



## Identification of point sources of polyfluoroalkyl compounds (PFCs) along the River Rhine watershed and their transportation into the North Sea

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### Abstract

Polyfluoroalkyl compounds (PFCs) have received increasing public attention because of their ubiquitous distribution in the aquatic environment. The concentration profile of PFCs in surface water along the River Rhine from the Lake Constance to the North Sea was investigated to identify point sources along the river and to examine their transportation into the marine environment. The water samples were preconcentrated by solid-phase extraction and analysed by a HPLC-MS/MS system. The short-chained compounds perfluorobutanoic acid (PFBA) and perfluorobutane sulfonate (PFBS) were found to be the dominating pollutants with concentrations up to 335 ng/L and 181 ng/L, respectively, while the concentrations of the other PFCs were mainly below 10 ng/L. The River Rhine downstream of the section Lower Rhine and the River Scheldt were found to be polluted by industrial point sources. Concentrations in the North Sea ranged from 0.4 to 11.6 ng/L total PFCs ( $\Sigma$ PFCs) while PFBA and PFBS were predominant at coastal stations, too. The results indicate that the River Rhine and in addition the River Scheldt seem to be major sources of PFCs in the North Sea whereas they might be transported into the German Bight via the easterly current.

### 1 Introduction and objectives

Poly- and perfluorinated compounds (PFCs) are one of the most illuminated environmental pollutants within the last years; the report about their worldwide distribution, environmental fate and transport pathways has rapidly increased since the end of the 1990s with continuously improving analytical methods. The public attention in Germany grew abruptly due to the contamination of surface and drinking water with PFCs in the region Sauerland in 2006 which originated from contaminated soil-improver which was spread on agricultural areas (Skutlarek et al. 2006).

PFCs are man-made chemicals which do not occur naturally in the environment. The industrial production started in the early 1950s with the invention of the electrochemical fluorination (ECF) for the large-scale production of PFCs. They consist of a hydrophilic head and both a hydrophobic and oleophobic carbon chain and are moderately water soluble. Because of their special chemical and physical properties due to their water, oil and soil repellence, they are used in a wide range of industrial applications and consumer products like paper, leather and textile coatings, in fire-fighting foam and in the polymer industry. The industrial interests and, therefore, the production has increased markedly in the last decades (Kissa 2001). A lot of toxic effects of PFCs have been verified and the lead compounds perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are under the suspicion to be carcinogenic (Fromme et al. 2008, Lau et al. 2007). They are persistent and bioaccumulative substances and have been detected in various environmental matrixes like freshwater (McLachlan et al. 2007) and marine waters (Ahrens et al. 2009a, Ahrens et al. 2009b, Yamashita et al. 2004), air (Jahnke et al. 2007), soil (Higgins & Luthy 2006) and organisms (Giesy & Kannan 2001). Some compounds meet the criteria of PBT compounds (persistent, bioaccumulative and toxic compounds) and PFOS was recently listed as a POP (persistent organic pollutant) by the Stockholm Convention (UNEP 2009).

With the commencement of the EU directive 2006/122/EC on July 27<sup>th</sup> 2008, the industrial usage of PFOS is already strictly limited Europe-wide (EPC 2006). The major PFC producing company 3M voluntarily phased out their PFOS production in 2002 and introduced perfluorobutane sulfonate (PFBS), a short-chained perfluoroalkyl sulfonate (PFSA), as substitute compound, which is told to be “practically non-toxic”, but still highly persistent (3M 2002). PFBS and additionally perfluorobutanoic acid (PFBA), a short-chained perfluorocarboxylic acid (PFCA), have already been detected in seawater of the North Sea while the River Rhine was proposed to be the source of the contamination of the North Sea by the short-chained PFCs (Ahrens et al. 2009b, Theobald et al. 2007).

The objective of this study was to examine the PFC profile in surface water along the entire course of the River Rhine from the Lake Constance to the North Sea. By a high number of samples in industrially marked regions, point sources of individual PFCs along the course were identified. Furthermore, the yearly discharge of PFCs from the River Rhine into the North Sea was calculated to estimate the influence on the contamination of the North Sea. Thereby, the little studied short-chained compounds PFBS and PFBA are focused, as they were found to be the dominating compounds and might be new lead compounds for PFCs in water.

## 2 Material and methods

### 2.1 Water sampling

In September and October 2008, 75 freshwater and marine water samples were taken along the River Rhine from the Lake Constance to the North Sea including the major tributaries and waters in the Rhine-Meuse delta (Figure 1).

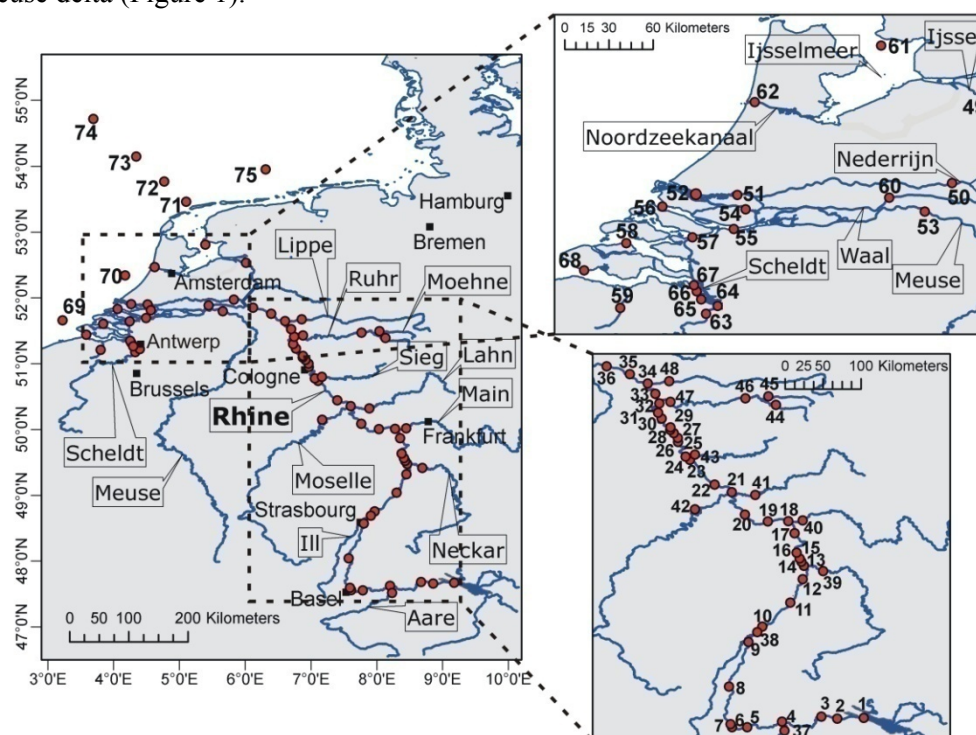


Figure 1: Maps showing the sampling stations along the River Rhine, in the tributary rivers, in the Rhine-Meuse delta and in the North Sea (Geographic data source: CCM River and Catchment Database, version 2.0 © European Commission–JRC 2007, Vogt et al. 2007)

The riverine samples were taken up- and downstream of possible point sources like the inflow of tributary rivers, industrial sites and wastewater treatment plants (WWTPs) in order to investigate their influence on the contamination. The seawater samples at stations 69 to 75 were taken by the

Rijkswaterstaat Waterdienst, The Netherlands (RWS) from the research vessel *R/V Zirfaea* via a ship intake system. Samples at the stations 36, 49, 51, 52, 54-57, 59, 61, 62 and 67 were taken by RWS via a ship intake system or from the shore. The remaining samples were taken via a stainless steel bucket from bridges, pontoons, public passenger ships or from the shore. All samples were taken at a water depth  $\leq 1$  metre and stored in 1 litre polypropylene bottles until analysis.

Table 1: Names, acronyms and formula of analysed PFCs (after Ahrens et al. 2009d, modified)

Analyte	Acronym	Formula
Perfluorobutane sulfonate	PFBS	C4F9SO2O-
Perfluoropentane sulfonate	PFPS	C5F11SO2O-
Perfluorohexane sulfonate	PFHxS	C6F13SO2O-
Perfluoroheptane sulfonate	PFHpS	C7F15SO2O-
Perfluorooctane sulfonate	PFOS	C8F17SO2O-
Perfluorononane sulfonate	PFNS	C9F19SO2O-
Perfluorodecane sulfonate	PFDS	C10F21SO2O-
6:2 fluorotelomer sulfonate	6:2 FTS	C6F13C2H4SO3-
Perfluoro-1-hexane sulfinate	PFHxSi	C6F13SO2-
Perfluoro-1-octane sulfinate	PFOSi	C8F17SO2-
Perfluoro-1-decane sulfinate	PFDSi	C10F21SO2-
Perfluorobutanoic acid	PFBA	C3F7COOH
Perfluoropentanoic acid	PFPeA	C4F9COOH
Perfluorohexanoic acid	PFHxA	C5F11COOH
Perfluoroheptanoic acid	PFHpA	C6F13COOH
Perfluorooctanoic acid	PFOA	C7F15COOH
Perfluorononanoic acid	PFNA	C8F17COOH
Perfluorodecanoic acid	PFDA	C9F19COOH
Perfluoroundecanoic acid	PFUnDA	C10F21COOH
Perfluorododecanoic acid	PFDoDA	C11F23COOH
Perfluorotridecanoic acid	PFTriDA	C12F25COOH
Perfluorotetradecanoic acid	PFTeDA	C13F27COOH
Perfluorotridecanoic acid	PFPDA	C14F29COOH
Perfluorohexadecanoic acid	PFHxDA	C15F31COOH
Perfluoroheptadecanoic acid	PFHpDA	C16F33COOH
Perfluorooctadecanoic acid	PFOcDA	C17F35COOH
Perfluoro-3,7-bis(trifluoromethyl)-octanoic acid	3,7m2-PFOA	C9F19COOH
Perfluorooctane sulfonamide	PFOSA	C8F17SO2NH2
N-methyl perfluorooctane sulfonamide	N-MeFOSA	C8F17SO2NH(CH3)
N-ethyl perfluorooctane sulfonamide	N-EtFOSA	C8F17SO2NH(C2H5)
N-methyl perfluorooctane sulfonamidoethanol	N-MeFOSE	C8F17SO2N(CH3)C2H4OH
N-ethyl perfluorooctane sulfonamidoethanol	N-EtFOSE	C8F17SO2N(C2H5)C2H4OH
N-methylperfluorobutane sulfonamide	MeFBSA	C4F9SO2NH(CH3)
N-methylperfluorobutane sulfonamidoethanol	MeFBSE	C4F9SO2N(CH3)C2H4OH
2-perfluorohexyl ethanoic acid	FHEA	C6F13CH2COOH
2-perfluorooctyl ethanoic acid	FOEA	C8F17CH2COOH
2-perfluorodecyl ethanoic acid	FDEA	C10F21CH2COOH
2H-perfluoro-2-octenoic acid	FHUEA	C6F12CHCOOH
2H-perfluoro-2-decenoic acid	FOUEA	C8F16CHCOOH
2H-perfluoro-2-dodecenoic acid	FDUEA	C10F20CHCOOH

## 2.2 Analysed compounds

In total, 40 PFCs were analysed including 16 PFCAs, 7 PFSAs, 6:2 Fluorotelomer sulfonate (6:2 FTS), 3 perfluoroalkyl sulfinates (PFSiAs), 4 perfluoroalkyl sulfonamides (FASAs), 3 perfluoroalkyl sulfonamidoethanols (FASEs), 3 fluorotelomercarboxylic acids (FTCAs) and 3 unsaturated fluorotelomercarboxylic acids (FTUCAs). All analytes and acronyms are included in Table 1.

## 2.3 Chemicals

Methanol (SupraSolv), acetonitrile (LiChrosolv), ammonium hydroxide (25 % for analysis) and ammonium acetate were purchased from Merck (Darmstadt, Germany). Millipore water was supplied by a Milli-Q Plus 185 system (Millipore).

## 2.4 Sample pre-treatment and extraction procedure

The surface water samples were filtered prior to the extraction using glass fiber filters (GC/C, Whatman,  $\varnothing$  47 mm, 1.2  $\mu$ m). The samples were extracted in a clean lab (class 10,000) based on the method described by Ahrens et al. (2009a) with some modifications. Briefly, 400 mL water samples (1 litre for the North Sea samples) were spiked with 10 ng of a mass labelled internal standard (IS) mix including 20 mass labelled internal standards (see Table 2 for internal standards).

Table 2: Names, acronyms and formula of internal standards (after Ahrens et al. 2009d, modified)

Internal Standard	Acronym	Formula
Perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate	[ <sup>18</sup> O <sub>2</sub> ]-PFHxS	C <sub>6</sub> F <sub>13</sub> S[ <sup>18</sup> O <sub>2</sub> ]O <sup>-</sup>
Perfluoro-1-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanesulfonate	[ <sup>13</sup> C <sub>4</sub> ]-PFOS	C <sub>4</sub> F <sub>9</sub> [1,2,3,4- <sup>13</sup> C <sub>4</sub> ]F <sub>8</sub> SO <sub>2</sub> O <sup>-</sup>
Perfluoro-1-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanesulfinate	[ <sup>13</sup> C <sub>4</sub> ]-PFOSi	C <sub>4</sub> F <sub>9</sub> [1,2,3,4- <sup>13</sup> C <sub>4</sub> ]F <sub>8</sub> SO <sub>2</sub> <sup>-</sup>
Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]butanoic acid	[ <sup>13</sup> C <sub>4</sub> ]-PFBA	2,3,4- <sup>13</sup> C <sub>3</sub> F <sub>7</sub> <sup>13</sup> COOH
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFHxA	C <sub>4</sub> F <sub>9</sub> [2- <sup>13</sup> C]F <sub>2</sub> <sup>13</sup> COOH
Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid	[ <sup>13</sup> C <sub>4</sub> ]-PFOA	C <sub>4</sub> F <sub>9</sub> [2,3,4- <sup>13</sup> C <sub>3</sub> ]F <sub>6</sub> <sup>13</sup> COOH
Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid	[ <sup>13</sup> C <sub>5</sub> ]-PFNA	C <sub>4</sub> F <sub>9</sub> [2,3,4,5- <sup>13</sup> C <sub>4</sub> ]F <sub>8</sub> <sup>13</sup> COOH
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFDA	C <sub>8</sub> F <sub>17</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]undecanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFUnDA	C <sub>9</sub> F <sub>19</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]dodecanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFDoDA	C <sub>10</sub> F <sub>21</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH
N-methyl-d <sub>3</sub> -perfluoro-1-octanesulfonamide	d <sub>3</sub> -N-MeFOSA	C <sub>9</sub> D <sub>3</sub> HF <sub>17</sub> NO <sub>2</sub> S
N-ethyl-d <sub>5</sub> -perfluoro-1-octanesulfonamide	d <sub>5</sub> -N-EtFOSA	C <sub>10</sub> D <sub>5</sub> HF <sub>17</sub> NO <sub>2</sub> S
2-(n-deuteriomethylperfluoro-1-octanesulfoneamido)-1,1,2,2-tetradeuterioethanol	d <sub>7</sub> -N-MeFOSE	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> N(CD <sub>3</sub> )C <sub>2</sub> D <sub>4</sub> OH
2-(n-deuterioethylperfluoro-1-octanesulfoneamido)-1,1,2,2-tetradeuterioethanol	d <sub>9</sub> -N-EtFOSE	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> N(C <sub>2</sub> D <sub>3</sub> )C <sub>2</sub> D <sub>4</sub> OH
2-perfluorohexyl-[1,2- <sup>13</sup> C <sub>2</sub> ]ethanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-FHEA	C <sub>6</sub> F <sub>13</sub> <sup>13</sup> CH <sub>2</sub> <sup>13</sup> COOH
2-perfluorooctyl-[1,2- <sup>13</sup> C <sub>2</sub> ]ethanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-FOEA	C <sub>8</sub> F <sub>17</sub> <sup>13</sup> CH <sub>2</sub> <sup>13</sup> COOH
2-perfluorodecyl-[1,2- <sup>13</sup> C <sub>2</sub> ]ethanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-FDEA	C <sub>10</sub> F <sub>21</sub> <sup>13</sup> CH <sub>2</sub> <sup>13</sup> COOH
2H-perfluoro-[1,2- <sup>13</sup> C <sub>2</sub> ]-2-octenoic acid	[ <sup>13</sup> C <sub>2</sub> ]-FHUEA	C <sub>6</sub> F <sub>12</sub> <sup>13</sup> CH <sup>13</sup> COOH
2H-perfluoro-[1,2- <sup>13</sup> C <sub>2</sub> ]-2-decenoic acid	[ <sup>13</sup> C <sub>2</sub> ]-FOUEA	C <sub>8</sub> F <sub>16</sub> <sup>13</sup> CH <sup>13</sup> COOH
2H-perfluoro-[1,2- <sup>13</sup> C <sub>2</sub> ]-2-dodecenoic acid	[ <sup>13</sup> C <sub>2</sub> ]-FDUEA	C <sub>10</sub> F <sub>20</sub> <sup>13</sup> CH <sup>13</sup> COOH

The samples were extracted via solid-phase extraction using Oasis WAX cartridges (Waters, 150 mg, 6 cc) which were conditioned with 5 mL 0.1 % ammonium hydroxide (NH<sub>4</sub>OH) in methanol, following 5 mL methanol and 5 mL Millipore water. The cartridges were loaded at approximately 1 drop/sec (3 drops/sec for the one litre North Sea samples), washed with 5 mL 0.1 % NH<sub>4</sub>OH in

Millipore water and then dried via centrifugation (2 min at 3000 rpm). Elution was done in two steps using first 14 mL acetonitrile and second 5 mL 0.1 % NH<sub>4</sub>OH in methanol. Method blanks using 1 litre or 400 mL Millipore water were extracted in the same way for each batch containing 10 to 12 samples.

## 2.5 Instrumental analysis

The extracts were analysed by a HPLC-MS/MS system with an electrospray interface in negative ionisation mode. An API 3000 triple-quadrupole mass spectrometer (Applied Biosystems/MDS Sciex) was used for detection (see Ahrens et al. 2009a for more details). An instrumental blank using methanol was injected with every batch.

## 2.6 Quantification and quality control

A five-point calibration from 0.5 ng/mL to 10 ng/mL (0.5, 1.0, 2.5, 5.0 and 10 ng/mL) was used for the quantification while two to four more calibration standards were added for higher concentrations (50, 100, 200 and 300 ng/mL). Response factors between analyte and the appropriate IS were used as calibration signal. As no analytical standards were available for perfluoropentane sulfonate (PFPS), perfluorononane sulfonate (PFNS), perfluoropentadecanoic acid (PFPeDA) and perfluoroheptadecanoic acid (PFHpDA), they were quantified using calibration parameters of the one carbon atom longer and shorter compounds. Thus, the results of these compounds should be seen just as estimation. All calibration graphs were linear and the correlation coefficients were > 0.99 for all analytes. PFOA was found in all method blanks above the method detection limit (MDL) in the pg/L range. However, as the concentrations in the real samples were about two orders of magnitude higher, the blind concentrations are negligible. Perfluorononanoic acid (PFNA), perfluoroundecanoic acid (PFUnDA), Perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA) were found occasionally slightly above the MDL. All blank concentrations were considered in the calculation of the sample concentration by subtraction from the sample concentrations. The instrumental blanks showed no contamination. The mean recoveries of the internal standards in the seawater samples ranged from 6 ± 1 % ([<sup>13</sup>C<sub>4</sub>]-PFBA) to 69 ± 12 % ([<sup>13</sup>C<sub>4</sub>]-PFDA), the mean recoveries of PFCAs and PFSAs were 38 ± 24 % and 44 ± 22 %, respectively. The recoveries in the river water samples were higher ranging from 22 ± 6 % ([<sup>13</sup>C<sub>4</sub>]-PFBA) to 105 ± 25 % ([<sup>13</sup>C<sub>4</sub>]-PFOSi) with mean recoveries for PFCAs and PFSAs of 55 ± 27 %. The relative recoveries of the analytes, which were corrected by the recoveries of the internal standards, ranged from 58 % (PFBS) to 182 % (6:2 FTS) with a mean recovery of PFCAs and PFSAs of 95 ± 28 % and 74 ± 10 %, respectively. The MDLs were determined at a signal to noise ratio (S/N) of three ranging from 0.0037 ng/L for perfluorooctane sulfinate (PFOSi) to 1.15 ng/L (PFBA) for the 1-litre seawater samples and from 0.014 ng/L for perfluoro-3,7-bis(trifluoromethyl)-octanoic acid (3,7m<sub>2</sub>-PFOA) to 1.60 ng/L (PFBA) for the 400 mL samples.

## 3 Results and discussion

### 3.1 PFCs along the River Rhine and its tributaries

Along the River Rhine and its tributaries, 27 PFCs were quantified including 6 PFSAs (C<sub>4</sub>-C<sub>9</sub> PFSAs), 6:2 FTS, 16 PFCAs (C<sub>4</sub>-C<sub>18</sub> PFCAs and 3,7m<sub>2</sub>-PFOA), perfluorohexane sulfinate (PFHxSi), perfluorooctane sulfonamide (PFOSA), N-methylperfluorobutane sulfonamide (MeFBSA), N-methylperfluorooctane sulfonamidoethanol (N-MeFOSE) and N-methylperfluorobutane sulfonamide (MeFBSA). The ΣPFC concentration ranged from 4.1 ng/L at the Lake Constance (station 1) to 267.5 ng/L in the section Lower Rhine (station 35). Figure 2 shows the concentration profile of major quantified PFCs along the River Rhine.

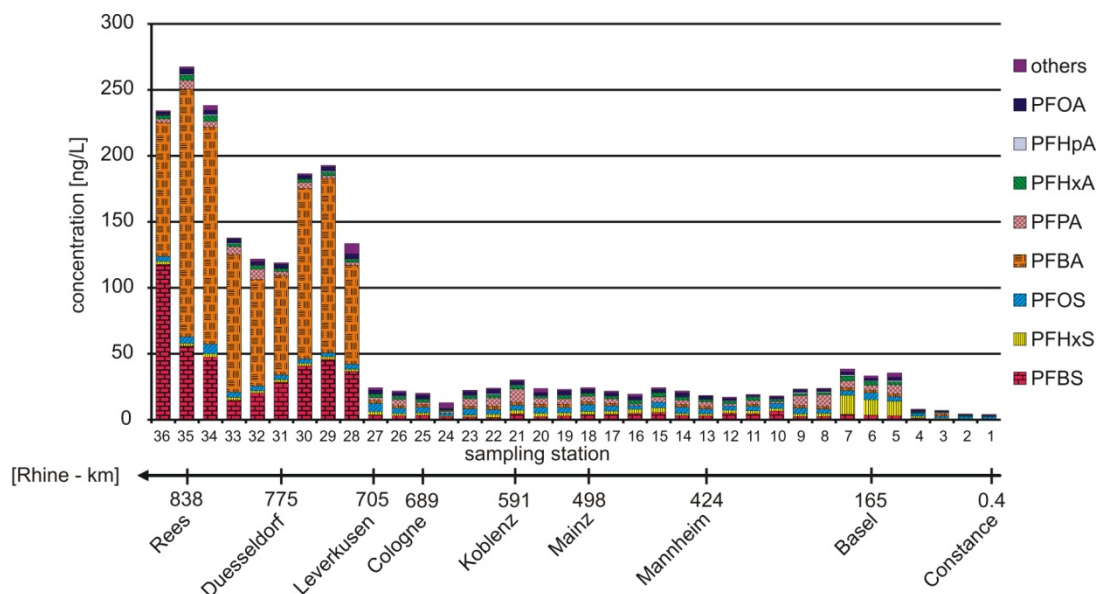


Figure 2: Concentration profile of major PFCs quantified along the River Rhine

The composition was dominated by the C<sub>8</sub>-based compounds PFOS and PFOA and the C<sub>4</sub>-based compounds PFBS and PFBA. Further, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFNA, perfluorodecanoic acid (PFDA) and perfluorohexane sulfonate (PFHxS) were detected in at least 90 % of the samples.

Along the River Rhine, two significant concentration increases were observed:

1. Station 4 to 5: PFHxS increased by a factor of ~10 with a maximum concentration of 14.5 ng/L at station 7.
2. Station 27 to 28: PFBS and PFBA increased by a factor of ~10 (from 3.8 to 36.7 ng/L) and ~33 (from 2.3 to 75.1 ng/L), respectively.

The C<sub>6</sub> compound PFHxS is industrially used in aqueous film-forming foams (AFFF) and for carpet treatments (Kärman et al. 2006). Hence, the first increase was likely caused by direct industrial emissions or indirect via WWTP effluents. Several paint, pharmaceuticals, plastic and textile manufacturing factories located in this section are conceivable sources. Due to the decrease of PFHxS by a factor of ~5 from station 7 to station 8, the increase seems to be based on a temporary or discontinuous pointwise immission of PFHxS.

The increases of PFBS and PFBA between station 27 and 28 were observed in an industrially marked region in the section Lower Rhine. Downstream of station 28, the mean concentrations were relatively constant with  $116.8 \pm 40.1$  ng/L for PFBA and  $45.4 \pm 30.2$  ng/L for PFBS. The source of the increase was found to be the discharge of treated wastewater by a WWTP located near the city of Leverkusen upstream of station 27 which treats industrial wastewaters. Obviously, the wastewater plume was not detected at station 27. In 2006, Lange et al. (2007) had already observed PFBS concentrations of 81 ng/L and 48 ng/L (mean values) in the Lower Rhine (sites Duesseldorf and Duisburg) and they reported a regional concentration increase of PFBS in the section Lower Rhine, too. The State Office of Nature, Environment and Consumer Protection North Rhine-Westphalia determined PFC concentrations in the wastewater effluent up to 68 µg/L for PFBA and 19 µg/L for PFBS, respectively (Bergmann 2009). Therefore, the operating company took actions to reduce the discharge of PFBS and PFBA into the River Rhine in the end of 2008 whereby the concentrations decreased to ~10 ng/L in the River Rhine downstream of the inflow (Bergmann 2009).

In the investigated tributaries of the River Rhine, the  $\Sigma$ PFC concentration ranged from 6.3 ng/L (station 43, River Sieg) to 308.8 ng/L (station 45, River Moehne) while PFBS, PFBA, PFPeA, PFOS and PFOA were the most common compounds (Figure 3).

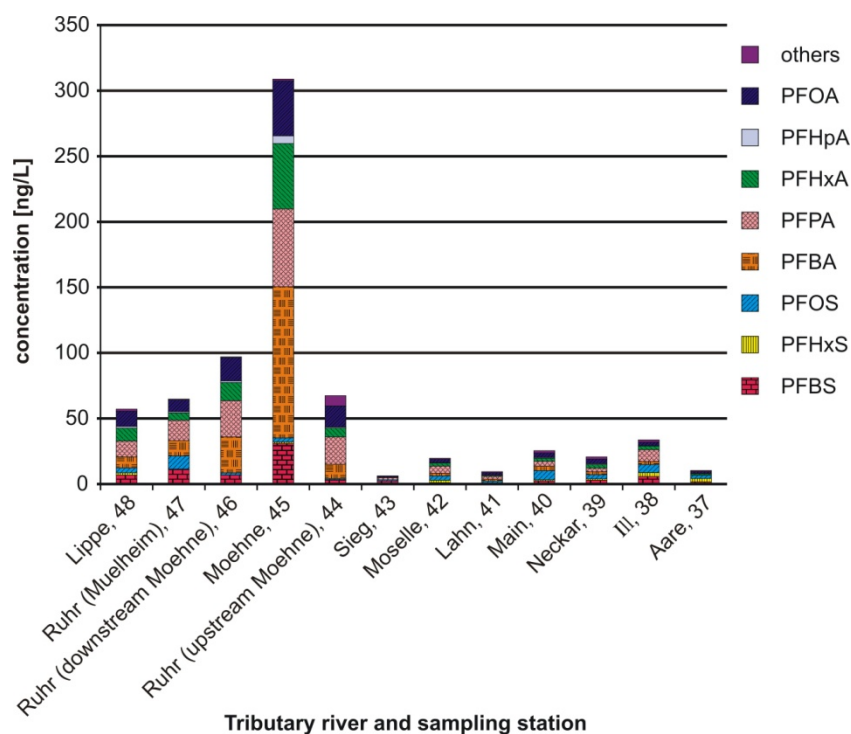


Figure 3: Concentrations of major PFCs quantified in the tributaries of the River Rhine

The rivers Moehne and Ruhr showed the highest concentrations of the investigated tributary rivers dominated by the C<sub>4</sub> to C<sub>8</sub> PFCAs. Since the dominating compounds in the rivers Ruhr and Moehne (i. e. PFBA, PFPeA, PFHxA and PFOA) were the main pollutants in the contamination scandal in the region Sauerland in 2006 (Skutlarek et al. 2006, Wilhelm et al. 2008), it is likely that the rivers Ruhr and Moehne are still polluted by runoff water from contaminated agricultural areas. The concentration in the River Ruhr downstream of the inflow of the River Moehne (station 46) increased by a factor of 1.4 ( $\Sigma$ PFCs) compared to station 44 upstream of the inflow showing the inflow's influence. The other tributaries showed no noteworthy concentration and no concentration increases were observed in the River Rhine downstream of their inflows.

In comparison, Skutlarek et al. (2006) reported approximately five times higher PFOS and PFOA concentrations in the River Rhine than observed in this study with concentrations up to 30 and 24 ng/L, respectively. The PFOS and PFOA concentrations along the River Rhine observed in this study are comparable to the concentrations in the River Elbe reported by Ahrens et al. (2009c) while the PFBS and PFBA concentrations are up to 50 times higher. McLachlan et al. (2007) reported PFHxA and PFNA concentrations in the River Rhine similar to this study, their observed PFHpA and PFOA concentrations were slightly higher. Further, the highest PFOA concentration in their study on 14 European rivers was found in the River Po with 200 ng/L, followed by the River Thames with 23 ng/L. A maximum PFBS concentration of 2,900 ng/L was reported for the River Aare (Lange et al. 2007). In a recent study, PFBS concentrations in the River Glatt comparable to the concentrations in the River Rhine downstream to station 27 were reported (Huset et al. 2008). In general, PFOA and PFOS concentrations in riverine water samples in this study are lower, while PFBS and PFBA concentrations are higher compared to riverine concentrations reported in recent studies. These results suggest the decreasing usage and emission of PFOA and PFOS into the aqueous environment and the replacement by the C<sub>4</sub>-based compounds PFBS and PFBA.

### 3.2 Transport of PFCs through the delta into the North Sea

The surface water samples along the course of the River Rhine in the delta showed similar concentrations and contributions as observed downstream of station 28 with PFBS and PFBA as the predominating PFCs. The  $\Sigma$ PFC concentration ranged from 20.8 ng/L (station 58, Eastern Scheldt) to 286.8 ng/L (station 60, River Waal). Figure 4 shows the concentrations of PFCs in the Rhine-Meuse delta. The main source of the pollution of the branches of the River Rhine is the WWTP at the Lower Rhine as mentioned above. Surely, there might be other sources discharging PFCs contributing to the pollution of the delta. Along the course of the Rhine, the  $\Sigma$ PFC concentration decreased towards stations influenced by seawater due to the tides like the New Waterway Canal (station 52) and the North Sea Canal (station 62). Conversely, higher PFOA concentrations were observed in the waters New Meuse (station 51) and in the New Waterway Canal pointing to the discharge of PFOA in the areas of the cities Dordrecht and Rotterdam located along the river. Sources might be the use of PFOA in the fluoropolymer production like Teflon®. The Western Scheldt estuary (station 68), which is the estuary of the River Scheldt, was found to be ~5 times higher polluted by PFCs compared to the Eastern Scheldt estuary (station 58), pointing to the influence of the discharge via the River Scheldt.

The second important river contributing to the delta, the River Meuse, showed a comparably low concentration (49.3 ng/L  $\Sigma$ PFCs) while the composition was dominated by PFBS, PFPeA and PFOA.

The third investigated river in the delta, the River Scheldt, was found to be the highest PFC-contaminated river among all investigated waters with a  $\Sigma$ PFC concentration up to 620.9 ng/L (station 67) while an increase by a factor of ~2.5 downstream of the city Antwerp was observed. PFBA was the most abundant PFC ranging from 87.8 ng/L (station 63) to 335.1 ng/L (station 67) and PFBS was also detected in high concentrations from 71.2 ng/L (station 63) to 153.0 ng/L (station 64). Apart from them, PFPeA and PFOA were found in quite high concentrations ranging from 16.7 ng/L (station 63) to 41.4 ng/L (station 67) and from 14.1 ng/L (station 63) to 69.5 ng/L (station 66), respectively.

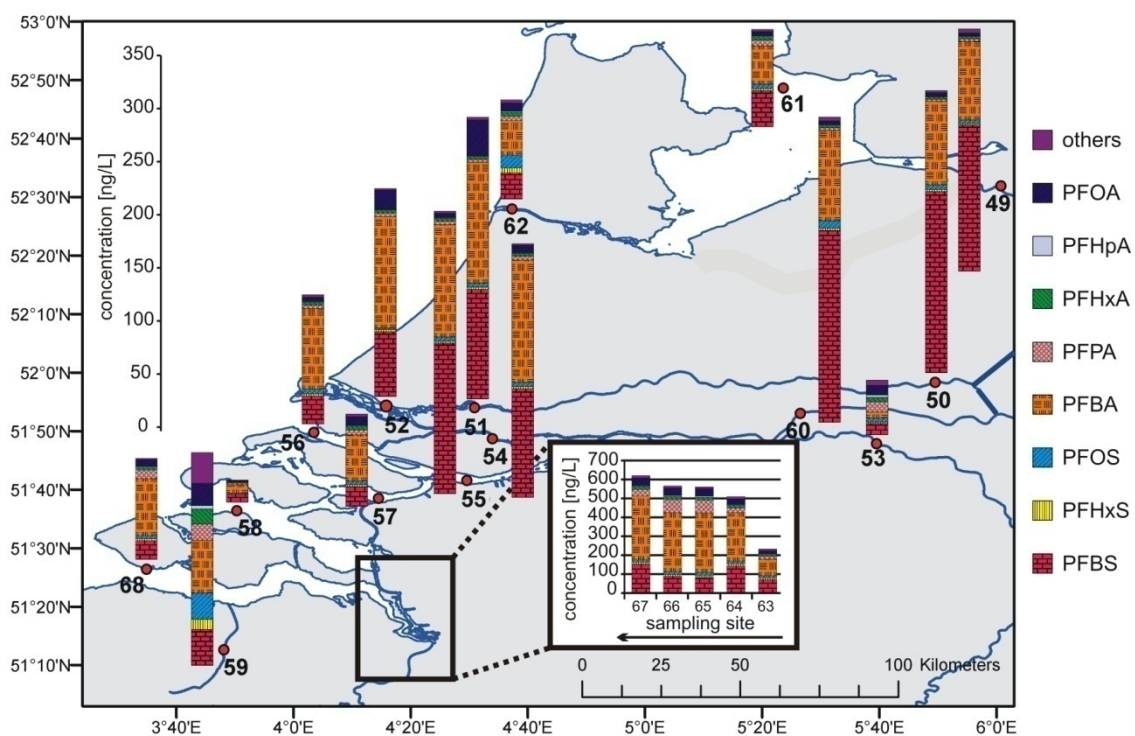


Figure 4: Concentrations of major PFCs quantified in the Rhine-Meuse delta.

Note: Measured salinity at the stations 52, 57, 58, 59, 62, 63, 64, 65, 66, 67 and 68 was 3.1, 0.8, 32.7, 2.8, 5.6, 1.8, 6.2, 9.9, 9.4, 9.4 and 29.8 psu, respectively. The salinity at the remaining stations was below 0.5 psu (Geographic data source: CCM River and Catchment Database, version 2.0 © European Commission-JRC 2007, Vogt et al. 2007).



Since the contamination of the River Scheldt was based on the same compounds as observed for the River Rhine, similar or related production processes and products might cause the contaminations of the River Rhine and the River Scheldt. Possible sources of the observed increase and the high contamination are industrial plants located in the harbour area of Antwerp, including a fluorochemical manufacturing facility.

Along the Dutch coastline in the North Sea, 14 compounds were found in concentrations above the MDL ( $C_4$ - $C_6$  and  $C_8$  PFSAs, PFOSi,  $C_4$ - $C_{11}$  PFCAs, PFOSA and N-MeFOSE). The  $\Sigma$ PFC concentration varied from 0.4 ng/L at station 74 (175 km from the shore of Terschelling) to 11.6 ng/L at station 71 (10 km from the shore of Terschelling) while a strong decrease with increasing offshore distance was observed from station 71 to 74. Figure 5 shows the observed concentrations along the Dutch coastline. The  $C_4$  compounds PFBS and PFBA were the dominating compounds at coastal stations with maximum concentrations of 4.8 ng/L for PFBS and 4.2 ng/L for PFBA. The same compounds were found to be dominant in the River Rhine distributaries and in the River Scheldt, indicating the rivers Rhine and Scheldt as sources of these compounds in the North Sea. Recently, the River Rhine was assumed to be a major source of PFCs in the North Sea by Theobald et al. (2007), who detected the highest concentrations in the North Sea close to the Rhine-Meuse delta estuaries. Furthermore, Ahrens et al. (2009b) observed significantly higher PFBS concentrations in the German Bight than in the River Elbe. It was supposed that the PFBS contamination originated from the River Rhine while PFCs are transported into the German Bight via the easterly current. The PFBS and PFBA concentrations observed in this study near the Dutch coastline are similar to the concentrations in the German Bight observed by Ahrens et al. (2009c). Therewith, the River Rhine seems to act as a major source of PFCs in the North Sea where they are transported via the easterly current along the coastline into the German Bight. Besides, the River Scheldt might have a considerable influence on the PFC contamination of the North Sea, too.

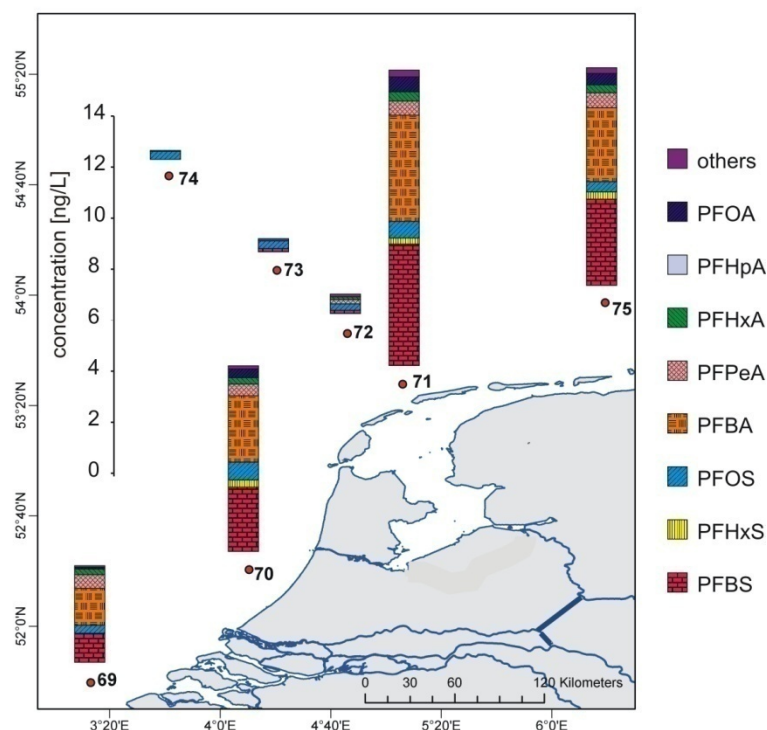


Figure 5: Concentrations of major PFCs quantified in the North Sea (Geographic data source: CCM River and Catchment Database, version 2.0 © European Commission–JRC 2007, Vogt et al. 2007)

At the more distant stations, the percentages of PFBA and PFBS decreased and PFOS became dominant. This can be explained by the transport of PFCs discharged via rivers predominantly along the coastline.

### 3.3 PFC mass flows and discharge into the North Sea

The daily PFC mass flows in the River Rhine were calculated with the riverine discharge data of the respective sampling day measured close to the sampling stations and the observed PFC concentrations in the surface water samples. The riverine water discharges were provided by the appropriate authorities. It should be noted that the calculation of the riverine mass flows is based on only one spot sample. The mass flows might vary due to seasonal trends, variations in water discharges and discontinuous immissions of PFCs by industrial plants or WWTPs. Huset et al. (2008) used 24-hour flow-proportional samples of seven consecutive days for the calculation of mass flows in the River Glatt, another tributary river of the River Rhine. Hence, the mass flows calculated in this study should be seen as rough estimations. The daily mass flow in the River Rhine increased from ~300 g/d at station 3 to ~39,000 g/d at station 35. The concentration increases between station 4 and 5 and between station 27 and 28 are reflected with mass flow increases of approximately 1,700 g/d and 23,000 g/d, respectively. The State Office of Nature, Environment and Consumer Protection North Rhine-Westphalia calculated a daily discharge by the WWTP located upstream of station 27 of approximately 8,000 g/d PFBS and 22,500 g/d PFBA in November 2008 (Bergmann 2009). This is in good comparison with the calculated increase of 23,000 g/d.

Based on the observed concentrations at the stations 34 to 36 close to the Dutch-German border and assuming a yearly mean water discharge of 2,200 m<sup>3</sup>/s, a yearly mass flow of ~17 tonnes PFCs from the River Rhine into the delta and further into the North Sea can be estimated. PFBA and PFBS have the highest impacts with 10.5 and 5.1 tonnes, respectively, followed by PFOS, PFPeA, PFHxA and PFOA with 0.4, 0.3, 0.2 and 0.2 tonnes, respectively. But, it should be noted that the discharge of PFBS and PFBA by the WWTP into the River Rhine decreased markedly at the end of 2008 as mentioned above. Therewith, the calculated flux might be overestimated. Assuming a riverine flow of 800 m<sup>3</sup>/s for the River New Meuse, an additional yearly discharge of 0.8 tonnes PFOA by the supposed source located in the areas of Dordrecht or Rotterdam can be estimated leading to a total discharge of ~1 tonne PFOA per year.

The River Meuse showed a total annual mass flow of 0.4 tonnes/year (based on a mean water discharge of 250 m<sup>3</sup>/s), whereby PFBS, PFPeA, PFOA, PFBA, PFHxA and PFOS dominated with 0.09, 0.08, 0.07, 0.05, 0.03 and 0.03 tonnes/year, respectively.

As described earlier, the River Scheldt seems to have an important influence on the contamination of the North Sea. Based on a mean discharge of 100 m<sup>3</sup>/s and in consideration of the influence of seawater due to the tides, a mass flow of ~2.5 tonnes PFCs per year was calculated. PFBA, PFBS, PFPeA, PFOA and PFOS have the highest impacts with 1.4, 0.5, 0.3, 0.2 and 0.07 tonnes.

As sum of the three important affluxes contributing to the delta, the rivers Rhine, Meuse and Scheldt, an overall amount of ~20 tonnes PFCs per year transported into the North Sea can be estimated. For the River Elbe, a total PFC mass flow of 802 kg/year in the dissolved phase was estimated with individual mass flows for PFBS and PFBA of 18 and 35 kg/year, respectively (Ahrens et al. 2009c). The total flow calculated for the Rhine-Meuse delta in this study is more than 20 times higher, while the flows for PFBS and PFBA are even more than 100 times higher. Again, this shows that the River Rhine is a major source of PFCs in the North Sea while the impact on the contamination of the North Sea by PFCs is supposed to be much higher compared to the River Elbe.

## 4 Conclusions

The present study shows the occurrence of a wide range of PFCs in the River Rhine watershed while the short-chained compounds PFBS and PFBA were found to be the predominating PFCs. Point sources discharging PFCs located in the section Lower Rhine and in the delta could be identified. The River Rhine and in addition the rivers Scheldt and Meuse were found to be important sources of PFCs, especially of PFBS and PFBA, in the North Sea discharging approximately 20 tonnes PFCs into the North Sea where they are transported via the easterly current along the coastline into the German Bight. Even though the short-chained compounds are told to be less (acutely) toxic and less bioaccumulative than longer chained PFCs ( $\geq C_8$ ), they are still highly persistent, can be transported over a wide range via the ocean currents and might have chronic toxic potential which is not yet sufficiently researched. Therefore, high concentrations as observed in this study in rivers and in their estuaries as well as considerable mass flows into the North Sea are of high emerging concern for the marine environment.

The dominance of PFBS and PFBA originates from the limitation of PFOS and decreasing usage of PFOA and the introduction of PFBS and PFBA as substitute compounds. PFBA and PFOS might be future lead compounds for PFCs in surface water, while these observations should be surveyed in further studies on other important European rivers. The ubiquitous occurrence of PFCs and especially the wide range of PFCs detected shows that the occurrence of PFCs, their sources and their fate in the environment, in particular in the aquatic environment, should be extensively investigated in the future.

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