



# Emerging per- and polyfluoroalkyl substances (PFASs) in surface water and sediment of the North and Baltic Seas

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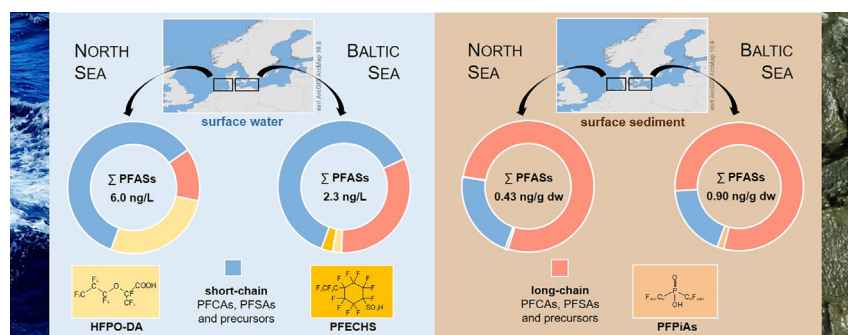
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## HIGHLIGHTS

- The replacement compound HFPO-DA was the most prevalent substance in North Sea water.
- In the Baltic Sea, legacy long-chain PFCAs and PFASs were still dominant.
- A shift to replacements is dependent on sources and geographical conditions.
- The cyclic compound PFECCHS was detected in 86% of the Baltic Sea water samples.
- In sediments, PFPiAs were identified as emerging PFASs in coastal areas.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Along with the phase-out of legacy long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFASs) and their precursors, attention has been drawn to emerging per- and polyfluoroalkyl substances (PFASs). This study is aimed at investigating the importance of selected emerging PFASs as pollutants in European coastal environments and a possible transition from legacy long-chain PFCAs and PFASs to replacement compounds. Therefore, the spatial distribution of 29 PFASs was analysed in surface water and sediment of the North and Baltic Seas sampled in 2017. Levels of the replacement compound HFPO-DA were approximately three times higher than those of its predecessor PFOA in surface water from the North Sea, which is characterised by the influence of point sources and constant exchange with open water. Reanalysis of sample extracts from the last decade showed that HFPO-DA had already been present in 2011, when it had not yet been in focus. In the Baltic Sea with a limited water exchange and dominance of diffuse sources, the proportion of HFPO-DA was negligible, whereas long-chain PFCAs and PFASs still contributed to  $\Sigma$ PFASs with about 30%. The emerging cyclic compound perfluoro-4-ethylcyclohexanesulfonate (PFECCHS), which has not yet been reported in European coastal environments, was detected in 86% of the Baltic Sea samples. Influenced by sediment characteristics in addition to source-specific contributions, the spatial distribution of PFASs in surface sediments was more variable than for water samples. The linear isomer of the long-chain legacy substance PFOS was the predominant compound found over the entire study area. Of the emerging PFASs, 6:6 and 6:8 perfluoroalkyl phosphinic acids (PFPiAs) were identified close to potential industrial inputs and in sedimentation areas. The results show that particular emerging PFASs play a relevant role in the investigated coastal environments and that a shift to replacements is dependent on sources and geographical conditions.

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic chemicals that have been used widely in industrial and consumer applications since the 1950s (Prevedouros et al., 2006; Kissa, 2001). Attention has been drawn to the role of long-chain perfluoroalkyl carboxylic acids (PFCAs,  $C_nF_{2n+1}COOH$ ,  $n \geq 7$ ), perfluoroalkane sulfonic acids (PFSAs,  $C_nF_{2n+1}SO_3H$ ,  $n \geq 6$ ) and their potential precursors as global contaminants of high concern due to their persistence, bioaccumulation potential, toxicity and long-range transport potential (Buck et al., 2011; Scheringer et al., 2014). This has led to a number of initiatives by regulatory authorities and industry aiming at restricting the production, use, and release of long-chain PFASs. In 2000, the major manufacturer 3M announced a global phase-out plan to be carried out by 2002 for products derived from perfluorooctane sulfonyl fluoride (POSF), including the  $C_6$  and  $C_{10}$  homologues (3M, 2000). Industrial initiatives were continued in 2006 when eight major producers joined in a global stewardship program and thereby committed working towards eliminating perfluorooctanoic acid (PFOA), its precursors and related higher-homologue chemicals by 2015 (US EPA, 2006a). At the international regulatory level, PFOS (perfluorooctane sulfonic acid), its salts and POSF (perfluorooctane sulfonyl fluoride) were added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in 2009, implementing restrictions on their production and use (BRS Secretariat, 2017). The evaluation of PFOA and perfluorohexane sulfonic acid (PFHxS) is currently ongoing (BRS Secretariat, 2019). Under REACH, the European chemicals regulation, PFOA, PFHxS as well as  $C_9$  to  $C_{14}$ -PFCAs, their salts and precursors were added to the Candidate List of Substances of Very High Concern from 2012 to 2017 (ECHA, 2019). In 2017, the Commission Regulation (EU) No 2017/1000 to restrict PFOA, its salts and precursors under REACH came into force and will be implemented beginning in 2020.

As a consequence of the gradual phase-out of legacy long-chain PFASs, an industrial transition to replacement substances has been taking place. In addition, production has been shifted from Western Europe, the United States and Japan to less regulated countries such as China (Wang et al., 2014). Replacement compounds include shorter-chain homologues, such as perfluorobutane sulfonic acid (PFBS), but also PFASs with different functionalities, such as per- and polyfluoroalkyl ether carboxylic and sulfonic acids (PFECAs and PFESAs). Several PFECAs are known to replace PFOA as processing aids in fluoropolymer manufacturing (Z. Wang et al., 2013). They include the dimer acid of hexafluoropropylene oxide (HFPO-DA), introduced into the market as its ammonium salt GenX, and 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propanoic acid, marketed as its ammonium salt ADONA. The latter has been identified mainly in river water from Germany thus far (LfU, 2019; Pan et al., 2018; Heydebreck, 2017), whereas the occurrence of HFPO-DA has already been reported worldwide, especially in river water downstream of fluoropolymer manufacturing plants or industries applying fluorochemicals in Europe (Heydebreck et al., 2015; Gebbink et al., 2017), the United States (Sun et al., 2016) and China (Heydebreck et al., 2015). A recent study showed that in addition to HFPO-DA, which is the dimer acid of HFPO, the trimer acid (HFPO-TrA) is also widely present in river water (Pan et al., 2018). Of the PFESAs, 6:2 Cl-PFESA has been used as an alternative for PFOS for the metal plating industry in China since the 1970s, marketed as its potassium salt—F-53B. In recent years, its presence in China as well as in European countries and the United States has been reported (Pan et al., 2018; S. Wang et al., 2013; Ruan et al., 2015).

In addition to replacements for long-chain PFCAs and PFSAs, emerging PFASs include legacy PFASs that have already been in use for several decades but have not yet been in focus. Among them are perfluoroalkyl phosphinic acids (PFPIAs), which are used as defoamers in pesticide formulations and wetting agents in consumer products (Z. Wang et al., 2016), as well as cyclic PFASs such as perfluoro-4-

ethylcyclohexanesulfonate (PFECHS), which is added to aircraft hydraulic fluids as an erosion inhibitor (de Silva et al., 2011).

Most of the studies discussed focus on the distribution and occurrence of emerging PFASs in the environment close to point sources and in adjacent rivers and lakes, whereas only limited data is available for PFECAs and PFESAs, PFPIAs and cyclic PFASs in the coastal and marine environment.

This study aims at investigating whether the emerging PFASs discussed are of relevance in the coastal environment of the North and Baltic Seas and if there has been a transition from legacy long-chain PFCAs and PFSAs to replacement compounds. For this, 92 surface water and 24 surface sediment samples were collected in the North and Baltic Seas and analysed for 29 PFASs. More specifically, the compounds' occurrence and composition profiles as well as their spatial distribution and potential sources were investigated. To examine the partitioning behaviour of PFASs between sediment and water, field-based partitioning coefficients were calculated. In addition, water sample extracts from the last decade were reanalysed using the current instrumental method to elucidate as to whether there has been a shift to emerging PFASs over time.

## 2. Materials and methods

### 2.1. Study area and sampling

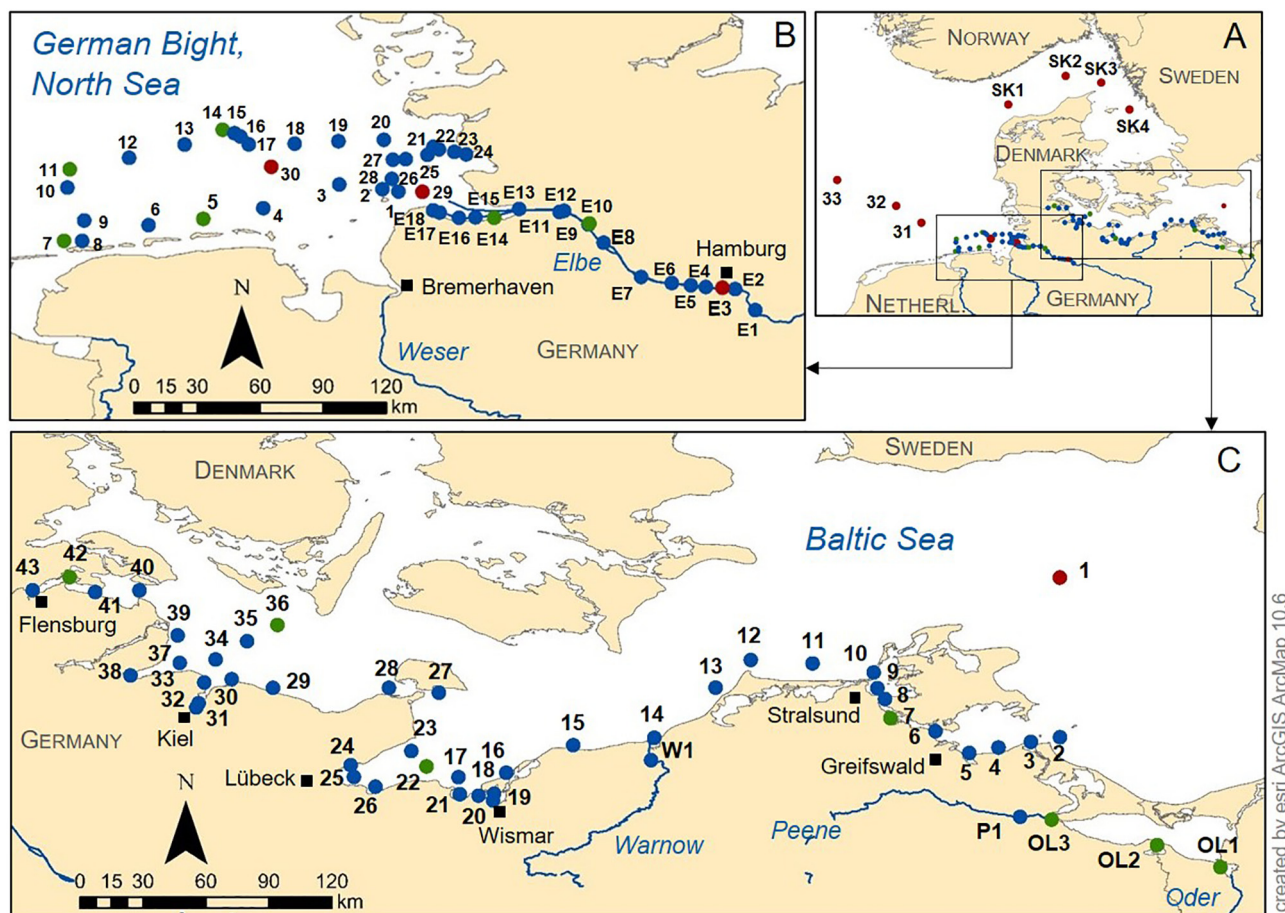
Surface water and sediment samples in coastal areas of the German Bight and the German Baltic Sea were collected during two sampling campaigns with the research vessel *Ludwig Prandtl* in June and September 2017. Additional sediment samples were taken during the *Maria S. Merian* cruise MSM50 in January 2016, covering not only coastal areas, but also open water regions of the North Sea, the Skagerrak and Kattegat as well as the Baltic Sea (see Fig. 1).

The North Sea is a North Atlantic shelf sea that connects to the Baltic Sea via the Skagerrak, the Kattegat and the Danish Straits. The semi-enclosed brackish Baltic Sea is characterised by the limited exchange with open waters and the long water residence times of approximately 30 years (Helcom, 2018). The catchment areas of the North and Baltic Seas are inhabited by approximately 184 (OSPAR Commission, 2010) and 85 million people (Helcom, 2018), respectively. Both seas are surrounded by highly industrialized countries, which include large river catchments, such as the Oder and Elbe Rivers in the study area.

Water samples were collected in 1 L polypropylene (PP) bottles 0.5 m below the surface, stored at 4 °C and processed in the lab within four weeks after sampling. Before sampling, the PP bottles were rinsed with methanol and water from the respective sampling site. Sediment samples were taken by a stainless-steel box corer or van Veen grabs. After homogenization and removal of large pieces, such as sea shells and stones, sediment samples were transferred to aluminium shells and stored at –20 °C until sample preparation. Aluminium shells were cleaned with acetone and baked at 250 °C before usage. Water temperature, salinity and pH were measured continuously by the in situ FerryBox system during the cruises (Petersen et al., 2011). The coordinates of the sampling locations and the physicochemical parameters are provided in Table A1.

### 2.2. Target analytes and chemicals

The analytical method included 29 target analytes: 11 PFCAs ( $C_4$  to  $C_{14}$ ), five PFSAs ( $C_4$ ,  $C_6$ ,  $C_7$ ,  $C_8$ ,  $C_{10}$ ), the cyclic PFAS PFECHS, six PFECAs and PFESAs (i.e. HFPO-DA, HFPO-TrA, HFPO-TeA; DONA; 6:2 and 8:2 Cl-PFESA), two PFPIAs (i.e. 6:6 PFPIA, 6:8 PFPIA) and four precursors (i.e. FOSA; 4:2 FTSA, 6:2 FTSA, 8:2 FTSA). A total of 13 mass-labelled internal standards (IS) was used, which included seven isotopically labelled PFCAs ( $^{13}C_4$ -PFBA,  $^{13}C_2$ -PFHxA,  $^{13}C_4$ -PFOA,  $^{13}C_5$ -PFNA,  $^{13}C_2$ -PFDA,  $^{13}C_2$ -PFUnDA,  $^{13}C_2$ -PFDoDA), three PFSAs ( $^{13}C_3$ -PFBS,  $^{18}O_2$ -PFHxS,  $^{13}C_4$ -PFOS), one PFECA ( $^{13}C_3$ -HFPO-DA) and two precursors



**Fig. 1.** Sampling locations A) over the entire study area, including Skagerrak and Kattegat (SK1-SK4) and open water regions of the North Sea (31–33), B) in coastal areas of the German Bight (1–30) including the Elbe River (E1–E18), C) in coastal areas of the German Baltic Sea (1–43) including the Oder Lagoon (OL1–OL3) and the Peene and Warnow Rivers (P1 and W1). Water was collected at blue stations; water and sediment at green stations; and sediment only at red stations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

( $^{13}\text{C}_2$ -6:2 FTSA and  $^{13}\text{C}_8$ -FOSA).  $^{13}\text{C}_8$ -PFOA was used as the injection standard. Detailed information on the target analytes as well as on the standards' purity and concentration is presented in Table A3. Table A4 provides information on chemicals used for sample preparation and cleaning.

### 2.3. Sample pretreatment

Water samples were filtered through glass microfiber filters (Whatman, grade GF/F, pore size 0.7  $\mu\text{m}$ , diameter 47 mm, GE Healthcare, USA), which had been heated at 450 °C over night. Wet sediment was freeze-dried prior to sample extraction (Gamma 1–16 LSCplus, Christ, Germany). Afterwards, small stones and sticks were removed with forceps and the samples were homogenized using an agate mortar and pestle. For the analysis of total organic carbon (TOC), separate sub-samples were dried to constant weight at 40 °C. TOC<sub>400</sub> values were determined in duplicates using a RC612 multiphase carbon/hydrogen/moisture determinator (LECO, USA). The method was based on dry combustion, applying a temperature ramp from 150 °C to 400 °C. The TOC content of the analysed samples ranged between 0.01% and 6.13% (Table A2).

### 2.4. Sample extraction

For PFAS analysis in 1 L water samples, weak anion exchange cartridges (Oasis WAX, 6 cc, 500 mg sorbent, 60  $\mu\text{m}$  particle size, Waters, USA) were preconditioned by 6 mL 0.1% ammonium hydroxide in methanol, 6 mL methanol and 6 mL water. Samples were spiked with

IS (3 ng each) and loaded onto the cartridges at a flow rate of 2–3 drops/s. A washing step with an 80:20 (v/v) water/methanol solution followed (Gremmel et al., 2017). To remove matrix components, especially sea salt, and to improve recovery rates for long-chain PFASs, a comparatively large volume of 15 mL of the washing solution was used per sample. After vacuum drying of the cartridges, the target compounds were eluted using 6 mL methanol and 6 mL 0.1% ammonium hydroxide in methanol. Finally, the eluates were reduced to 150  $\mu\text{L}$  under nitrogen, before 1 ng of the injection standard  $^{13}\text{C}_8$ -PFOA (10  $\mu\text{L}$  of a 100 pg/ $\mu\text{L}$  solution) and 40  $\mu\text{L}$  water (20% v/v) were added.

For sediments, the methanol- and acetic acid-based extraction method by Higgins et al. (2005) was taken as a basis. Because of the expected low concentrations of PFASs in the marine environment, it was adapted to a larger sample amount as described by Yan et al. (2015). 5 g of the freeze-dried, homogenized sediment samples were transferred to 50 mL polypropylene tubes and spiked with IS (3 ng each). 30 mL of a 1% acetic acid in water solution was added before the samples were vortexed, put into an ultrasonic bath, heated at 60 °C for 15 min and centrifuged at 3000 rpm for 5 min. The supernatant was transferred to a 125 mL HDPE bottle. Subsequently, 7.5 mL of a mixture of methanol and 1% acetic acid in water (90:10, v/v) was added to the original PP tube and the process of vortexing, ultrasonication, centrifugation and transferring the supernatant to the 125 mL HDPE bottle was repeated. This combination of acetic acid wash and methanol extraction was repeated twice for each sample. To clean and concentrate the sample extracts, an SPE extraction was performed for the pooled supernatants in the same way as for the water samples. The eluent was reduced in volume under nitrogen to 1 mL and passed through a syringe filter

(Spartan Whatman, pore size 0.2  $\mu\text{m}$ , diameter 13 mm, GE Healthcare, USA) to remove further matrix components. Afterwards, the filtered eluate was concentrated to 300  $\mu\text{L}$  and 2 ng of the injection standard  $^{13}\text{C}_8$ -PFOA (20  $\mu\text{L}$  of a 100 pg/ $\mu\text{L}$  solution) as well as 80  $\mu\text{L}$  water (20% v/v) were added.

## 2.5. Instrumental analysis

Instrumental analysis was performed by HPLC-MS/MS, using an HP 1100 LC system (Agilent Technologies, USA) coupled to an API 4000 triple quadrupole mass spectrometer (AB Sciex, USA). It was equipped with a Turbo V ion source (AB Sciex, USA), operating in negative electrospray ionisation mode. For chromatographic separation, a polar embedded reversed phase C18 separation column (Synergi Fusion-RP C18, Phenomenex, USA) was combined with a reversed phase guard column (Phenomenex, USA). As solvents for the gradient elution, 2 mM ammonium acetate aqueous solution (A) and 0.05% acetic acid in methanol (B) were used. The injection volume was 10  $\mu\text{L}$  for samples and standards, both dissolved in 80:20 (v/v) methanol/water. Detailed information on the instrumental method can be found in Tables A5 and A6.

In addition to the samples taken for this study in 2017, water sample extracts and blanks from 2007, 2011 and 2014 were reanalysed using the current instrumental method. The extracts had been stored in vials at  $-20\text{ }^\circ\text{C}$ , beginning from the first analysis onward. Before instrumental analysis, the vials were put into an ultrasonic bath for 30 min and vortexed for 5 min.

## 2.6. Quality assurance and quality control

The internal standard method was used for quantification of the target analytes. On the basis of standards prepared in 80:20 (v/v) methanol/water, a 10-point calibration curve in the range of 0 to 25 pg/ $\mu\text{L}$  was generated and measured before and after each sample batch. The linear regression model was applicable and resulted in correlation coefficients of  $r > 0.99$  for all analytes. Curves were weighted, applying a factor of  $1/x$  to improve accuracy for low concentration levels.

For PFOS and FOSA, the linear isomer and the sum of branched isomers were quantified separately versus their respective linear calibration standards. Structural isomers of other compounds like PFECHS and PFOA were not baseline-separated and consequently not quantified individually. Reported concentrations refer to the sum of the linear and branched isomers, if not stated otherwise in case of linear and branched PFOS and FOSA (L-/Br-PFOS and L-/Br-FOSA).

For most of the PFCAs, PFASs and precursors, isotopically labelled analogues were available, but for emerging PFASs from other groups of PFASs only  $^{13}\text{C}_3$ -HFPO-DA could be obtained. To assign substances without isotopically labelled analogues to structurally similar IS and to test the method performance, matrix spike recovery tests were conducted. In general, relative recovery rates for PFASs in seawater samples at a spiking level of 3 ng/L ranged from  $(73 \pm 1)\%$  to  $(117 \pm 7)\%$ , except for the long-chain compounds PFTeDA  $(54 \pm 4)\%$  and 6:8 PFPiA  $(60 \pm 2)\%$  as well as 4:2 FTSA  $(61 \pm 3)\%$ . The results for these three compounds must be considered as semiquantitative as they are most likely underestimated. Relative recoveries for PFASs in sediment samples varied between  $(80 \pm 12)\%$  to  $(120 \pm 6)\%$  at a spiking level of 0.6 ng/g dw. Results for the individual compounds as well as average recoveries for the internal standards in the actual samples are presented in Tables A7 and A8.

The results of the reanalysed sample extracts from the last decade cannot be determined quantitatively, because it is not known how the long storage period affects the target analytes and internal standards. However, peak area ratios were used for indications of trends.

To minimize background contamination, contact of the samples and standards to fluoropolymers was avoided throughout the analysis. All containers and equipment were rinsed three times with methanol

prior to usage. As instrumental blank, methanol was injected after every sixth sample. Ultrapure water and purified sea sand (Merck, Germany), baked at  $450\text{ }^\circ\text{C}$ , were used as procedural laboratory blanks for water and sediment analysis, respectively, and analysed with every batch of seven samples. Additionally, five field blanks were taken, filling sampling bottles with ultrapure water at different sampling sites and treating them as if they were samples from this step forward. No PFASs were detected in the instrumental blanks, whereas particular compounds were quantified in the procedural laboratory blanks in the pg/L and pg/g dw range, respectively (see Table A9). In the field blanks, the same PFASs as in the laboratory blanks were quantified at comparable levels. This indicates that PFASs were not introduced into the blank samples during the sampling process and transportation, but by sample preparation in the laboratory. All results were blank-corrected by subtracting the average PFAS concentration in the procedural laboratory blanks from the concentrations in the samples. For compounds present in the procedural blanks, method detection limits (MDLs) and method quantification limits (MQLs) were calculated as the mean blank values plus 3 or 10 times the standard deviation, respectively. For PFASs other than those mentioned, the MDLs and MQLs were derived from a signal-to-noise ratio of 3 or 10, observed in low-level samples or spiked matrices. MQLs were in a range of 0.0069 to 0.48 ng/L for seawater samples and 0.0065 to 0.49 ng/g dw for sediments (Table A9). Replicate samples showed standard deviations of  $<20\%$  for the single compounds in seawater triplicates ( $n = 7$ ) and sediment duplicates ( $n = 3$ ) (Table A10).

## 2.7. Data analysis

Calculation of arithmetic means and further statistical analysis was performed only for PFASs with a detection frequency  $> 50\%$ . Results  $<$  MDL were considered as zero and the calculated values between MDL and MQL were used unaltered for calculations.

Statistical analysis was performed with OriginPro 2018 (version 9.5), setting the significance level at  $\alpha = 0.05$ . Normality was tested by the Kolmogorov-Smirnov test, before further statistical analysis followed. If data was normally distributed, a Pearson correlation analysis was conducted to investigate the relationship among individual PFASs and between PFASs and physicochemical parameters. Otherwise, Spearman's correlation analysis was used. To test for significant differences in PFAS patterns, two-sample *t*-tests were conducted. If data sets did not show homogeneity of variance according to Leuvene's test, the Welch correction was applied.

Sediment-water partitioning coefficients ( $K_D$ ) [L/kg dw] were calculated by dividing the concentration of a compound in sediment [ng/kg dw] by the concentration of this compound in water [ng/L], given that the substance was detected in both the sediment and water phase of a sampling location. Organic carbon normalized sediment-water partitioning coefficients were derived from the equation  $K_{OC} = K_D \cdot 100 / \text{TOC}$  where TOC is the content of total organic carbon [%].

## 3. Results and discussion

### 3.1. PFASs in surface water

#### 3.1.1. Levels and composition profiles

Of the 29 analysed PFASs, 15 were detected in surface water from coastal areas of the German Bight and the Baltic Sea: the replacement compound HFPO-DA, the cyclic PFAS PFECHS,  $\text{C}_{4-11}$  PFCAs, PFBS, PFHxS, L-PFOS/Br-PFOS as well as the precursors 6:2 FTSA and L-FOSA/Br-FOSA (Fig. 2). Detection frequency, concentration range, mean and median of these compounds in the different sampling areas are shown in Table A11. Levels of individual PFASs at all sampling sites are given in Tables A14 to A19.

The sum of PFASs ranged from 4.7 to 7.4 ng/L in the German Bight (mean 6.0 ng/L), whereas in the Baltic Sea, levels were two to three

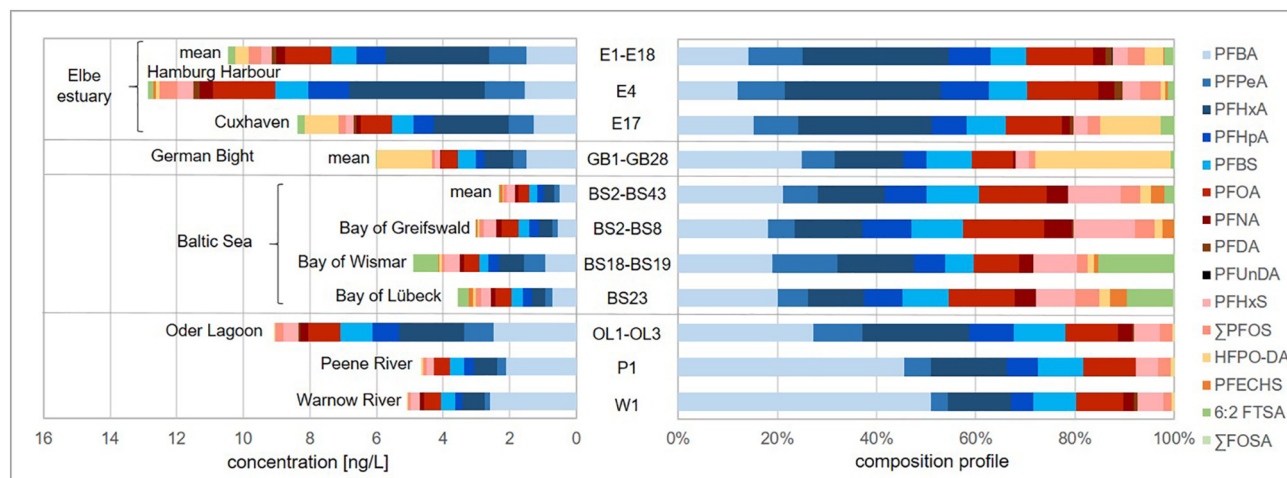


Fig. 2. Concentrations [ng/L] and composition profiles of individual PFASs over the entire study area. Short-chain PFCAs and PFASs are shown in blue; long-chain PFCAs and PFASs in red; emerging PFASs in yellow; and precursors in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

times lower, ranging from 1.6 to 5.2 ng/L (mean 2.3 ng/L). The replacement compound HFPO-DA was detected in all seawater samples along the German coastline. With a mean concentration of  $(1.6 \pm 0.3)$  ng/L, it contributed to  $\Sigma$ PFASs by  $(27 \pm 5)$  % in the German Bight and was the compound with the highest proportion. In contrast, the proportion of HFPO-DA was negligible in the Baltic Sea. In addition to HFPO-DA, the emerging cyclic compound PFECHS was detected in 86% of the seawater samples from the Baltic Sea. However, it was below the detection limit in all samples from the German Bight. The short-chain compounds PFBA, PFPeA, PFHxA, PFHpA and PFBS accounted for the sum of PFASs with about 60% and had comparable proportions in both seas. On the contrary, the long-chain compounds PFOA, PFNA, PFHxS and  $\Sigma$ PFOS had a significantly higher proportion in the Baltic Sea than in the German Bight ( $(32 \pm 4)$  % versus  $(13 \pm 2)$  %). In both water bodies, L-PFOS and Br-PFOS contributed approximately equally to  $\Sigma$ PFOS. For the precursors 6:2 FTSA and L-FOSA/Br-FOSA, detection frequencies were below 30%.

### 3.1.2. Spatial distribution and potential sources

To explain the differences between the two seas and to find indications of sources, samples from river mouths were analysed and a correlation analysis was conducted to study relationships between individual PFASs and between PFASs and physicochemical parameters.

Concentrations of the replacement compound HFPO-DA in the Elbe estuary increased towards the German Bight and showed a statistically significant positive correlation with the salt content (Pearson's  $r = 0.99$ ,  $p = 3.3 \cdot 10^{-11}$ ; see Table A22). Because fresh water from the Elbe River mixes with seawater moving in from the North Sea, salinity in the Elbe water samples increased towards the sea (0.5 to 17.8 psu). Consequently, the positive correlation between HFPO-DA and salinity in the Elbe estuary indicates that HFPO-DA enters the estuary with seawater from the North Sea and that the Elbe River is not a relevant source for HFPO-DA in the North Sea. In the investigated area of the German Bight itself, HFPO-DA was distributed homogeneously. Previous studies identified a fluoropolymer production plant as a point source in the Rhine-Meuse delta, in which PFOA has been completely replaced by HFPO-DA in fluoropolymer production since 2012 (Heydebreck et al., 2015; RIVM, 2016). River samples taken downstream from the chemical park showed HFPO-DA concentrations up to 812 ng/L in 2016 (Gebbinck et al., 2017), which is about 2000 times higher than the mean concentration in the Elbe estuary in this study (0.40 ng/L). It can be hypothesized that HFPO-DA is transported from the Rhine River to the Dutch North Sea water and from there to the German Bight by the easterly coastal current.

A positive correlation between HFPO-DA and salinity was also observed in the Baltic Sea (Pearson's  $r = 0.57$ ,  $p = 8.4 \cdot 10^{-5}$ ). In its westernmost region, the semi-enclosed Baltic Sea is connected to the North Sea via the Danish Straits, Kattegat and Skagerrak. Reflecting the growing influence of water inflow from the North Sea with a salinity of 35 psu in the Kattegat, salinity in the analysed samples from the brackish Baltic Sea increased from east (7.5 psu) to west (18.0 psu). Thus, the positive correlation between HFPO-DA and salinity indicates that the water inflow from the North Sea can be a relevant source for HFPO-DA in the Baltic Sea. Interestingly, HFPO-DA was the only compound positively correlated with salinity in the Baltic Sea (see Table A23).

The occurrence of PFECHS in the European coastal environment has not yet been reported. The compound has already been identified in the North American Great Lakes (de Silva et al., 2011); in Canadian water bodies close to Ontario airport (de Solla et al., 2012); in environmental samples from the area around Beijing airport in China (Y. Wang et al., 2016); and in Chinese coastal areas (Liu et al., 2019). Additionally, it was detected in the Devon ice cap in the High Arctic (MacInnis et al., 2017). The authors mainly explained the occurrence of PFECHS with its usage as an erosion inhibitor in aircraft hydraulic fluids, but it was also pointed out that PFECHS can be present as an impurity in POSF-based products such as aqueous film forming foams (AFFFs) for fire fighting (MacInnis et al., 2017). In this study, PFECHS was detected in one sample from the Elbe River (E4). It was taken in direct proximity to the Finkenwerder Airport and near the industrialized port of Hamburg, both considered potential sources. In addition, PFECHS was primarily detected in the eastern part of the coastline investigated (Baltic Sea samples BS2-BS32). In samples from the Oder Lagoon, as well as the Warnow and Peene Rivers, which are potential sources in this coastal area, PFECHS could not be identified. PFECHS showed a weak significant positive correlation to Br-PFOS (Pearson's  $r = 0.35$ ,  $p = 0.022$ ) and L-PFOS (Pearson's  $r = 0.49$ ,  $r = 0.0011$ ). A positive relationship could result from emissions of PFECHS present as an impurity in POSF-based products. However, PFECHS levels are in the same range as those of  $\Sigma$ PFOS, indicating that distinct emissions, for example from hydraulic fluids, can play a role as well.

In general, the semi-enclosed Baltic Sea is susceptible to accumulation of pollutants because of its limited water exchange with open waters, its shallowness and its large catchment area. As the residence time of water in the Baltic Sea is approximately 30 years, the system reacts more slowly to changes in source patterns than other water bodies (Helcom, 2018). This may explain the significantly higher proportion of long-chain PFCAs and PFASs in the investigated coastal areas of the Baltic Sea in comparison to the German Bight as well as in comparison to the inflowing Oder, Peene and Warnow Rivers. A higher proportion

of long-chain compounds was also found in Baltic Sea water in comparison to Swedish rivers (Nguyen et al., 2017). In addition to river inflow, atmospheric deposition can be a relevant source of long-chain PFASs to the Baltic Sea (Filipovic et al., 2013).

Despite the long water residence times in the Baltic Sea, the sum of PFASs is two to three times lower than in coastal areas of the North Sea. This has also been described for samples taken in 2007 and 2016 (Ahrens et al., 2010; Heydebreck, 2017) and can be explained by the continuous input of PFASs from the Rhine-Meuse delta to the North Sea related to point sources, whereas diffuse sources are dominant in the Baltic Sea region.

The riverine influences on PFCA and PFSA levels can be clearly seen in both study areas. In the Baltic Sea, the sum of PFASs and the proportion of short-chain compounds was significantly higher in the Bay of Greifswald (BS2–BS8), which is close to the Oder Lagoon, than in the western portion of the study area. In the other samples from the Baltic Sea (BS9–BS43), PFASs were homogeneously distributed, with exception of the three samples BS18, BS19 and BS23, taken in the Bay of Wismar and the Bay of Lübeck. In these samples, the precursor compound 6:2 FTSA was comparatively high in proportion (17%, 12% and 9%, respectively). This observation suggests a local source in this area, such as the effluents of a wastewater treatment plant or the use of AFFFs, which typically contain 6:2 FTSA and related compounds as substitutes for PFOS.

In the German Bight, levels of PFCAs and PFSAs generally decreased with increasing distance to the Elbe estuary and the coast, with exception of the short-chain compounds PFBS and PFBA as well as the replacement compound HFPO-DA. These differences were also reflected in Pearson correlations as all compounds showed significant positive correlations to each other ( $r > 0.67$ ,  $p < 0.05$ ) and significant negative relationships with salinity ( $r < -0.74$ ,  $p < 0.05$ ), with exception of PFBS, PFBA and HFPO-DA (Table A24). This points to different sources (e.g. the Rhine River) or to a different environmental behaviour (e.g. the higher mobility of short-chain compounds).

### 3.2. PFASs in surface sediment

#### 3.2.1. Levels and composition profiles

In surface sediment from coastal areas of the German Bight and the Baltic Sea as well as from the Kattegat and Skagerrak, 16 PFASs were detected: 6:6 and 6:8 PFPiAs, PFBA and C<sub>6–14</sub> PFCAs, PFHxS, L-PFOS/Br-PFOS, and the precursors 6:2 FTSA and L-FOSA/Br-FOSA (Fig. 3). Detection frequency, concentration range, mean and median are shown in Tables A12 and A13. Additionally, levels of individual PFASs at all sampling sites are given in Tables A20 to A21.

The spatial variation of PFASs in sediment was more variable than for water samples with regard to concentration levels and composition. Over the entire study area, the sum of PFASs ranged from 0.018 ng/g dw to 2.6 ng/g dw (mean: 0.64 ng/g dw, median: 0.36 ng/g dw). As mean values were skewed by single samples with high concentrations, median values are used to describe central tendencies for sediment samples in the following. The median concentration of  $\sum$ PFASs in the German Bight was significantly lower than in the Skagerrak/Kattegat area and the Baltic Sea (0.12 ng/g dw versus 1.0 ng/g dw and 0.72 ng/g dw, respectively). However, the highest concentrations were found for sample GB7 from the North Sea, taken close to the East Frisian island of Norderney, and sample E3, taken in the Elbe estuary at Hamburg Harbour. Of the emerging PFASs, 6:6 and 6:8 PFPiAs were identified in coastal sediment for the first time. They were detected in 8% and 25% of the sediment samples, respectively. Concentrations of 6:6 PFPiA were always below MQL, whereas 6:8 PFPiA was quantified in a range of 0.013 ng/g dw to 0.052 ng/g dw, contributing to the sum of PFASs with 1% to 8%. Regarding PFCAs and PFSAs, L-PFOS was the dominant compound over the entire study area with a median concentration of 0.085 ng/g dw and a proportion of (20 ± 12)% of  $\sum$ PFASs. In contrast to L-PFOS, with a high detection frequency of 83%, Br-PFOS was detected

in only 17% of the samples. In addition to L-PFOS, the long-chain C<sub>9</sub>–C<sub>14</sub> PFCAs (67% to 100%) as well as the short-chain compound PFBA (67%) were frequently detected. Due to comparatively high blanks, PFOA had a detection frequency of only 42%. C<sub>9</sub>–C<sub>11</sub> PFCAs and PFBA contributed to the sum of PFASs with 10% to 17% each. Of the precursors, L-FOSA and Br-FOSA were detected in 75% and 63% of the samples, accounting for the sum of PFASs with an average proportion of (6 ± 4)%. 6:2 FTSA was detected only in sample E3 from the Port of Hamburg with a concentration of 0.40 ng/g dw and a proportion of 18%.

#### 3.2.2. Spatial distribution and potential sources

The emerging compounds 6:6 PFPiA and 6:8 PFPiA were identified mainly in areas with potential inputs from industrial sources, such as Hamburg Harbour (E3) and Flensburg Firth (BS43), as well as in known sedimentation areas, such as the Skagerrak (SK4), the Helgoland mud area in the North Sea (GB30) and the Arkona Basin in the Baltic Sea (BS1). Although there has been an increasing interest in PFPiAs in recent years, PFPiAs have not yet been reported in the coastal or marine environment. In Germany, the use of pesticide formulations containing PFPiAs and perfluoroalkyl phosphonic acids (PFPAAs) as antifoaming agents, such as Fluowet PL80-B and Masurf FS-780, is still permitted in contrast to the United States (BVL, 2018; US EPA, 2006b). The use of these products on the German mainland might explain the occurrence of PFPiAs in different areas of the investigated coastlines. However, quantified levels of PFPiAs were generally about an order of magnitude lower than those of L-PFOS. These lower levels might be explained by lower production volumes and releases, as well as degradation or biotransformation of PFPiAs yielding to perfluoroalkyl phosphonic acids (PFPAAs) (Z. Wang et al., 2016).

In addition to source-specific contributions, sediment characteristics can play an important role for the sorption of PFASs (Higgins and Luthy, 2006; Ahrens et al., 2011). This is reflected in the spatial distribution of PFCAs and PFSAs in this study. Over the entire study area, correlation analysis showed no significant relationship between the TOC content and levels of individual PFASs with the exception of PFNA (Spearman's  $r = 0.70$ ,  $p = 1.4 \cdot 10^{-4}$ ). Disregarding the four samples with the highest TOC contents (samples BS22, BS7, BS1 and E10; TOC 4.57% to 6.13%), concentrations of all PFCAs and PFSAs showed a significant positive relationship to the TOC content (Pearson's  $r > 0.5$ ,  $p < 0.05$ ). In particular, the long-chain compounds PFNA, PFUnDA, PFTrDA, L-PFOS and  $\sum$ PFASs were strongly correlated with TOC (Pearson's  $r > 0.7$ ,  $p < 0.001$ ) (Table A25). This is in accordance with the results from other field studies in the coastal environment (Zhao et al., 2015; Theobald et al., 2012). In addition to TOC, sediment characteristics that were not considered in this study may play a role for PFAS sorption, especially for short-chain compounds and the four samples with the highest TOC contents. They include the black carbon content of the sediment, grain size, density, pH and metal ion concentrations (Munoz et al., 2017; Ahrens et al., 2011; Higgins and Luthy, 2006).

Sediment samples from the German Bight were mostly sandy and their TOC contents were generally lower than those of the more muddy samples from the Baltic Sea and the Skagerrak/Kattegat area. In addition, sediment processes in the North Sea are strongly influenced by tides and waves and there is a continuous redistribution with only a few depositional areas, such as the Helgoland mud area and the Skagerrak/Kattegat (Hebbeln et al., 2003). These differences in sediment characteristics and processes can serve as an explanation for the significantly lower  $\sum$ PFASs in sediment from the German Bight in comparison to samples from the Baltic Sea and Skagerrak/Kattegat. Showing the highest concentrations in this study, sample GB7, which was taken close to the East Frisian island of Norderney in the German Bight, was an exception ( $\sum$ PFASs: 2.6 ng/g dw). In contrast to other samples from the North Sea, PFHxA, PFHpA, PFOA could be detected in this sample, pointing to a local source. Comparatively high concentrations ( $\sum$ PFASs: 2.2 ng/g dw) were also found in sample E3 from the Elbe estuary, taken close to the Port of Hamburg in the Elbe River. It was the

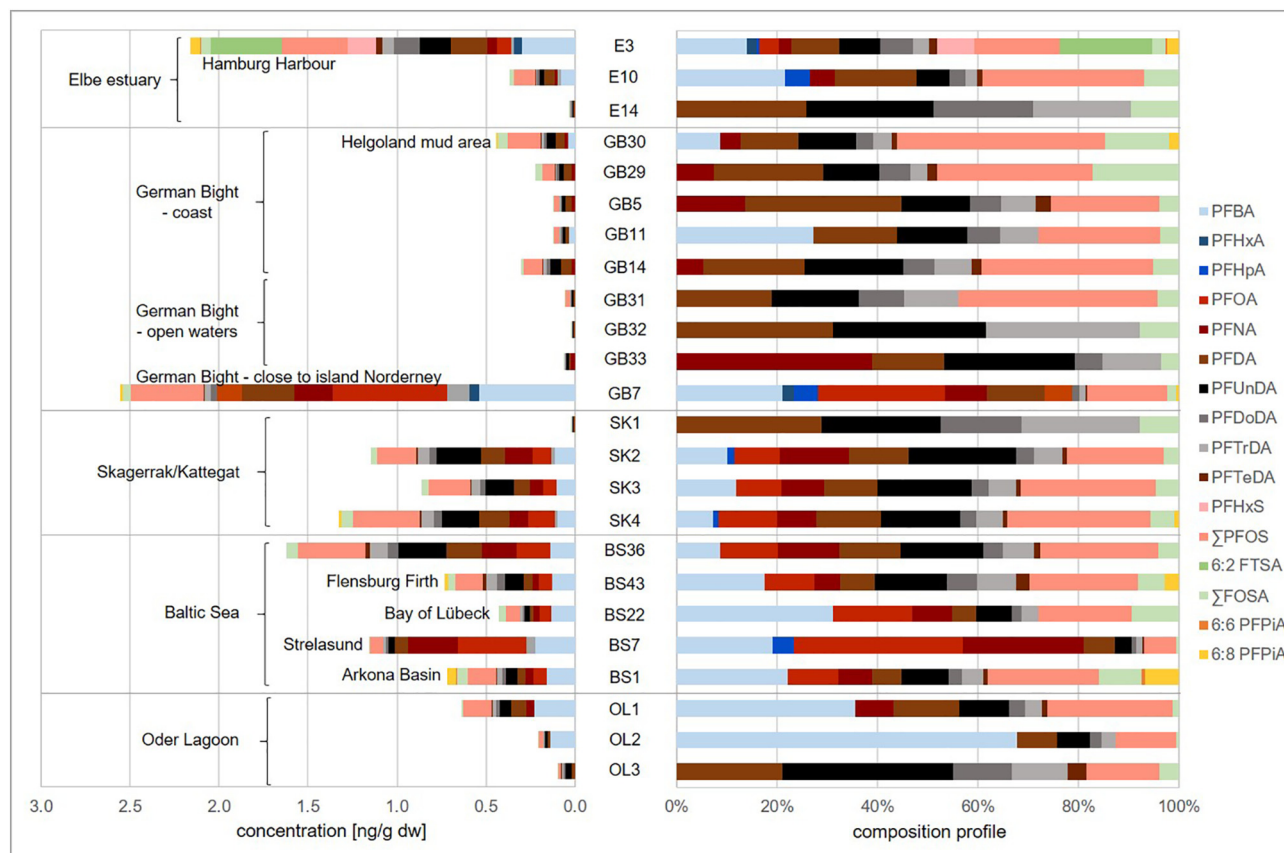


Fig. 3. Concentrations [ng/g dw] and composition profiles of individual PFASs in surface sediment samples over the entire study area.

only sampling location where PFHxS and the precursor 6:2 FTSA were identified. Together with the presence of the precursors L-FOSA and Br-FOSA, this is an indication of local inputs.

### 3.3. Partitioning of PFASs between sediment and water

The emerging PFASs identified in this study were detected either in the sediment phase or in the water phase. HFPO-DA was identified only in water samples while its predecessor PFOA occurred in both matrices. Lower sorption to sediment of HFPO-DA than of PFOA is supported by laboratory experiments showing that HFPO-DA is less adsorbable to powdered activated carbon than its predecessor PFOA (Sun et al., 2016). Additionally, modelling results by Gomis et al. (2015) predicted a more hydrophilic behaviour of HFPO-DA than of PFOA, resulting from the smaller molecule size, which requires less energy for cavity formation among the strongly-bonded water molecules. The cyclic compound PFECBS was also detected only in the water phase although having eight perfluorinated moieties like L-PFOS, which was one of the dominant compounds in sediment over the entire study area. In an airport-impacted ecosystem, in which levels of PFECBS in surface water were two to four orders of magnitude higher than in this study, PFECBS had a lower detection frequency in sediment samples as well. The field-based sediment-water partitioning coefficients calculated by the authors of that study indicate a lower sorption affinity for solid environmental matrices of cyclic PFASs compared to linear and branched PFASs (Y. Wang et al., 2016). The lower hydrophobicity of linear PFASs in comparison to cyclic PFASs is underlined by the retention times on C18 columns, which is lower for PFECBS (11.7 min in this study) than for L-PFOS (12.8 min). The presence of 6:6 PFPiA and 6:8 PFPiA in sediment is consistent with laboratory sorption experiments, which indicated that PFPiAs would preferentially be retained by environmentally solid phases, as their partitioning coefficients are comparable to those

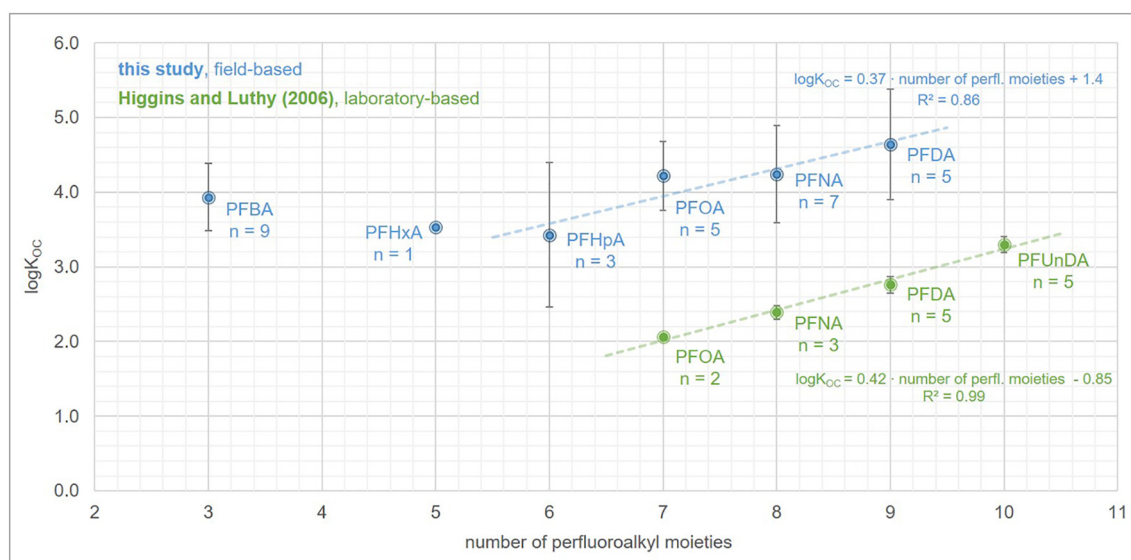
of the long-chain compounds PFUnDA and PFDS (Lee and Mabury, 2017).

For PFCAs, PFASs and FOSA, which were detected in both the sediment and water phase, sediment-water partitioning coefficients were calculated and compared to values reported in literature (Table A26). To reduce the influence of sediment characteristics, the partitioning coefficients  $\log K_D$  were normalized to organic carbon ( $\log K_{OC}$ ).

For PFCAs, an increase of the  $\log K_{OC}$  values with increasing number of perfluoroalkyl moieties could be observed from PFHpA to PFDA ( $R^2 = 0.86$ , see Fig. 4). This trend is consistent with field studies conducted in different areas (Zhu et al., 2014; Ahrens et al., 2010; Habibullah-Al-Mamun et al., 2016) and a laboratory study by Higgins and Luthy (2006). It can be explained by the increase of hydrophobicity with an increasing number of  $CF_2$  units and underlines the importance of van der Waals interactions in PFAS sorption.

Despite its small number of perfluoroalkyl moieties, PFBA had a comparatively high  $\log K_{OC}$  value (see Fig. 4). That the short-chain compounds PFBA and PFPeA do not follow the chain-length dependent trend observed for PFCAs with a larger chain length was initially found in batch sorption experiments with soils (Guelfo and Higgins, 2013) and was also reported in other field studies (Zhu et al., 2014; Habibullah-Al-Mamun et al., 2016). These findings indicate that mechanisms other than van der Waals interactions may play an important role for the water-sediment partitioning of short-chain compounds; for instance, ion exchange or the interaction with sorptive sites that are not available to larger molecules due to steric effects (Guelfo and Higgins, 2013).

Additionally, differences in the partitioning of isomers could be observed. Linear and branched PFOS were approximately equal in proportion in the water phase, whereas L-PFOS was the predominant isomer in sediment. This is reflected in the  $\log K_{OC}$  value, which is approximately one log unit higher for L-PFOS (5.2) than for Br-PFOS (3.9). A similar



**Fig. 4.** Sediment/water partitioning coefficients  $\log K_{OC}$  for individual PFCAs in this study in comparison to a laboratory study by Higgins and Luthy (2006). Linear regression lines were calculated for PFCAs from PFHpA to PFDA (this study) and from PFOA to PFUnDA (Higgins and Luthy, 2006), respectively. *n* gives the number of sampling locations at which the compound was detected in both the sediment and water phase and for which partitioning coefficients were calculated.

trend was observed for L-FOSA and Br-FOSA (5.5 vs. 4.4). Higher sediment-water partitioning coefficients for the linear than for the branched isomers of PFOS and FOSA have also been reported for the Liao River Basin and Taihu Lake in China (Chen et al., 2015). A possible explanation is the higher hydrophobicity of the linear isomers, reflected in the higher retention times using a reversed phase C18 column. Moreover, isomer-specific biotransformation of precursors might play a role in the differences between linear and branched isomers (Benskin et al., 2010).

$\log K_{OC}$  values in the field studies discussed were generally higher than in laboratory studies. In this study, they were approximately two log units higher than in the laboratory study by Higgins and Luthy (2006) (see Fig. 4). This variation can be attributed to the different experimental conditions. In contrast to laboratory experiments, an equilibrium between sediment and the overlying water column is rarely achieved in the dynamic coastal ecosystem. The water phase reacts faster to changes in source patterns, which include decreasing trends of long-chain PFASs over the last decade (see 3.4). The slower reaction of the sediment phase might explain higher  $\log K_{OC}$  values of the long-chain PFCAs and PFASs in current field studies than in laboratory studies. Moreover, additional environmental factors and sediment characteristics that were not considered in this field study can influence the sediment-water partitioning process.

### 3.4. Temporal trends

In surface water from coastal areas of the German Bight, decreasing levels of the long-chain compound L-PFOS were observed, from a median concentration of 1.3 ng/L in 2007 (Ahrens et al., 2009) to 0.043 ng/L in 2017 (this study). For PFOA and the short-chain compound PFBS, a downward trend was observed as well (see Table 1). It can be assumed that these decreasing trends in the German Bight are effects of the industrial transition that has been taking place in Europe since the 2000s, including the phase-out of long-chain PFCAs and PFASs and the shift to replacement compounds such as HFPO-DA.

When analytical standards became available, HFPO-DA was analysed for the first time in German Bight samples collected in 2014. In those samples, HFPO-DA had already been one of the dominant PFASs (Heydebreck et al., 2015). To investigate whether there has been a shift to HFPO-DA over time, stored sample extracts and blanks from 2007, 2011 and 2014 were reanalysed using the current

instrumental method. All samples were taken in the German Bight, within the area of the East Frisian Islands, close to the coastline. The blanks and the sample extract from 2007 showed no peak for HFPO-DA, but the compound could be detected in the sample extract from 2011. At that time, replacement compounds for long-chain PFCAs and PFASs had not yet been in focus and analytical standards were not available. From 2011 to 2014, the peak area of HFPO-DA strongly increased in relation to the peak area of its predecessor PFOA, changing the peak area ratio from 0.1:1.0 in 2011 to 0.8:1.0 in 2014 and further to 1.1:1.0 in 2017 (this study) (see chromatograms in Fig. A1). This is consistent with the information that the fluoropolymer manufacturing plant in the Rhine-Meuse delta, which is assumed to be the major source of HFPO-DA in the German Bight, completely replaced PFOA with HFPO-DA from 2012 onward (RIVM, 2016).

In the investigated coastal areas of the Baltic Sea, the levels of L-PFOS, PFOA and PFBS in seawater also showed downward trends, but these were not as clear as in the German Bight (see Table 1). A slower reaction of the Baltic Sea in comparison to the North Sea can be explained by the long residence times of water in the Baltic Sea and the dominance of diffuse sources. This is underlined by the results for the sediment samples. In the German Bight, median concentrations of L-PFOS decreased from 0.14 ng/g dw in 2004 (Theobald et al., 2012) to 0.029 ng/g dw in 2017 (this study). As for the water samples, the trend was not as clear in the western Baltic Sea with a median value of 0.27 ng/g dw in 2004 and 0.15 ng/g dw in 2017.

## 4. Conclusion

The spatial distribution and partitioning of 29 PFASs was analysed in surface water and sediment from coastal areas of the North and Baltic Seas. The analytical method included 11 PFCAs, five PFASs and four precursors as well as emerging PFASs from different sub-classes, among them six per- and polyfluoroether carboxylic and sulfonic acids (PFECAs and PFESAs), two perfluoroalkyl phosphinic acids (PFPIAs) and the cyclic compound perfluoro-4-ethylcyclohexanesulfonate (PFECHS).

In North Sea surface water, levels of the ether-based replacement compound HFPO-DA were approximately three times higher than those of its predecessor PFOA. With a mean concentration of  $(1.6 \pm 0.3)$  ng/L, it contributed to  $\sum$ PFASs by  $(27 \pm 5)\%$  and was the compound with the highest proportion. In addition to HFPO-DA, the emerging cyclic compound PFECHS was detected in 86% of the seawater



**Table 1**  
Comparison of PFBS, L-PFOS and PFOA levels in this study to previous studies in the same investigation areas.

Location	Reference	Year	PFBS	L-PFOS	PFOA
			Range (median) [ng/L]		
Surface water					
German Bight	[1]	2007	3.4–18 (5.4)	0.69–4.0 (1.3)	2.7–7.8 (3.7)
	This study	2017	0.44–0.72 (0.53)	0.020–0.077 (0.043)	0.27–0.71 (0.51)
Baltic Sea	[2]	2007	0.26–0.88 (0.57)	<MDL–0.35 (0.23)	0.25–4.55 (1.30)
	This study	2017	0.15–0.43 (0.24)	<MQL–0.082 (0.040)	0.20–0.70 (0.27)
Location	Reference	Year	PFBS	L-PFOS	PFOA
Surface sediment					
German Bight	[3]	2004	<MQL	0.032–2.1 (0.14) <sup>a</sup>	0.079–1.6 (0.14)
	This study	2017	<MDL	<MDL–0.39 (0.029)	<MDL–0.65 (<MDL)
Baltic Sea	[3]	2004	<MQL	0.021–0.56 (0.27) <sup>a</sup>	0.061–0.68 (0.12)
	This study	2017	<MDL	0.074–0.38 (0.15)	<MQL–0.39 (0.073)

[1] Ahrens et al. (2009) - [2] Ahrens et al. (2010) - [3] Theobald et al. (2012).

<sup>a</sup> PFOS values reported in Theobald et al. (2012) generally include a portion of 18% branched isomers (Theobald et al., 2007). This was subtracted to obtain the values for L-PFOS given in the table.

samples from the Baltic Sea in concentrations up to 0.14 ng/L. In sediment, 6:6 and 6:8 PFPIAs were identified close to potential industrial inputs and in sedimentation areas.

The shift to the replacement compound HFPO-DA as one of the dominant PFASs in surface water from the German Bight shows changes in pollution levels as a consequence of action taken by regulatory authorities and industry aiming to restrict long-chain PFASs. Environmental exposure to controversial replacements such as HFPO-DA demonstrates the necessity to evaluate these substances in regard to future regulations.

The occurrence of HFPO-DA in samples from periods when fluorinated alternatives had not yet been in focus shows the limitations of target analysis focussing on a predefined scope of well-known PFASs. Moreover, the detection of PFECHS and PFPIAs as “overlooked” PFASs that have already been in use for decades underlines the importance of new analytical approaches aimed at addressing the unknown pool of PFASs. These include the total oxidizable precursor assay to estimate the amount of unknown precursors in a sample (Houtz and Sedlak, 2012), but also non-target and suspect screening strategies to identify novel PFASs of relevance.

### CRedit authorship contribution statement

**Hanna Joerss:** Conceptualization, Methodology, Validation, Investigation, Writing - original draft. **Christina Apel:** Writing - review & editing. **Ralf Ebinghaus:** Supervision, Conceptualization, Writing - review & editing.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.05.363>.

### References

3M, 2000. Letter to US EPA, Re: Phase-out Plan for POSF-Based Products (226-0600). US EPA Administrative Record. vol. 226 pp. 1–11.

- Ahrens, L., Felizeter, S., Ebinghaus, R., 2009. Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight. *Chemosphere* 76 (2), 179–184. <https://doi.org/10.1016/j.chemosphere.2009.03.052>.
- Ahrens, L., Gerwinski, W., Theobald, N., Ebinghaus, R., 2010. Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface water. *Mar. Pollut. Bull.* 60 (2), 255–260. <https://doi.org/10.1016/j.marpolbul.2009.09.013>.
- Ahrens, L., Yeung, L.W., Taniyasu, S., Lam, P.K., Yamashita, N., 2011. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment. *Chemosphere* 85 (5), 731–737. <https://doi.org/10.1016/j.chemosphere.2011.06.046>.
- Benskin, J.P., Yeung, L.W.Y., Yamashita, N., Taniyasu, S., Lam, P.K.S., Martin, J.W., 2010. Perfluorinated acid isomer profiling in water and quantitative assessment of manufacturing source. *Environ. Sci. Technol.* 44 (23), 9049–9054. <https://doi.org/10.1021/es102582x>.
- BRS Secretariat, 2017. Secretariat of the Basel, Rotterdam and Stockholm Conventions. The 16 new POPs. <http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-PUB-Brochure-16NewPOPs-201706.English.pdf>, Accessed date: 1 May 2019.
- BRS Secretariat, 2019. Secretariat of the Basel, Rotterdam and Stockholm Conventions. POPRC recommendations for listing chemicals – chemicals under review. <http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx>, Accessed date: 3 February 2019.
- Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., van Leeuwen, S.P., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr. Environ. Assess. Manag.* 7 (4), 513–541. <https://doi.org/10.1002/ieam.258>.
- BVL, 2018. German Federal Office of Consumer Protection and Food Safety. Beistoffe in zugelassenen Pflanzenschutzmitteln. [https://www.bvl.bund.de/SharedDocs/Downloads/04\\_Pflanzenschutzmittel/zul\\_info\\_liste\\_beistoffe.html?nn=1489180](https://www.bvl.bund.de/SharedDocs/Downloads/04_Pflanzenschutzmittel/zul_info_liste_beistoffe.html?nn=1489180), Accessed date: 6 March 2019 (in German).
- Chen, X., Zhu, L., Pan, X., Fang, S., Zhang, Y., Yang, L., 2015. Isomeric specific partitioning behaviors of perfluoroalkyl substances in water dissolved phase, suspended particulate matters and sediments in Liao River Basin and Taihu Lake, China. *Water Res.* 80, 235–244. <https://doi.org/10.1016/j.watres.2015.04.032>.
- de Silva, A.O., Spencer, C., Scott, B.F., Backus, S., Muir, D.C.G., 2011. Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the Great Lakes of North America. *Environ. Sci. Technol.* 45 (19), 8060–8066. <https://doi.org/10.1021/es200135c>.
- de Solla, S.R., De Silva, A.O., Letcher, R.J., 2012. Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada. *Environ. Int.* 39 (1), 19–26. <https://doi.org/10.1016/j.envint.2011.09.011>.
- ECHA, 2019. European Chemicals Agency. Candidate list of substances of very high concern for authorisation. <https://echa.europa.eu/candidate-list-table>, Accessed date: 5 March 2019.
- Filipovic, M., Berger, U., McLachlan, M.S., 2013. Mass balance of perfluoroalkyl acids in the Baltic Sea. *Environ. Sci. Technol.* 47 (9), 4088–4095. <https://doi.org/10.1021/es400174y>.
- Gebbink, W.A., van Asseldonk, L., van Leeuwen, S.P.J., 2017. Presence of emerging per- and polyfluoroalkyl substances (PFASs) in river and drinking water near a fluorochemical production plant in the Netherlands. *Environ. Sci. Technol.* 51 (19), 11057–11065. <https://doi.org/10.1021/acs.est.7b02488>.
- Gomis, M.I., Wang, Z., Scheringer, M., Cousins, I.T., 2015. A modeling assessment of the physicochemical properties and environmental fate of emerging and novel per- and polyfluoroalkyl substances. *Sci. Total Environ.* 505, 981–991. <https://doi.org/10.1016/j.scitotenv.2014.10.062>.
- Gremmel, C., Frömel, T., Knepper, T.P., 2017. HPLC-MS/MS methods for the determination of 52 perfluoroalkyl and polyfluoroalkyl substances in aqueous samples. *Anal. Bioanal. Chem.* 409 (6), 1643–1655. <https://doi.org/10.1007/s00216-016-0110-z>.

- Guelfo, J.L., Higgins, C.P., 2013. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol.* 47 (9), 4164–4171. <https://doi.org/10.1021/es3048043>.
- Habibullah-Al-Mamun, M., Ahmed, M.K., Raknuzzaman, M., Islam, M.S., Negishi, J., Nakamichi, S., Masunaga, S., 2016. Occurrence and distribution of perfluoroalkyl acids (PFAAs) in surface water and sediment of a tropical coastal area (Bay of Bengal coast, Bangladesh). *Sci. Total Environ.* 571, 1089–1104. <https://doi.org/10.1016/j.scitotenv.2016.07.104>.
- Hebbeln, D., Scheurle, C., Lamy, F., 2003. Depositional history of the Helgoland mud area, German Bight, North Sea. *Geo-Mar. Lett.* 23 (2), 81–90. <https://doi.org/10.1007/s00367-003-0127-0>.
- HELCOM, Baltic Marine Environment Protection Commission, 2018. State of the Baltic Sea – Second HELCOM Holistic Assessment 2011–2016. *Baltic Sea Environment Proceedings*. p. 155.
- Heydebreck, F., 2017. Per- and Polyfluoroalkyl Substances in the Environment - Shifting Toward Fluorinated Alternatives?. Dissertation. University of Hamburg
- Heydebreck, F., Tang, J., Xie, Z., Ebinghaus, R., 2015. Alternative and legacy perfluoroalkyl substances: differences between European and Chinese river/estuary systems. *Environ. Sci. Technol.* 49 (14), 8386–8395. <https://doi.org/10.1021/acs.est.5b01648>.
- Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* 40 (23), 7251–7256. <https://doi.org/10.1021/es061000n>.
- Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* 39 (11), 3946–3956. <https://doi.org/10.1021/es048245p>.
- Houtz, E.F., Sedlak, D.L., 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ. Sci. Technol.* 46 (17), 9342–9349. <https://doi.org/10.1021/es302274g>.
- Kissa, E., 2001. Fluorinated Surfactants and Repellents. 2nd edition. Marcel Dekker, New York.
- Lee, H., Mabury, S.A., 2017. Sorption of perfluoroalkyl phosphonates and perfluoroalkyl phosphinates in soils. *Environ. Sci. Technol.* 51 (6), 3197–3205. <https://doi.org/10.1021/acs.est.6b04395>.
- LFU; Bavarian Environment Agency, 2019. Per- und polyfluorierte Chemikalien in Bayern – Untersuchungen 2006–2018. [https://www.bestellen.bayern.de/application/applstarter?APPL=eshop&DIR=eshop&ACTIONxSETVAL\(artdtl.htm,APGXNODENR:200594,AAARTxNR:lfu\\_all\\_00153,AAARTxNODENR:353133,USERxBODYURL:artdtl.htm,KATALOG:StMUG,AKATxNAME:StMUG,ALLE:x\)=X](https://www.bestellen.bayern.de/application/applstarter?APPL=eshop&DIR=eshop&ACTIONxSETVAL(artdtl.htm,APGXNODENR:200594,AAARTxNR:lfu_all_00153,AAARTxNODENR:353133,USERxBODYURL:artdtl.htm,KATALOG:StMUG,AKATxNAME:StMUG,ALLE:x)=X), Accessed date: 15 March 2019 (in German).
- Liu, Y., Zhang, Y., Li, J., Wu, N., Li, W., Niu, Z., 2019. Distribution, partitioning behavior and positive matrix factorization-based source analysis of legacy and emerging polyfluorinated alkyl substances in the dissolved phase, surface sediment and suspended particulate matter around coastal areas of Bohai Bay, China. *Environ. Pollut.* 246, 34–44. <https://doi.org/10.1016/j.envpol.2018.11.113>.
- MacInnis, J.J., French, K., Muir, D.C.G., Spencer, C., Criscitiello, A., De Silva, A.O., Young, C.J., 2017. Emerging investigator series: a 14-year depositional ice record of perfluoroalkyl substances in the High Arctic. *Environ. Sci. Process Impacts* 19 (1), 22–30. <https://doi.org/10.1039/C6EM00593D>.
- Munoz, G., Budzinski, H., Labadie, P., 2017. Influence of environmental factors on the fate of legacy and emerging per- and polyfluoroalkyl substances along the salinity/turbidity gradient of a macrotidal estuary. *Environ. Sci. Technol.* 51 (21), 12347–12357. <https://doi.org/10.1021/acs.est.7b03626>.
- Nguyen, M.A., Wiberg, K., Ribeli, E., Josefsson, S., Futter, M., Gustavsson, J., Ahrens, L., 2017. Spatial distribution and source tracing of per- and polyfluoroalkyl substances (PFASs) in surface water in Northern Europe. *Environ. Pollut.* 220 (Part B), 1438–1446. <https://doi.org/10.1016/j.envpol.2016.10.089>.
- OSPAR Commission, 2010. Quality Status Report 2010. OSPAR Commission, London.
- Pan, Y., Zhang, H., Cui, Q., Sheng, N., Yeung, L.W.Y., Sun, Y., Dai, J., 2018. Worldwide distribution of novel perfluoroether carboxylic and sulfonic acids in surface water. *Environ. Sci. Technol.* 52 (14), 7621–7629. <https://doi.org/10.1021/acs.est.8b00829>.
- Petersen, W., Schroeder, F., Bockelmann, F.D., 2011. FerryBox - application of continuous water quality observations along transects in the North Sea. *Ocean Dynam* 61 (10), 1541–1554. <https://doi.org/10.1007/s10236-011-0445-0>.
- Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* 40 (1), 32–44. <https://doi.org/10.1021/es0512475>.
- RIVM; Netherlands National Institute for Public Health and the Environment, 2016. Evaluation of Substances Used in the GenX Technology by Chemours, Dordrecht. RIVM Letter Report 2016-0174.
- Ruan, T., Lin, Y., Wang, T., Liu, R., Jiang, G., 2015. Identification of novel polyfluorinated ether sulfonates as PFOS alternatives in municipal sewage sludge in China. *Environ. Sci. Technol.* 49 (11), 6519–6527. <https://doi.org/10.1021/acs.est.5b01010>.
- Scheringer, M., Trier, X., Cousins, I.T., de Voogt, P., Fletcher, T., Wang, Z., Webster, T.F., 2014. Helsingor statement on poly- and perfluorinated alkyl substances (PFASs). *Chemosphere* 114, 337–339. <https://doi.org/10.1016/j.chemosphere.2014.05.044>.
- Sun, M., Arevalo, E., Strynar, M.J., Lindstrom, A.B., Richardson, M., Kearns, B., Knappe, D.R.U., 2016. Legacy and emerging perfluoroalkyl substances are important drinking water contaminants in the Cape Fear River watershed of North Carolina. *Environ. Sci. Technol. Lett.* 3 (12), 415–419. <https://doi.org/10.1021/acs.estlett.6b00398>.
- Theobald, N., Gerwinski, W., Caliebe, C., Heerich, M., 2007. Development and Validation of a Method for the Determination of Polyfluorinated Organic Substances in Sea Water, Sediments and Biota; Occurrence of These Compounds in the North and Baltic Seas. UBA-Texte 41/2007 (ISSN 1862-4804 (in German)).
- Theobald, N., Caliebe, C., Gerwinski, W., Hühnerfuss, H., Lepom, P., 2012. Occurrence of perfluorinated organic acids in the North and Baltic Seas. Part 2: distribution in sediments. *Environ. Sci. Pollut. R.* 19 (2), 313–324. <https://doi.org/10.1007/s11356-011-0559-4>.
- US EPA, 2006a. United States Environmental Protection Agency, 2010/15 PFOA Stewardship Program. <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/and-polyfluoroalkyl-substances-pfas-under-tsca#tab-3>, Accessed date: 4 February 2019.
- US EPA, 2006b. United States Environmental Protection Agency, Inert ingredient; revocation of the tolerance exemption of mono- and bis-(1H, 1H, 2H, 2H-perfluoroalkyl) phosphates where the alkyl group is even numbered and in the C6–C12 range; final rule. *Fed. Regist.* 71 (153), 45408–45411.
- Wang, Z., Cousins, I.T., Scheringer, M., Hungerbühler, K., 2013a. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCA), perfluoroalkane sulfonic acids (PFSA) and their potential precursors. *Environ. Int.* 60, 242–248. <https://doi.org/10.1016/j.envint.2013.08.021>.
- Wang, S., Huang, J., Yang, Y., Hui, Y., Ge, Y., Larssen, T., Harman, C., 2013b. First report of a Chinese PFOS alternative overlooked for 30 years: its toxicity, persistence, and presence in the environment. *Environ. Sci. Technol.* 47 (18), 10163–10170. <https://doi.org/10.1021/es401525n>.
- Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K., 2014. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part I: production and emissions from quantifiable sources. *Environ. Int.* 70, 62–75. <https://doi.org/10.1016/j.envint.2014.04.013>.
- Wang, Z., Cousins, I.T., Berger, U., Hungerbühler, K., Scheringer, M., 2016a. Comparative assessment of the environmental hazards of and exposure to perfluoroalkyl phosphonic and phosphinic acids (PFPA and PFPIA): current knowledge, gaps, challenges and research needs. *Environ. Int.* 89–90, 235–247. <https://doi.org/10.1016/j.envint.2016.01.023>.
- Wang, Y., Vestergren, R., Shi, Y., Cao, D., Xu, L., Cai, Y., Wu, F., 2016b. Identification, tissue distribution, and bioaccumulation potential of cyclic perfluorinated sulfonic acids isomers in an airport impacted ecosystem. *Environ. Sci. Technol.* 50 (20), 10923–10932. <https://doi.org/10.1021/acs.est.6b01980>.
- Yan, H., Zhang, C., Zhou, Q., Yang, S., 2015. Occurrence of perfluorinated alkyl substances in sediment from estuarine and coastal areas of the East China Sea. *Environ. Sci. Pollut. R.* 22 (3), 1662–1669. <https://doi.org/10.1007/s11356-014-2838-3>.
- Zhao, Z., Xie, Z., Tang, J., Zhang, G., Ebinghaus, R., 2015. Spatial distribution of perfluoroalkyl acids in surface sediments of the German Bight, North Sea. *Sci. Total Environ.* 511, 145–152. <https://doi.org/10.1016/j.scitotenv.2014.12.063>.
- Zhu, Z., Wang, T., Wang, P., Lu, Y., Giesy, J.P., 2014. Perfluoroalkyl and polyfluoroalkyl substances in sediments from South Bohai coastal watersheds, China. *Mar. Pollut. Bull.* 85 (2), 619–627. <https://doi.org/10.1016/j.marpolbul.2013.12.042>.