_2]O^-$	Well. Lab.[a] (>98%)	402.981/ 83.9
perfluoro-1-[1,2,3,4-13C]octanesulfonate	[$^{13}C_4$]-PFOS	$C_4F_9[1,2,3,4\text{-}^{13}C_4]F_8SO_2O^-$	Well. Lab.[a] (>98%)	502.899/ 79.5
perfluoro-1-[1,2,3,4-13C]octanesulfinate	[$^{13}C_4$]-PFOSi	$C_4F_9[1,2,3,4\text{-}^{13}C_4]F_8SO_2^-$	Well. Lab.[a] (>90%)	486.859/ 422.9
perfluoro-n-(1,2,3,4-$^{13}C_4$)butanoic acid	[$^{13}C_4$]-PFBA	$2,3,4\text{-}^{13}C_3F_7{}^{13}COOH$	Well. Lab.[a] (>98%)	216.823/ 171.8
perfluoro-n-(1,2-$^{13}C_2$)hexanoic acid	[$^{13}C_2$]-PFHxA	$C_4F_9[2\text{-}^{13}C]F_2{}^{13}COOH$	Well. Lab.[a] (>98%)	314.891/ 269.9
perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	[$^{13}C_4$]-PFOA	$C_4F_9[2,3,4\text{-}^{13}C_3]F_6{}^{13}COOH$	Well. Lab.[a] (>98%)	416.978/ 371.8
perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	[$^{13}C_5$]-PFNA	$C_4F_9[2,3,4,5\text{-}^{13}C_4]F_8{}^{13}COOH$	Well. Lab.[a] (>98%)	467.907/ 423.0
perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	[$^{13}C_2$]-PFDA	$C_8F_{17}{}^{13}CF_2{}^{13}COOH$	Well. Lab.[a] (>98%)	514.944/ 469.8
perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	[$^{13}C_2$]-PFUnDA	$C_9F_{19}{}^{13}CF_2{}^{13}COOH$	Well. Lab.[a] (>98%)	564.959/ 519.8
perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	[$^{13}C_2$]-PFDoDA	$C_{10}F_{21}{}^{13}CF_2{}^{13}COOH$	Well. Lab.[a] (>98%)	614.913/ 569.9
N-methyl-d$_3$-perfluoro-1-octanesulfonamide	d$_3$-N-MeFOSA	$C_9D_3HF_{17}NO_2S$	Well. Lab.[a] (>98%)	514.920/ 168.8
N-ethyl-d$_5$-perfluoro-1-octanesulfonamide	d$_5$-N-EtFOSA	$C_{10}D_5HF_{17}NO_2S$	Well. Lab.[a] (>98%)	530.984/ 168.8
2-(n-deuteriomethylperfluoro-1-octanesulfoneamido)-1,1,2,2-tetradeuterioethanol	d$_7$-N-MeFOSE	$C_8F_{17}SO_2N(CD_3)C_2D_4OH$	Well. Lab.[a] (>98%)	623.058/ 58.9
2-(n-deuterioethylperfluoro-1-octanesulfoneamido)-1,1,2,2-tetradeuterioethanol	d$_9$-N-EtFOSE	$C_8F_{17}SO_2N(C_2D_5)C_2D_4OH$	Well. Lab.[a] (>98%)	639.054/ 58.9
2-perfluorohexyl-[1,2-$^{13}C_2$]ethanoic acid	[$^{13}C_2$]-FHEA	$C_6F_{13}{}^{13}CH_2{}^{13}COOH$	Well. Lab.[a] (>98%)	378.912/ 294.0
2-perfluorooctyl-[1,2-$^{13}C_2$]ethanoic acid	[$^{13}C_2$]-FOEA	$C_8F_{17}{}^{13}CH_2{}^{13}COOH$	Well. Lab.[a] (>98%)	478.911/ 393.8
2-perfluorodecyl-[1,2-$^{13}C_2$]ethanoic acid	[$^{13}C_2$]-FDEA	$C_{10}F_{21}{}^{13}CH_2{}^{13}COOH$	Well. Lab.[a] (>98%)	579.017/ 494.1
2H-perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid	[$^{13}C_2$]-FHUEA	$C_6F_{12}{}^{13}CH{}^{13}COOH$	Well. Lab.[a] (>98%)	358.907/ 294.0
2H-perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid	[$^{13}C_2$]-FOUEA	$C_8F_{16}{}^{13}CH{}^{13}COOH$	Well. Lab.[a] (>98%)	458.903/ 393.8
2H-perfluoro-[1,2-$^{13}C_2$]-2-dodecenoic acid	[$^{13}C_2$]-FDUEA	$C_{10}F_{20}{}^{13}CH{}^{13}COOH$	Well. Lab.[a] (>98%)	558.955/ 494.0
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid	d$_5$-EtFOSAA	$C_8F_{17}SO_2N(C_2D_2C_2D_3)C_2H_2CO_2H$	Well. Lab.[a] (>98%)	589.015/ 418.7

Notes: [a] Well. Lab. = Wellington Laboratories; [b] Lanc. Syn. = Lancaster Synthesis; n.a. = not available.

The dissolved phase was extracted by solid phase extraction (SPE), and the suspended particulate matter (SPM, >1.2 μm) was extracted by sonication. The natural water samples were spiked before the filtration with 10 ng of an IS-mix A (i.e., [$^{13}C_4$]-PFOA, [$^{13}C_4$]-PFNA, [$^{13}C_4$]-PFDA, [$^{13}C_2$]-PFUnDA, [$^{13}C_2$]-PFDoA, [$^{13}C_4$]-PFOS, [$^{13}C_4$]-PFOSi, d_3-MeFOSA, d_5-EtFOSA, d_7-MeFOSE, d_9-EtFOSE, and 50 μL of 0.2 μg/mL solution) to control any loss or adsorption effects of the IS during the storage, transportation, and filtration. In addition, after the filtration both dissolved and particulate phases were spiked separately with 10 ng of an IS-mix B (i.e., [$^{13}C_2$]-FHEA, [$^{13}C_2$]-FOEA, [$^{13}C_2$]-FDEA, [$^{13}C_2$]-FHUEA, [$^{13}C_2$]-FOUEA, [$^{13}C_2$]-FDUEA, [$^{13}C_4$]-PFBA, [$^{13}C_2$]-PFHxA, [$^{18}O_2$]-PFHxS, and 50 μL of 0.2 μg/mL solution) to correct for matrix effects as well as losses during sampling, sample extraction, concentration, and analysis. The extraction recoveries were examined by spiking separately the dissolved and particulate phases of water samples taken from Tesperhude/Geesthacht in October 2007 with 10 ng of the IS-mix A and B. For the instrumental blank 10 μL of methanol was injected, and for the method blank 1 L of Millipore water (Millipore, Elix 5 and Millipore Milli Q Plus) was extracted in the same way as the natural samples.

The SPE of the dissolved phase was similar to that described elsewhere [19] with some modifications. Briefly, Oasis WAX cartridges (Waters, 150 mg, 6 cc, 30 μ) were preconditioned with 5 mL of methanol and Millipore water. The 1−2 L of sample was extracted at approximately 2 drops/sec (approximately 5 mL/min), and the cartridges were washed with 5 mL of 0.1% formic acid in Millipore water. The cartridges were dried for 30 min, and then eluted in two steps using 14 mL of acetonitrile for the sulfonamides and 5 mL of 0.1% ammonium hydroxide in methanol for the acids. Both eluates were combined and further reduced to 200 μL under a nitrogen stream. 20 ng of the InjS (i.e., d_5-EtFOSAA, 10μL of 2 μg/mL solution) was spiked to the final extract to correct for instrument variations.

Sonication was used for the extraction of the SPM [3,20]. The GFF was placed into a glass fibre thimble in a beaker and sonicated with 100 mL of methanol for 1 h. This was carried out twice and the two fractions were combined. The extract was evaporated to approximately 2 mL and transferred over a nylon filter (Syringe, 0.2 μm) into a vial. It was further reduced to 200 μL and spiked with the InjS in the same way as the dissolved phase extracts.

2.3 Instrument analysis and quantification

An high-performance liquid chromatography (HPLC)-system (HP 1100, Agilent Technologies, USA) was used with a Synergi Hydro RP 80A column (150 × 2 mm, 4 micron) by Phenomenex plus a suitable guard column: Synergi 2 μ Hydro RP Mercury (20 × 2 mm, 2 micron). Modifications to the HPLC system were made to eliminate instrumental blank contamination [21]. All Teflon-containing tubing was replaced with polypropylene tubing, and stainless steel filters were used for the mobile phase solvents. The degasser was excluded from the system and helium was pumped into the mobile phase before every analysed sample batch. A cartridge (Gemini 5 μ C18 110A Mercury, 20 × 2 mm by Phenomenex) was installed behind the pump to trap all contaminants resulting from the mobile phase. Barrier septums (Supelco) made of silica and aluminium were used for the vials. Millipore water [A] and methanol [B] were employed as mobile phases, both with 10 mmol/L ammonium acetate as an ionisation aid. The acquisition time of the final method was set to 40 min plus 7 min equilibration. The gradient was started with 30% methanol. After this, it was increased to 70% [B] over 3 min, and then continuously increased to 100% [B] over 28 min. Finally 100% methanol was held over 7 min. The flow was set to 200 μL/min, 10 μL of the sample was injected and the temperature of the column oven was kept constantly at 30°C.

An API 3000 triple-quadrupole mass spectrometer (MS/MS) supplied by Applied Biosystems/MDS SCIEX with an ESI interface in negative ionisation mode was used. Precursor and product ions and all other optimised parameters are listed in Table S2 in the SI. The instrument was operated in multiple reaction monitoring (MRM) mode with a dwell time of 15 msec. Nebulizer, curtain, and collision gas were set to 14 L/min, 8 L/min, and 6 L/min, respectively. The ion spray voltage was set to −4500 V and the temperature of the source block was adjusted to 300°C.

Quantification was done using response factors calculated by an eight-point calibration curve from 0.1 ng/mL to 50 ng/mL. The PFSAs and sulfonamides revealed more than one peak, which is due to the different isomers of the compounds, resulting from the production process [22]. As the ratio of the isomers was sometimes different when the calibration standards were compared to the real samples, only the linear isomer was integrated for the quantification because of the lack of standards for the branched isomers. Therefore, concentrations of the branched isomers are not included in the evaluation. As the analytical standards are not available for PFPS, PFNS, PFPDA, and PFHpDA, they were integrated into the method taking the MS/MS parameters of the compound having one carbon atom less in the carbon chain. Their calibration was used for the quantification. Hence, the quantification of PFPS, PFNS, PFPDA, and

PFHpDA must be considered only as an estimation, as it is not sure that they have the same response factors.

2.4 Quality control

The analytical quality of the laboratory has been approved in interlaboratory studies [23]. As the standard procedure, field blanks, instrument detection limits (IDLs), method detection limits (MDLs), recoveries of spiked samples, and duplicate samples were examined in the dissolved and particulate phase for the water samples. A detailed list of analytical parameters and quality control data can be found in Tables S3 to S6 in the SI.

In order to evaluate the instrumental precision, within-day precision was tested by a tenfold injection of the same calibration solution at 25 ng/mL. The relative standard deviation (RSD) ranged from 2.1% (PFTriDA) to 7.2% (PFBA, PFBS). Between-day precision at 25 ng/mL ranged between 5.7% (PFNA) and 16.8% (FHEA) RSD. Instrumental blanks showed no contamination after all the above mentioned modifications were applied to the HPLC system. Before these modifications were made, PFBA, PFHxA, PFOA, FOSA, and MeFBSE were detected. Field blanks were all under the MDLs. IDLs and MDLs were determined at a signal to noise (S/N) of 3. The IDLs were calculated from the calibration standards and ranged from 0.191 pg absolute (PFBS) to 3.918 pg absolute (FHEA). These values are comparable to results from previously reported methods [19,24]. The MDLs for substances which were found in real samples ranged from 0.010 ng/L (PFHxSi) to 0.530 ng/L (PFBA) for the dissolved phase, and from 0.006 ng/L (PFOSi) to 0.228 ng/L (PFDoDA) for the particulate phase (for details see Table S3 in the SI).

One litre of water samples from the river Elbe close to location 22 were used for the recovery experiments. The dissolved and particulate phase were spiked separately with a low (5 ng/L) and high (20 ng/L) concentration of standard-mix. Absolute recoveries, which were corrected by the background concentration (see Table S4 in the SI) in the sample, as well as relative recoveries which were corrected for IS recoveries (see Table S5 in the SI) and background concentration in the sample are shown in Table S6 in the SI. As far as we know, this is the first report where the particulate matter was analysed separately from surface water samples. Sludge, particle matter of waste water samples, and sediments were analysed by a method applying sonication as well [3,20]. It is shown that the recovery values for the particulate phase corrected by IS and background concentration usually ranging between 67% (PFHxS) and 112% (PFBS, PFHpS and MeFBSE). Only PFDS and PFDSi (125% to 127%) showed higher values. The relative recoveries of the analytes for the dissolved phase were generally between 77% (PFTeDA and EtFOSA) and 126% (FOSA) for both spiking levels. The recoveries of PFBS, PFDS, 6:2 FTS, and PFDSi were higher (147% to 157%), while those of PFHxS, PFHxDA, and PFOcDA were lower (52% to 73%) (Table S6 in the SI). Breakthrough tests were carried out by putting two cartridges in series and applying both direct spiking and extraction of 1 L of spiked Millipore water. These tests showed that everything was retained on the first cartridge.

In the dissolved phase, the IS which were spiked before the filtration (IS-mix A) usually showed the higher recoveries of 72% to 99%, lower recoveries for [$^{13}C_2$]-PFDoA (41%) and the sulfonamides (21% to 34%). The latter may be the result of adsorption effects during the storage, transportation, and filtration. None of the IS (IS-mix A) was observed in the particulate phase. For the dissolved and particulate phase nine IS, spiked after the filtration (IS-mix B), were used to quantify the loss of the analytes due to sample preparation. Parallel samples taken at locations 7, 12, 20, and 22 showed good agreements. The RSD of these were generally lower than 20% for each compound.

3 Results and discussion

3.1 Concentration of PFCs in the particulate and dissolved phase

Overall 20 of the 40 examined analytes were found at the 24 sampling locations. The PFCs quantified included C_4-C_8 PFSAs, 6:2 FTS, C_6 and C_8 PFSiAs, C_4-C_{12} PFCAs, 3,7m$_2$-PFOA, FOSA, and EtFOSE. In this study, the compounds PFPS, PFHpS, PFHxSi, 3,7m$_2$-PFOA, and EtFOSE were observed for the first time in surface water, and the first particle-bound PFC data in surface water were reported. The uneven carbon chained analytes PFPS and PFHpS may be by-products of the POSF-based and PBSF-based production, respectively. 3,7m$_2$-PFOA could be a by-product of the production of PFCAs, while EtFOSE is a precursor of PFSAs [15,16]. The concentration ranges, which were found in the dissolved and particulate phases, are shown in Table 2 for five areas (North Sea, Elbe Estuary, Elbe brackish water, Hamburg City, and Hamburg to Lauenburg). All concentrations at each location are summarized in Table S7 and Fig. S1 in the SI.

Table 2 Concentration range and mean concentration in brackets for individual PFCs and ∑PFCs in the dissolved and particulate phases in ng/L, and particulate associated fraction range (φ) in % for five different areas from the North Sea and the river Elbe

area		North Sea	Elbe estuary	Elbe brackish water	Hamburg City	Lauenburg to Hamburg
location number[a]		1—4	5—8	9—15	16—18	19—24
samples size		4	4	7	3	6
PFBS	dissolved	1.1—3.9 (2.5)	1.3—1.7 (1.5)	n.d.—2.0 (1.2)	1.1—2.5 (1.6)	0.53—1.5 (1.1)
	particulate	n.d.	n.d.	n.d.—0.81 (0.12)	n.d.	n.d.
	φ (%)	0	0	0—34	0	0
PFPS[b]	dissolved	n.d.	n.d.	n.d.—0.67 (0.96)	1.3—2.8 (1.8)	0.47—2.1 (1.1)
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFHxS	dissolved	0.15—0.54 (0.31)	n.d.—0.72 (0.24)	0.37—0.91 (0.66)	0.56—0.67 (0.60)	0.24—0.49 (0.36)
	particulate	n.d.	n.d.	n.d.—0.20 (0.029)	n.d.	n.d.—0.098 (0.029)
	φ (%)	0	0	0—21	0	0—17
PFHpS	dissolved	n.d.	n.d.	n.d.	n.d.—0.072 (0.024)	n.d.
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFOS	dissolved	1.2—4.2 (2.2)	0.18—2.2 (1.1)	1.3—7.3 (3.7)	5.5—7.5 (6.4)	2.8—8.2 (5.5)
	particulate	n.d.	n.d.—0.76 (0.22)	n.d.—0.88 (0.48)	1.3—1.8 (1.6)	0.90—2.3 (1.6)
	φ (%)	0	0—34	0—29	15—24	18—30
6:2 FTS	dissolved	n.d.	n.d.	n.d.	n.d.—0.47 (0.16)	n.d.
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFHxSi	dissolved	n.d.	n.d.—0.060 (0.015)	n.d.	n.d.	n.d.
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFOSi	dissolved	n.d.—0.085 (0.041)	0.074—0.46 (0.20)	n.d.—0.85 (0.27)	n.d.—1.0 (0.61)	n.d.—1.4 (0.62)
	particulate	n.d.—0.067 (0.045)	n.d.—0.36 (0.13)	0.052—0.15 (0.097)	0.18—0.53 (0.38)	0.065—0.42 (0.27)
	φ (%)	27—100	24—44	7—100	34—100	6—100
PFBA	dissolved	1.5—5.0 (3.0)	1.0—2.5 (1.8)	n.d.—4.2 (2.4)	2.5—3.3 (3.0)	0.59—2.6 (2.2)
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFPA	dissolved	0.81—1.5 (1.1)	1.0—1.6 (1.3)	2.0—4.7 (3.4)	4.0—6.4 (5.4)	2.1—4.1 (3.3)
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFHxA	dissolved	1.1—1.3 (1.1)	1.7—2.0 (1.8)	2.7—4.6 (3.4)	5.2—6.0 (5.6)	3.0—5.5 (4.4)
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFHpA	dissolved	0.48—0.61 (0.56)	0.76—1.1 (0.87)	1.2—2.6 (1.8)	2.7—2.8 (2.7)	2.2—3.9 (2.9)
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
PFOA	dissolved	3.6—4.0 (3.8)	3.7—5.3 (4.5)	2.9—10.8 (7.4)	10.6—12.5 (11.4)	6.2—9.8 (8.0)
	particulate	n.d.	n.d.—0.35 (0.15)	n.d.—0.19 (0.071)	0.18—0.30 (0.24)	n.d.—0.30 (0.15)
	φ (%)	0	0—8	0—6	1—3	0—3
PFNA	dissolved	0.094—0.21 (0.13)	0.20—0.58 (0.38)	0.78—2.0 (1.4)	1.7—2.0 (1.8)	0.6—2.1 (1.7)
	particulate	n.d.	n.d.—0.13 (0.039)	n.d.—0.022 (0.008)	n.d.—0.088 (0.040)	0.003—0.074 (0.044)
	φ (%)	0	0—18	0—2	0—4	0—8
PFDA	dissolved	0.043—0.30 (0.13)	0.042—0.31 (0.16)	0.24—1.8 (0.77)	0.81—2.1 (1.4)	n.d.—0.69 (0.40)
	particulate	n.d.	n.d.	n.d.—0.12 (0.059)	0.087—0.18 (0.13)	0.12—0.19 (0.14)
	φ (%)	0	0	0—14	8—10	0—100
PFUnDA	dissolved	n.d.	n.d.—0.13 (0.06)	n.d.—0.49 (0.17)	0.099—0.47 (0.28)	n.d.—0.23 (0.11)
	particulate	n.d.	n.d.	n.d.—0.11 (0.019)	0.12—0.19 (0.15)	0.15—0.15 (0.15)
	φ (%)	0	0	0—19	0—100	0—40
PFDoDA	dissolved	n.d.—0.065 (0.016)	n.d.	n.d.—0.25 (0.035)	n.d.—0.12 (0.068)	n.d.—0.15 (0.07)
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
3,7m$_2$-PFOA	dissolved	n.d.	n.d.—0.22 (0.11)	n.d.—0.53 (0.094)	n.d.—0.78 (0.28)	n.d.—0.12 (0.027)
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.
	φ (%)	0	0	0	0	0
FOSA	dissolved	0.44—1.2 (0.85)	0.92—2.8 (1.8)	1.2—7.8 (3.8)	3.5—6.7 (4.9)	4.8—8.9 (6.1)
	particulate	0.14—0.37 (0.22)	0.31—0.95 (0.61)	0.36—1.2 (0.87)	1.3—2.0 (1.8)	1.7—4.0 (2.5)
	φ (%)	13—25	13—38	9—39	23—37	20—45
EtFOSE	dissolved	n.d.	n.d.	n.d.	n.d.	n.d.
	particulate	n.d.—0.023 (0.006)	n.d.	n.d.—0.12 (0.023)	n.d.—0.009 (0.003)	n.d.—0.047 (0.008)
	φ (%)	0—100	0	0—100	0—100	0—100
∑PFCs	dissolved	13.3—18.4 (16.0)	13.4—15.8 (15.7)	21.7—41.2 (30.5)	44.0—50.7 (48.0)	30.1—47.7 (38.0)
	particulate	0.16—0.41 (0.27)	0.34—2.2 (1.2)	0.41—2.6 (1.8)	3.3—4.8 (4.3)	3.1—6.0 (4.9)

Notes: [a] The locations of the numbers can be found in the map displayed in Fig. 1;
[b] Have to be considered as estimates, because no standard was available for this compound.;
n.d. = not detected.

In the particulate phase 10 PFCs were detected, however, only PFOSi and FOSA were found in all samples. PFOS was found in three-quarters of the samples and the occurrence of C_8 to C_{11} PFCAs decreased from 63% to 21% in the samples taken. A maximal ∑PFC concentration was observed with 6.0 ng/L (location 23). The average ∑PFC concentrations decreased by a factor of 3.6 and 16 from Hamburg towards the Elbe Estuary and the North Sea, respectively. The large decrease in ∑PFC concentration towards the North Sea could be a result of sedimentation processes and/or dilution with sea-borne particulates in the estuary. However, the concentrations in the particulate phase of the single compounds were usually lower than 1 ng/L except FOSA and PFOS with a few ng/L, while towards the North Sea the concentrations decreased to the MQL.

In the dissolved phase the compounds, PFOS, FOSA, and C_5 to C_9 of PFCAs were detected in all water samples. In contrast to the particulate phase, the occurrence of PFCs in the dissolved phase decreased with increasing chain length. A maximal ∑PFC concentration of 50.7 ng/L was observed at location 16 in Hamburg City. This indicates the major influence of the urban area at Hamburg City as a source of PFC contamination of the river Elbe. The average ∑PFC concentration dropped by a factor of 3 towards the North Sea. Just PFOS and both short-chained PFBA and PFBS showed a different behaviour along the river Elbe towards the North Sea. PFOS had a maximum concentration of 7.5 ng/L in Hamburg, and in addition a second maximum in the North Sea of 4.2 ng/L. Over the entire course down to the North Sea the concentration of PFBS and PFBA was relatively constant at 1.3 and 2.3 ng/L, respectively, but towards the North Sea (locations 1 to 4) the concentration increased to 2.5 ng/L and 3.0 ng/L, respectively.

FOSA and EtFOSE, which are precursors of PFSAs [15,16], were detected. FOSA was quantified in the dissolved phase at a concentration of up to 8.9 ng/L and in the particulate phase of up to 4.0 ng/L. EtFOSE was only observed in the particulate phase up to 0.1 ng/L. FTCAs and FTUCAs, intermediates during the degradation of fluorotelomer alcohols to PFCAs [17], were not detected.

Investigations by Caliebe et al. [25] determined mean concentrations of PFCs in the river Elbe in 2003 of about 20 ng/L for PFOA and PFOS, and 1 ng/L to 3 ng/L for other PFCs like PFHxA, PFNA, PFDA, PFHxS, and FOSA. Towards the open sea, PFOA and PFOS concentrations decreased to between 0.5 ng/L and 1.2 ng/L. The concentrations of PFOA and PFOS in 2003 were twice as high as in this study from 2006, which may be a result of the phased out of the production of POSF from 3M. McLachlan et al. [2] presented the riverine discharge for 2005/2006 of four PFCAs of 14 major rivers in Europe with a maximal concentration of PFOA of 200 ng/L in the river Po. In comparison to this study the concentrations in the river Elbe were in the same range, with the exception of PFHxA which was three times higher in their study.

Particulate related PFC fraction ($\varphi = [PFC]_{SPM}/([PFC]_{dissolved}+[PFC]_{SPM}) \times 100$) was calculated from the concentrations in the dissolved and particulate phase, which varied from compound to compound and depended on the location from where the samples were taken (Table 2). The lowest particulate associated fraction was found in the North Sea and the highest in the brackish water zone. The PFCs were mostly distributed in the dissolved phase, only EtFOSE was exclusively found in the particulate phase. PFOSi and FOSA were detected in every particulate phase with a proportion of 7% to 100% and 9% to 45%, respectively. The mean percentages of the particulate associated fraction were also relatively high for PFOS (14%), PFUnDA (12%), and PFDA (10%). PFSAs and longer-chained PFCAs, and perfluorinated sulfonamides and sulfonamido ethanols were more associated to particles than the shorter-chained PFCAs. This indicates that these compounds could rather settle down and accumulate in the sediment depending on their solid-water distribution coefficients [3]. No significant correlation was found between the particle behaviour and either water temperature or salinity. PFCs which exist predominantly in the dissolved phase such as the shorter-chained PFCAs, will be rapidly dispersed in the aquatic environment and can be transported over long distances [1].

3.2 Composition profile of individual PFCs

The relative composition of individual PFCs in the particulate and dissolved phase can be found in Fig. 2 and Table S7 in the SI. Most of the PFCs observed were in the dissolved phase. An average of 93% of the total PFCs were in the dissolved fraction, while 7% were on the particulate fraction. In the particle phase FOSA dominated with 60% and PFOS with 22%. The composition of the dissolved phase was quite different. The highest percentage was found for PFOA (24%), followed by PFOS and FOSA (both 12%), PFHxA (11%), and PFPA and PFBA (both 9%). In contrast to the particulate phase, a gradient from location 12 to 24 was observed in the dissolved phase with a change of the percentage depending on the chain length of the PFCAs and PFSAs. While the percentage of the longer-chained PFCs decreased, it increased for the shorter-chained PFCs. An explanation of this behaviour would be the better sorption of longer-chained PFCs to particles. Thereby, the longer-chained PFCs would be sedimented to a higher

proportion than the shorter-chained PFCs, i.e., the sediment acts as a sink of longer-chained PFCs. Higgins et al. [3] also found an increasing sorption of PFCs to sediment with increasing chain length. Location 11 differed in the composition compared to the other locations. At this location, FOSA had its highest percentage of about 32%, whereas PFBS and PFBA were not found. This may be the influence of an external source, such as the Kiel Canal with a mean discharge of 19 m^3/s or the industrial park in Brunsbüttel, where petroleum, textile-colouring, and polymer industries are located. At location 5 and 6 the composition of PFOA and FOSA increased, which could be caused by the mixing zone between the North Sea and the river Elbe. The other tributaries or wastewater treatment plants along the sampling location had no significant influence to the composition of PFCs, which suggested that diffuse sources also had an influence on the distribution of PFCs in surface water.

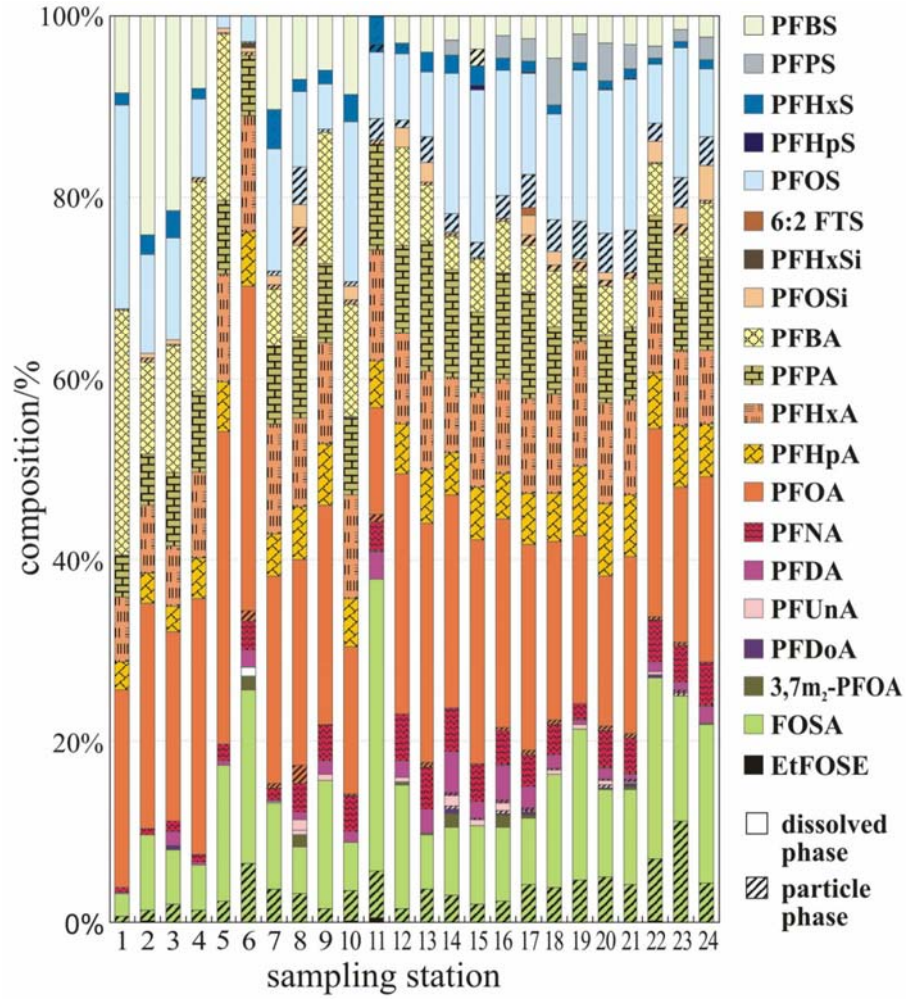

Fig. 2 Relative composition of individual PFCs for the dissolved and particulate phases in the river Elbe and the North Sea

3.3 Identification of common sources of individual PFCs

Table S8 in the SI shows the matrix of linear correlations among all detected PFCs at the 24 sampling locations. C_5 to C_{12} PFCAs were significantly correlated with each other and also with PFPS, PFOS, and mostly with PFOSi and FOSA. These positive correlations suggested that these PFCs had a common pollution source. Possible sources could be the effluents of waste water treatment plants (WWTPs) [26] and rain or surface runoff [27]. PFOS was positively correlated with PFOSi and FOSA, respectively. This agrees with the observations that PFOS is a degradation product of FOSA [16] and possibly also of PFOSi. So et al. [28] also found a positive correlation between the C_6 to C_{10} PFCAs and among PFOS and FOSA. It is noteworthy that PFHpS and 6:2 FTS had a high positive correlation with each other but not with any other PFC. This might suggest another source to the river Elbe compared to the other detected PFCs. The source of 6:2 FTS could be aqueous film-forming foams (AFFF) used to fight hydrocarbon-fueled fire [29]. The similar was found for PFBS and PFBA, which had a low correlation with each other. Additionally, in contrast to the other PFCs, significantly higher concentrations of PFBA and PFBS were

observed at locations 1 to 4 in the North Sea in comparison to the river Elbe (Mann-Whitney U-test, $p < 0.01$). This may be the result of an additional source, where PFBS and PFBA were transported into the North Sea with the westerly current. It is possible that this contamination of PFBS was originating from the river Rhine. Skutlarek et al. [30] took samples in the spring of the same year of the present sampling campaign, and they found PFBS as the major PFC in the river Rhine with a maximum concentration of 46 ng/L.

3.4 Total PFC flux from the river Elbe into the North Sea

The riverine discharge at individual locations is outlined in Table S1 in the SI. These calculations are based on data from the ARGE Elbe (personal communication), a consortium of German states for the prevention of pollution in the river Elbe. At the sampling day riverine discharge showed only a 7% higher amount compared to the mean annual riverine discharge. Because of this good agreement, or similarity, the total estimated flux per year was calculated with the riverine discharge of 736 m^3/s for the sampling day, which represents a riverine discharge of 2.32E+10 m^3 water per year. For this estimation the mean concentration of the water samples at 0.5, 1.0, 2.0, 2.5, and 2.8-m depth at location 23 was used, which is a rough estimation assuming a constant load over the whole year. The depth profile sampling was carried out at location 23 because this sampling point was behind the water dam at Geesthacht and was not influenced by the tides. The total estimated flux per year for the dissolved and the particulate phase is presented in Table 3. In the particulate phase the total riverine PFC flux was 152 kg/year, where the greatest proportions were observed for FOSA, PFOS, PFOSi, and PFOA with 63 kg, 35 kg, 27 kg, and 10 kg per year, respectively. A much higher riverine PFC flux was estimated for the dissolved phase with a total flux of 802 kg/year. The highest fluxes of PFOA, FOSA, PFOS, PFHxA, PFDA, PFHpA, PFPA, PFNA, and PFBA were 169 kg, 139 kg, 106 kg, 88 kg, 66 kg, 54 kg, 50 kg, 36 kg, and 35 kg per year, respectively. The calculation of the flux of FOSA may be too high, because the downstream concentrations were lower and it can be degraded to PFOS.

Table 3 Total estimated flux of individual PFCs in the dissolved and particulate phases in the river Elbe towards the North Sea[a]

analytes	total flux/(kg·year^{-1})	
	dissolved phase	particulate phase
PFBS	18	0
PFPS[b]	21	0
PFHxS	8	0
PFOS	106	35
PFOSi	13	27
PFBA	35	0
PFPA	50	0
PFHxA	88	0
PFHpA	54	0
PFOA	169	10
PFNA	36	3
PFDA	66	5
PFUnDA	0	3
PFDoDA	0	0
3,7m$_2$-PFOA	0	0
FOSA	139	63
EtFOSE	0	6
∑PFCs	802	152

Notes: [a] The mean concentration of the five water samples collected at 0.5-, 1.0-, 2.0-, 2.5-, and 2.8-m depth at location 23 (for details see text) was used for the calculation;
[b] Have to be considered as estimates, because no standard was available for this compound.

Total estimated fluxes of C_6 to C_9 PFCA for 14 major rivers in Europe were given by McLachlan et al. [2]. They estimated a total flux of 0.26 (PFNA) to 14.3 (PFOA) tonnes per year. In another study from the major rivers in Japan a maximum of 6.5 t of PFOA per year was calculated at the Aigawa Ryuiki disposal site [31]. In the present study, a riverine flux for all analysed PFCs in the river Elbe was estimated to be 954 kg/year, and separately for the groups of PFCAs, PFSAs, PFSiAs, and perfluorinated sulfonamides/sulfonamido ethanols was 517 kg, 189 kg, 40 kg, and 208 kg per year, respectively.

4 Conclusions

The present study is the first to determine PFCs in the particulate phase in surface water. In addition, PFPS, PFHpS, PFHxSi and 3,7m$_2$-PFOA were determined for the first time in the dissolved phase in surface water. The PFCs were mostly distributed in the dissolved phase (~93%), only EtFOSE was exclusively found in the particulate phase. Particles are subject to sedimentation and can therefore be important for bioavailability to benthic organisms. Further investigations are necessary to clarify if this leads to adverse effects such as a reduction of biodiversity. The total riverine PFC flux was 802 kg/year for the dissolved phase and 152 kg/year for the particulate phase. Discharge from the river Elbe contributed to a contamination of the North Sea with PFCs. This study found that PFBS and PFBA had other unknown sources in addition to the river Elbe, making research on the short-chained PFCs even more important. Further studies should therefore include a separate analysis of the dissolved and particulate phases. The particle mass and its content of organic matter should be determined to obtain a better understanding of the exchange processes between the dissolved and particulate phases, and to calculate partition coefficients between them.

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