



Spatial distribution of perfluoroalkyl acids in surface sediments of the German Bight, North Sea

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HIGHLIGHTS

- Declining PFOA and PFOS levels implied the effect of regulating C8-based products
- PFBA and PFBS occurred in the sediments of the German Bight
- PFOS in marine sediment may present a risk for benthic organisms in the German Bight

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ABSTRACT

Perfluoroalkyl acids (PFAAs) have been determined in the environment globally. However, studies on the occurrence of PFAAs in marine sediment remain limited. In this study, 16 PFAAs are investigated in surface sediments from the German Bight, which provided a good overview of the spatial distribution. The concentrations of ΣPFAAs ranged from 0.056 to 7.4 ng/g dry weight. The highest concentration was found at the estuary of the River Ems, which might be the result of local discharge source. Perfluorooctane sulfonic acid (PFOS) was the dominant compound, and the enrichment of PFOS in sediment might be strongly related to the compound structure itself. The geographical condition of the German Bight influenced the movement of water and sediment, resulting in complex distribution. Following normalization according to total organic carbon (TOC) content, PFAA distributions showed a different picture. Significant linear relationships were found between total PFAA concentrations and TOC ($R^2 = 0.50$, $p < 0.01$). Compared with a previous study conducted in the same area, a declining trend was presented for the concentrations of PFOS and perfluorooctanoic acid (PFOA). Compound structure, geographical condition, and organic carbon in the sediment influence the distribution of PFAAs in the German Bight. Environmental risk assessment indicated that the risk from PFOA is negligible, whereas PFOS in marine sediment may present a risk for benthic organisms in the German Bight.

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1. Introduction

Perfluoroalkyl acids (PFAAs) have been produced and utilized worldwide in high volumes for several decades, in consumer products such as polymerization aids; stain repellents in carpets; textile, and leather and paper products; and constituents of firefighting foams and fluoropolymer manufacturing, owing to their unique physical and chemical properties of thermal stability, surfactant property, hydrophobicity, and oleophobicity (Giesy and Kannan, 2001; Lindstrom et al., 2011; Prevedouros et al., 2006). PFAAs can be directly discharged into the aquatic environment via wastewater treatment plants, and from production and application processes (Ahrens, 2011; Armitage et al.,

2006; Sinclair and Kannan, 2006). They can be transformed from neutral poly-/per-fluoroalkyl substances (PFASs) via atmospheric oxidation and biotic degradation (Ellis et al., 2004; Martin et al., 2006; Tomy et al., 2004; Wallington et al., 2006). Neutral PFASs have been released to the environment in large quantities (Paul et al., 2009; Prevedouros et al., 2005) and are known to be long-range-transported pollutants (Ahrens et al., 2009a; Dreyer et al., 2009; Jahnke et al., 2007; Shoeib et al., 2006, 2010).

Previous studies of PFAAs have raised considerable concern regarding their global distribution (Ahrens et al., 2009a; Butt et al., 2010; Cai et al., 2012; Kannan, 2011; Taniyasu et al., 2013; Yamashita et al., 2005), bioaccumulation and/or biotransformation in organisms and marine mammals, environmental degradation and potential toxicity (Giesy et al., 2010; Naile et al., 2010). In recent years, PFAAs have been reported in different environmental compartments such as air (Dreyer

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et al., 2009; Li et al., 2011), water (Ahrens, 2011; Benskin et al., 2012), sediment (Bao et al., 2010; Higgins et al., 2005; Lam et al., 2014; Pan et al., 2014; Theobald et al., 2012; Zhao et al., 2013), and in biota (Giesy and Kannan, 2001; Houde et al., 2006; Kannan et al., 2006). Among the PFAAs, perfluorinated sulfonate acids (PFSAs) and perfluorinated carboxylic acids (PFCAs), e.g. PFOA and PFOS, have been well studied in aquatic environments, including their presence in the polar regions (Butt et al., 2010; Kwok et al., 2013). Because of their ubiquity and potential toxicity (Andersen et al., 2008; Hekster et al., 2003), the production and use of PFOS and PFOA are regulated worldwide. EU Directive 2006/122/EC required European countries to restrict the manufacture and use of PFOS from 2008 (EPC, 2006). National programs in the United States and Canada are attempting to regulate the use of PFOA, its salts and precursors (USEPA, 2006; Vierke et al., 2012). In 2009, PFOS and its salts, and perfluorooctanesulfonyl fluoride (PFOSF) were added to Annex B of the Stockholm Convention as new persistent organic pollutants.

PFAAs can be transported into coastal and marine environments via both riverine and atmospheric pathways. The sediment is highly important for the evaluation of their accumulation in coastal basins and potential impacts on benthic organisms. Several studies have reported PFAAs in sediment from China (Bao et al., 2009, 2010, 2012; Pan et al., 2014; Pan and You, 2010; Zhao et al., 2013), Japan (Ahrens et al., 2011), the United States (Senthil et al., 2009), and Europe (Becker et al., 2008; Beškoski et al., 2013; Campo et al., 2015; Hloušková et al., 2014; Labadie and Chevreuil, 2011a,b; Perra et al., 2013; Theobald et al., 2012). PFOS and PFOA were found as dominant homologues in PFAAs in most studies. Higgins and Luthy (2006) reported that the sorption of PFAAs onto sediment was influenced by organic carbon content, pH, and electrolytes in the solution, and by the compounds' structure.

The German Bight is the southeastern Bight of the North Sea, which receives large volumes of water containing particulate matter from

the Rhine (2260 m³/s), Ems (85 m³/s), Weser (350 m³/s) and Elbe (750 m³/s) rivers (Kampa et al., 2003). PFAAs have been frequently detected in seawater of the German Bight and its tributaries. The annual fluxes of PFAAs in the North Sea were estimated to be 335 ± 100 kg/year from the River Elbe and 102 ± 22 kg/year from the River Weser (Zhao et al., 2014). PFAAs were also identified in sediment collected from the German Bight in 2004 and 2005 (Theobald et al., 2012). However, there is less information on the latest status of PFAAs in sediment of the German Bight compared with that in seawater.

In this study, we collected sediment samples in the German Bight including the estuaries of the rivers Ems, Weser, and Elbe (Fig. 1). The distribution of PFAAs was discussed owing to the estuarine and offshore sampling program and total organic carbon content. The obtained PFAA data are compared with previous studies to evaluate the effect of regulatory controls. Furthermore, the potential risks of PFOS and PFOA in the aquatic ecosystem were assessed for the German Bight.

2. Materials and methods

2.1. Chemicals and standards

The native standards mixture including 16 PFAAs (i.e. C₄-, C₆-, C₈- and C₁₀-PFSAs and C₄-, C₁₄-PFCAs, >99%) was purchased from Wellington Laboratories. The mass-labeled standards were obtained from the same company, which contained 9 compounds (i.e. ¹³C-labeled C₄-, C₆-, C₈-, C₁₂-PFCAs, C₈-PFSAs, and perfluorooctane sulfonamide (FOSA) and ¹⁸O-labeled C₆-PFSAs, >99%). Methanol (Suprasolv grade), ammonium hydroxide (25%, Suprapur), sodium hydroxide, and hydrochloric acid were purchased from Merck (Darmstadt, Germany). Millipore water was produced by a Milli-Q Plus 185 system (Zug, Germany).

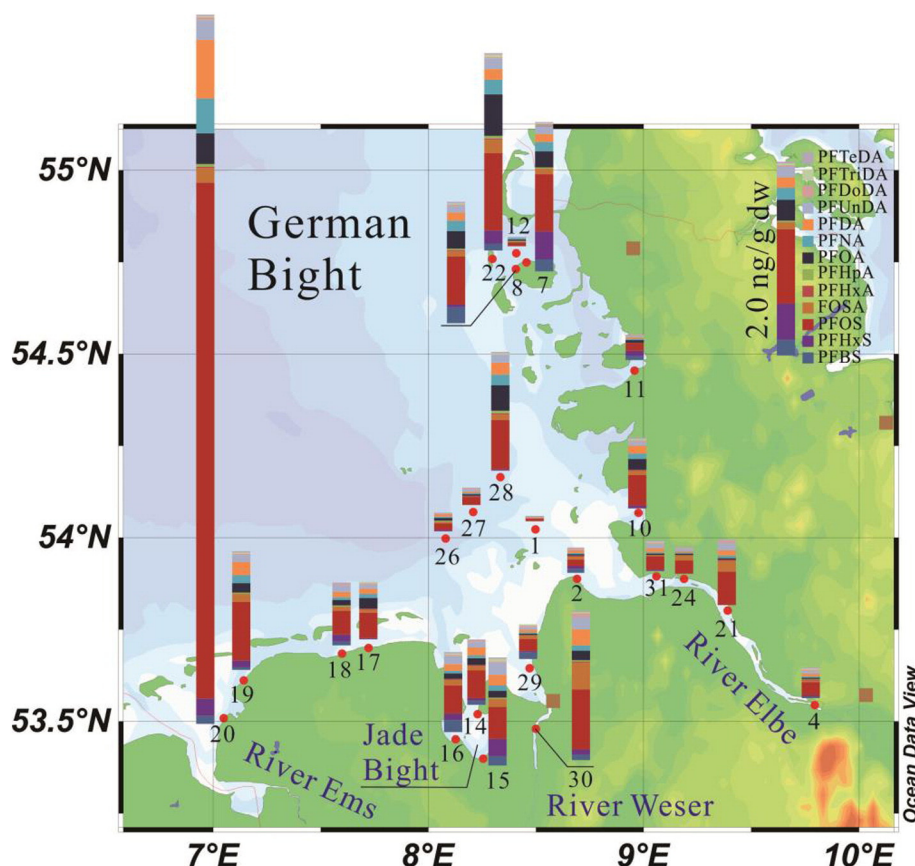


Fig. 1. Concentrations (ng/g dw) and spatial distribution of PFAAs in German Bight surface sediment.

2.2. Sampling and extraction

From February to May 2011, 24 surface sediment samples were collected at the German Bight coast (Fig. 1). In the region where sediment emerged during low tide, samples were collected by stainless steel spoon, and where sediment could not be reached by hiking, samples were obtained by a grab during cruise aboard the research vessels *Ludwig Prandtl*, and *Heincke*. The top 0–5 cm layer of sediment was sealed in aluminum boxes, frozen and stored at -20°C until analysis. The aluminum boxes were rinsed using methanol twice before being used. Sediments were freeze-dried (Martin Christ GAMMA 1–20) for 72 h, homogenized by agate mortar and pestle and sealed in methanol-rinsed brown jars until extraction.

The extraction and clean-up methods were modified from those reported by Higgins et al. (2005) and were described elsewhere (Zhao et al., 2013). Briefly, 8 g sediments were transferred to 50 mL methanol-rinsed polypropylene (PP) tubes and spiked with mass-labeled standard mixture (1 ng). 10 mL methanol was added and the mixture was soaked for 30 min and centrifuged for 8 min at 3000 rpm. The supernatant was collected in a methanol-rinsed glass flask. Sonication was repeated three times, yielding a total of 30 mL supernatant. The combined supernatant was concentrated to 3 mL by a rotary evaporator for clean-up.

An ENVI-Carb tube (3 mL, 0.25 g) was employed for clean-up. All the cartridges were washed by 10 mL methanol prior to use. After spiking the sample, 10 mL 0.1% NH_4OH methanol was added and the eluent was collected in glass tubes, before being further concentrated to 150 μL under gentle nitrogen stream. All samples were spiked with 1 ng mass-labeled 8:2 fluorotelomer unsaturated acid (8:2 FTUCA) as injection standard prior to analysis.

2.3. Instrument analysis

The instrument analysis was performed using a high-performance liquid chromatography electrospray ionization-tandem mass spectrometry system (HPLC–ESI–MS/MS) operating in negative ionization mode that consisted of an HP 1100 HPLC system (Agilent Technologies) coupled to an API 3000 triple-quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX). All Teflon parts were replaced by polypropylene parts to avoid possible contamination. The separation column was a Synergi Hydro RP 80A column ($150 \times 2 \text{ mm}$, $4 \mu\text{m}$) from Phenomenex, which was combined with a suitable guard column: Synergi 2 μm Hydro RP Mercury ($20 \times 2 \text{ mm}$, $2 \mu\text{m}$). The mobile phases employed were Millipore water and methanol both containing with 10 mmol/L ammonium acetate. The gradient of the mobile phase started with 30% methanol and then increased to 70% methanol over 3 min. After continuously increasing to 100% methanol over 28 min, the gradient was held for 7 min. The acquisition time was 40 min with 7 min equilibration. An API 3000 mass spectrometer was operated in multiple reaction monitoring (MRM) mode. Details of the instrument parameters, precursors, and product ions were described and listed in Ahrens et al. (2009a) and Zhao et al. (2013). Total organic carbon (TOC) was determined via an elemental analyzer (LECO RC 612).

2.4. Quality assurance and quality control

All the standards were checked before use, to avoid possible contamination from storage. No contamination was found in the standard mixtures. Chemicals (i.e. methanol, ammonium hydroxide, sodium hydroxide, and hydrochloric acid) were all examined, and no PFAAs were detectable. The blank ENVI-Carb cartridges were eluted and no PFAAs were found. One procedural blank was analyzed for every 8 samples. PFOS and FOSA were detected in procedural blanks at concentrations of $2 \pm 0.5 \text{ pg/g}$ and $3 \pm 1 \text{ pg/g}$, respectively.

The instrumental detection limit (IDL) was determined using a signal-to-noise ratio of 3 at the lowest level (0.2 ng/mL) in the

calibration. IDLs varied from 2 pg (perfluorohexane sulfonate acid, PFHxS) to 16 pg (perfluorobutanoic acid, PFBA). The method detection limit (MDL) was determined in two ways: 1) for the target analytes that were not detected in procedural blanks, MDLs were determined using a signal-to-noise ratio of 10, and MDL varied from 1 pg/g dry weight (dw, PFHxS) to 11 pg/g dw (PFBA); 2) for PFOS and FOSA, MDLs were extrapolated under 98% confidence intervals using the standard deviations and values in the blanks, giving MDLs for PFOS and FOSA of 3 pg/g dw and 8 pg/g dw, respectively.

To determine the precision of the method, sediments from the Arctic Ocean were employed. First, Arctic sediments from three sampling sites were extracted and analyzed, and no PFAAs were detectable. The PFAA-free sediments were spiked with PFAA standards. Sediments were then extracted, cleaned-up and analyzed, and recoveries of PFAAs were determined from 52% (PFBA) to 125% (PFUnDA) with mean value of $87\% \pm 16\%$.

Recoveries for German Bight sediments were calculated using mass-labeled standards. The values ranged from $61 \pm 11\%$ ($^{13}\text{C}_8\text{FOSA}$) to $106 \pm 13\%$ ($^{13}\text{C}_4\text{PFBA}$). In each extraction series (8 samples), one parallel sample was added, and the deviations of target analytes were within 25%.

3. Results and discussion

3.1. Distribution of PFAAs in German Bight surface sediment

All 16 of the PFAAs (PFBA is excluded from discussion) were detected in German Bight surface sediment. Concentrations of individual PFAAs and ΣPFAAs are listed in Table 1. Concentrations of ΣPFAAs ranged from 0.056 to 7.4 ng/g dw (mean 1.0 ng/g dw). ΣPFSA concentrations ranged from 0.023 to 5.7 ng/g dw (mean 0.61 ng/g dw), which were higher than those of ΣPFCAs (0.032–1.6 ng/g dw, mean 0.34 ng/g dw). PFOS was the dominant compound (range 0.023–5.4 ng/g dw, mean 0.27 ng/g dw), accounting for 24–72% of ΣPFAA concentration. With the exception of PFOS, all the other PFSAs had average compositions less than 8%. PFOA and PFDA were the dominant PFCAs, each accounting for 10% ΣPFAA . The average concentrations of longer-chained PFCAs, i.e. PFUnDA, PFDoDA and perfluorotridecanoic acid (PFTrIDA), were 0.059, 0.015, and 0.014 ng/g dw, respectively, whereas, shorter-chained PFCAs i.e. perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid (PFHpA), exhibited higher concentrations of 0.05, 0.07, and 0.08 ng/g dw, respectively. Ahrens et al. (2009b) reported a different situation for PFAA concentrations in German Bight surface water in 2007. In water phase, perfluorobutane sulfonate acid (PFBS) was the dominant compound (maximum concentration 17.7 ng/L), and among PFCAs, shorter-chained PFAAs had greater contribution than longer-chained PFAAs. That means the composition of PFAAs in sediment highly related to that in water. Higgins and Luthy (2006) revealed the relationship between the structural features of compounds and the sorption of PFAAs onto sediments. PFAAs with sulfonate heads that showed stronger affinity than those of carboxylates, and longer-chained compounds had stronger affinity than shorter-chained ones, as a result of more CF_2 moieties in their chemical structure. The significant differences between PFAA profiles in water and in sediments from German Bight suggested that the compound properties strongly influenced the distribution of PFAAs.

The spatial distribution of PFAAs is presented in Fig. 1. The highest concentration of ΣPFAAs was detected at the estuary of the River Ems (site 20, 7.4 ng/g dw), which was more than ten times higher than that from the River Weser estuary (site 29, 0.47 ng/g dw) and twenty to thirty times higher than that from the River Elbe Estuary (sites 2 and 31, 0.26–0.31 ng/g dw). The River Ems has smaller discharge volume than the Weser and Elbe, and the cities along the River Ems are much smaller than Bremen (River Weser) and Hamburg (River Elbe) (Ahrens et al., 2009b). The domestic sources may not be the major contributors of PFAAs. Southwest of the River Ems estuary, the River Rhine discharges heavily contaminated water to the North Sea (Möller et al.,

Table 1

Concentrations (ng/g dry weight) of individual PFAAs and ΣPFAAs in surface sediment of German Bight and the TOC content (%).

Site	TOC	PFBS	PFHxS	PFHpS	PFOS	PFDS	FOSA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	ΣPFSAAs	ΣPFCAAs	ΣPFAAs
GB1	0.023	<0.006	<0.001	<0.01	0.023	<0.006	<0.008	<0.003	<0.001	<0.001	0.007	0.003	0.016	0.007	<0.003	<0.005	<0.003	0.023	0.032	0.056
GB2	0.544	0.040	0.028	<0.01	0.069	<0.006	0.035	<0.003	0.004	0.002	0.019	0.017	0.028	0.013	0.007	<0.005	<0.003	0.14	0.090	0.26
GB4	0.534	0.011	0.012	<0.01	0.14	<0.006	0.018	<0.003	0.004	0.002	0.008	0.006	0.031	0.031	0.018	0.008	0.005	0.17	0.11	0.30
GB7	3.02	0.12	0.30	0.022	0.59	<0.006	0.051	<0.003	0.005	0.010	0.17	0.094	0.092	0.073	0.016	0.022	0.007	1.0	0.49	1.6
GB8	3.75	0.17	0.035	0.014	0.49	<0.006	0.059	<0.003	0.008	0.017	0.19	0.10	0.088	0.063	0.015	0.018	0.005	0.71	0.50	1.3
GB10	1.17	0.006	0.018	<0.01	0.33	<0.006	0.039	<0.003	0.009	0.008	0.10	0.059	0.081	0.050	0.013	0.009	0.004	0.35	0.34	0.73
GB11	0.370	0.042	0.058	<0.01	0.078	<0.006	<0.008	<0.003	0.003	0.001	0.022	0.013	0.017	0.016	0.003	<0.005	<0.003	0.18	0.076	0.25
GB12	0.150	<0.006	0.002	<0.01	0.035	<0.006	0.009	0.005	0.005	0.003	0.017	0.013	0.009	0.010	<0.003	<0.005	<0.003	0.037	0.060	0.11
GB14	1.67	0.037	0.038	<0.01	0.29	<0.006	0.043	<0.003	0.005	0.005	0.063	0.037	0.074	0.058	0.011	0.011	0.003	0.37	0.27	0.68
GB15	4.68	0.10	0.17	0.011	0.34	<0.006	0.070	<0.003	0.006	0.010	0.077	0.050	0.12	0.11	0.024	0.022	0.008	0.63	0.43	1.1
GB16	1.19	0.12	0.074	<0.01	0.29	<0.006	0.056	<0.003	0.007	0.004	0.059	0.031	0.064	0.077	0.016	0.015	0.004	0.49	0.28	0.82
GB17	0.625	<0.006	0.022	<0.01	0.25	<0.006	0.031	0.003	0.011	0.010	0.10	0.041	0.059	0.046	0.010	0.010	<0.003	0.27	0.29	0.60
GB18	1.28	0.042	0.066	<0.01	0.25	<0.006	0.045	<0.003	0.004	0.004	0.056	0.033	0.060	0.060	0.012	0.011	0.005	0.36	0.24	0.65
GB19	1.24	0.033	0.067	<0.01	0.61	<0.006	0.074	<0.003	0.008	0.007	0.11	0.086	0.13	0.078	0.012	0.011	0.004	0.71	0.44	1.2
GB20	4.10	0.091	0.18	0.044	5.4	<0.006	0.15	0.005	0.019	0.017	0.33	0.35	0.61	0.21	0.028	0.018	0.007	5.7	1.6	7.5
GB21	0.993	<0.006	0.007	<0.01	0.35	<0.006	0.11	<0.003	0.007	0.002	0.021	0.016	0.055	0.072	0.024	0.010	0.008	0.35	0.22	0.68
GB22	4.53	0.067	0.15	<0.01	0.80	<0.006	0.13	<0.003	0.016	0.031	0.43	0.15	0.12	0.10	0.021	0.023	0.007	1.0	0.90	2.0
GB24	3.93	<0.006	0.004	<0.01	0.13	<0.006	0.051	<0.003	0.005	0.002	0.014	0.009	0.024	0.020	0.005	<0.005	<0.003	0.14	0.079	0.27
GB26	0.169	<0.006	0.012	<0.01	0.068	<0.006	0.016	0.004	0.006	0.004	0.037	0.018	0.019	0.015	<0.003	<0.005	<0.003	0.080	0.10	0.20
GB27	0.267	<0.006	<0.001	<0.01	0.081	<0.006	0.010	<0.003	0.002	<0.001	0.018	0.014	0.016	0.021	0.003	<0.005	<0.003	0.081	0.075	0.17
GB28	0.920	<0.006	0.015	<0.01	0.51	<0.006	0.057	0.004	0.014	0.021	0.27	0.12	0.13	0.072	0.012	0.009	0.003	0.53	0.65	1.2
GB29	0.479	0.070	0.022	0.11	0.11	<0.006	0.042	<0.003	0.002	0.002	0.019	0.011	0.032	0.026	0.011	0.008	<0.003	0.32	0.11	0.47
GB30	3.88	0.054	0.056	<0.01	0.62	0.014	0.28	0.007	0.018	0.009	0.091	0.065	0.16	0.13	0.040	0.024	0.009	0.75	0.55	1.6
GB31	1.83	<0.006	0.011	<0.006	0.14	<0.006	0.008	<0.003	0.005	0.002	0.015	0.009	0.040	0.044	0.017	0.008	0.004	0.15	0.14	0.31
Max	4.68	0.17	0.30	0.11	5.4	0.014	0.28	0.007	0.019	0.031	0.43	0.35	0.61	0.21	0.040	0.024	0.009	5.7	1.6	7.5
Min	0.023	0.006	0.002	0.011	0.023	0.014	0.008	0.003	0.002	0.001	0.007	0.003	0.009	0.007	0.003	0.008	0.003	0.023	0.032	0.056
Mean	1.72	0.067	0.061	0.041	0.50	0.014	0.063	0.005	0.007	0.008	0.093	0.056	0.086	0.059	0.015	0.014	0.006	0.61	0.34	1.0
Median	1.18	0.054	0.031	0.022	0.27	0.014	0.048	0.004	0.006	0.004	0.057	0.032	0.059	0.054	0.013	0.011	0.005	0.35	0.26	0.66

2010). North Sea currents have the potential to transport pollutants from the River Rhine estuary and other areas of the North Sea to German Bight (Ahrens et al., 2009c). The high concentrations of PFAAs detected at the River Ems estuary might be attributed to their transportation from other areas of the North Sea. Relatively high Σ PFAA concentrations were found at the northeast coast of German Bight, e.g., sites 7, 8, and 22 (1.3–2.0 ng/g dw). These sampling sites were located at the inner area of the coast where the water exchange was relatively weak, which influenced the diffusion of contaminants. In the semi-enclosed Jade Bight (sites 14, 15, and 16, 0.68–1.2 ng/g dw), Σ PFAA concentrations were

relatively stable and higher than those detected at the Weser and Elbe estuaries. Considering the difficulty of dilution and diffusion, PFAAs easily accumulated to relatively high levels in Jade Bight even though the sources were not highly concentrated. The sources were not very strong. Low Σ PFAA concentrations were found at open areas of German Bight (sites 1, 26, and 27, 0.056–0.20 ng/g dw). The PFAA concentrations in water were reported to be relatively low in open areas (Ahrens et al., 2009b) and the suspended particles had to be transported long distances to deposit. The spatial distribution of PFAAs was related to the geography in German Bight.

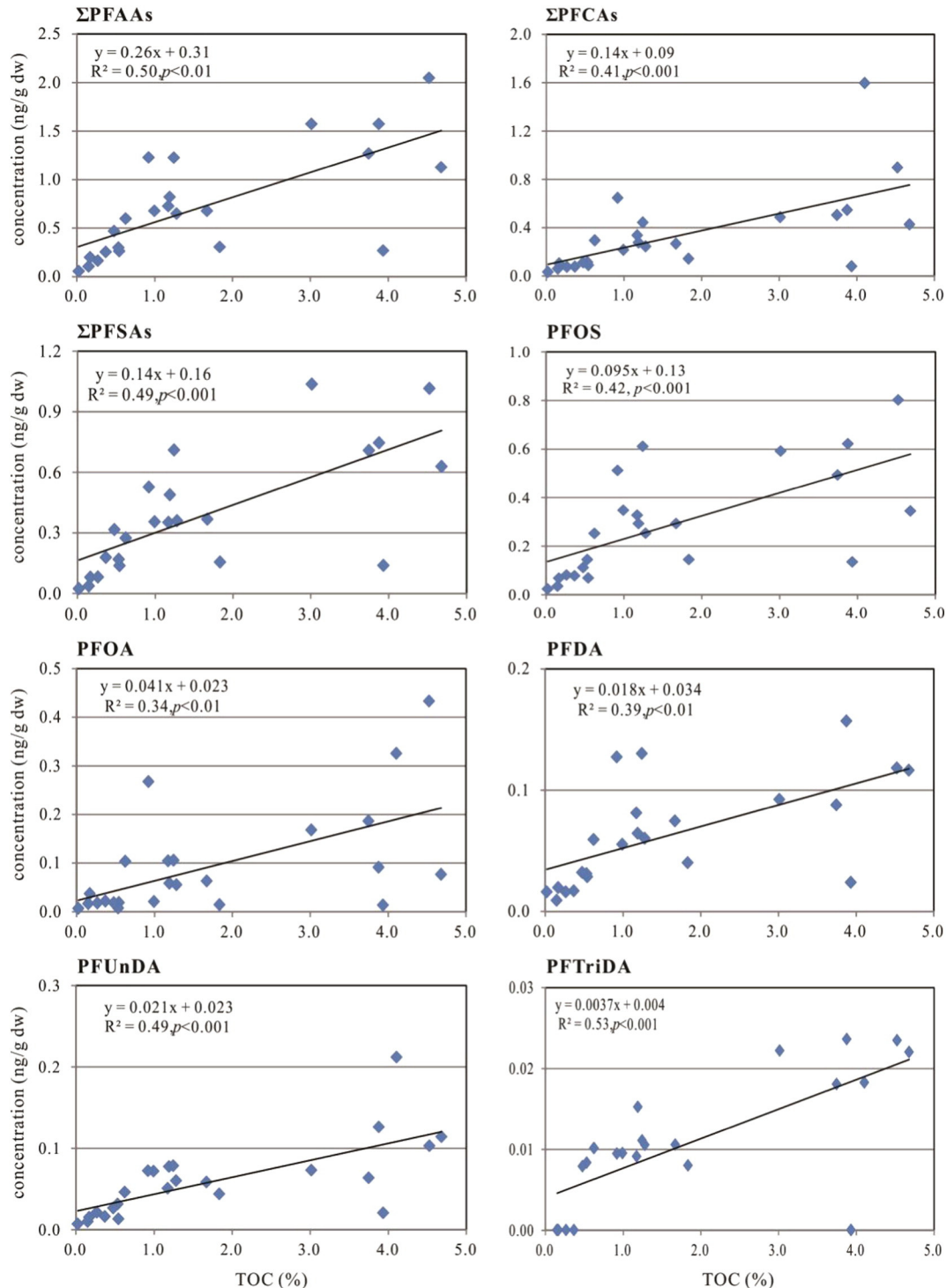


Fig. 2. Relationships between TOC content (%) and PFAA concentrations (ng/g dw).

The relationship between TOC contents and PFAA/ Σ PFAA concentrations was studied in German Bight sediment (see Fig. 2). A significant relationship was found between TOC and Σ PFAA concentrations ($R^2 = 0.50$, $p < 0.01$) without considering the highest concentration. The regression for Σ PFCAs ($R^2 = 0.49$, $p < 0.001$) showed comparable relationship with that for Σ PFASs ($R^2 = 0.41$, $p < 0.001$). For individual PFAAs, PFOS concentrations (except the highest one) were significantly related to TOC content ($R^2 = 0.42$, $p < 0.001$). Longer-chained PFCAs, i.e. PFUnDA and PFTriDA, showed strong correlation to TOC content than PFOS ($R^2 = 0.49$, $p < 0.001$ for PFUnDA and $R^2 = 0.53$, $p < 0.001$ for PFTriDA). PFOA and PFDA were less strongly correlated with TOC than were longer-chained PFCAs ($R^2 = 0.34$, $p < 0.01$ for PFOA and $R^2 = 0.39$, $p < 0.01$ for PFDA). The positive relationship between TOC and PFAA concentration was consistent with the discussion about sorption theory in Higgins and Luthy (2006), and the sorption affinity strongly related to the structure of the compounds. To reduce the influence of organic carbon, the concentrations were normalized by TOC content and the distributions are shown in Fig. 3. The highest value (2.42 ng/g TOC) was found at sampling site 1, which had the lowest TOC content. Site 20 showed the second-highest TOC of 1.81 ng/g and the highest TOC content. At the open offshore areas, e.g. sites 1, 26, 27, and 28, the values were significantly elevated, while at the inner areas, e.g. sites 20, 15, 30, and 4, the values were reduced. These findings indicate that, at offshore areas where sediments were homogenized, TOC strongly influenced the sorption of PFAAs.

3.2. Comparison with previous studies

In most previous studies (see Table 2), PFOS and PFOA were the predominant compounds detected in sediments, and PFOS usually presented higher concentration than PFOA. PFOS concentrations in German Bight in 2011 were comparable with those detected at Sydney Harbor, Australia (0.80–6.2 ng/g dw) (Thompson et al., 2011). Previous studies of coastal China, Japan, and USA reported lower PFOS concentrations than those recorded here for German Bight. Becker et al. (2008) reported lower PFOS concentrations (0.07–0.31 ng/g dw) in surface sediments

of the Red Main River in Germany than those found in this study. The PFOA concentrations in German Bight were lower than those reported in Laizhou Bay, China (0.07–1.8 ng/g dw) (Zhao et al., 2013) and Ariake Sea, Japan (0.84–1.1 ng/g dw) (Nakata et al., 2006). Comparable PFOA concentrations were reported for the North Bohai coast, China (nd–0.542 ng/g dw) (Wang et al., 2011), Tokyo Bay, Japan (0.45 ng/g dw) (Zushi et al., 2010), San Francisco coast, USA (nd–0.625 ng/g dw) (Higgins et al., 2005), and western Baltic Sea, Germany (0.06–0.68 ng/g dw) (Theobald et al., 2012).

Theobald et al. (2012) investigated PFAAs in sediment from German Bight in 2004. PFOS and PFOA were dominant, and PFNA and PFDA were detectable at most sites. Excluding the highest concentration in 2011, PFOS presented a declining trend from 2004 (0.04–2.4 ng/g dw) to 2011 (0.023–0.80 ng/g dw). Germany ceased production of PFOS in 2007, after which PFOS was only used in some non-substitutable applications, e.g. metal plating, photographic applications and semiconductors (Carroll et al., 2009). The decreasing release from former sources might be the major reason for the observed lower concentrations, since PFOS is relatively stable in the environment. For PFOA, concentrations decreased from 0.08–1.6 ng/g dw in 2004 to 0.007–0.43 ng/g dw in 2011, a trend that might be attributed to the voluntary phase-out by manufacturers (3M, 2011). The median concentrations of PFBS and PFHxS were 0.054 ng/g dw and 0.056 ng/g dw in 2011 which are slightly higher than those measured in 2004 (median <0.03 ng/g for PFBS and PFHxS). Whereas, PFNA and PFDA showed comparable concentrations in 2004 (0.055 ng/g dw for PFNA, 0.064 ng/g dw for PFDA) and in 2011 (0.032 ng/g dw for PFNA, 0.059 ng/g dw for PFDA).

3.3. Environmental risk assessment of PFOS and PFOA

Environmental risk assessment (ERA) was conducted for PFOS and PFOA in German Bight utilizing risk quotient (RQ), which is defined as the ratio of measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC), where $RQ < 1$ indicates no potential risk. The PNEC selected in this study is derived by the equilibrium partitioning method, which has been calculated for PFOS and PFOA

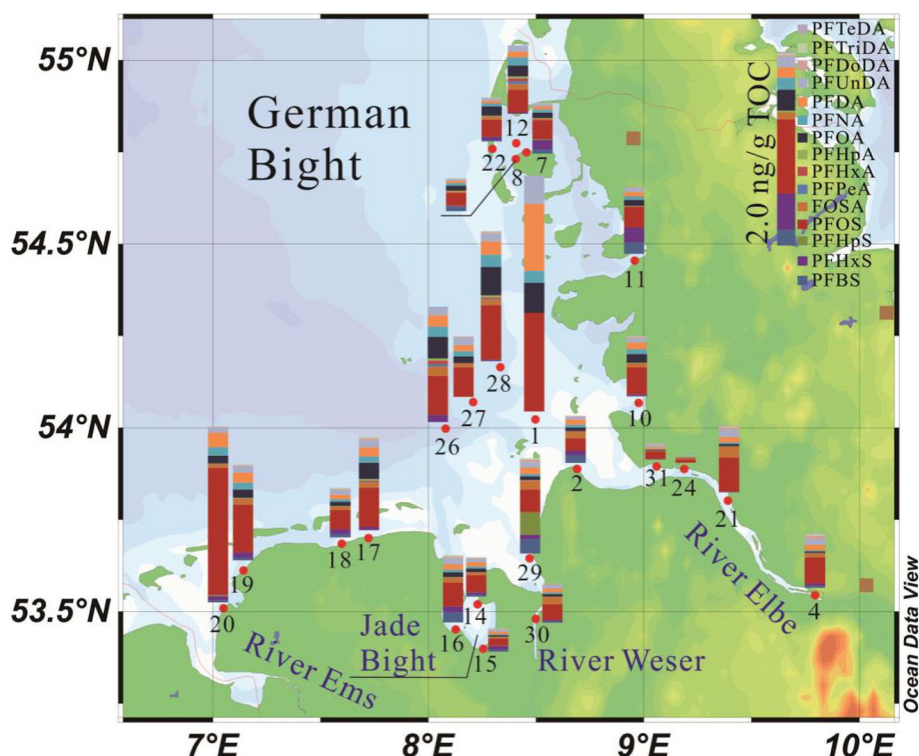


Fig. 3. TOC-normalized concentrations (ng/g TOC) and spatial distribution of PFAAs in German Bight surface sediment.

Table 2

Comparisons of PFOA and PFOS level in the German Bight and other coastal zones in the world.

Location	Sampling year	PFOS	PFOA	Reference
North Bohai Sea Coast, China	2008	nd–1.97	nd–0.542	Wang et al. (2011)
Laizhou Bay, China	2009	<0.03–0.06	0.07–1.8	Zhao et al. (2013)
Tokyo Bay, Japan	2004	1.66	0.45	Zushi et al. (2010)
Ariake Sea, Japan	2004	0.09–0.14	0.84–1.1	Nakata et al. (2006)
Savannah River Estuary, USA	2007	0.3–0.8	nd–0.2	Senthil et al. (2009)
LCP Superfund Site, USA	2006	0.1–0.4	nd–0.2	Senthil et al. (2009)
San Francisco Coast, USA	2002, 2004	nd–3.07	nd–0.625	Higgins et al. (2005)
Sydney Harbor, Australia	2009	0.80–6.2	0–0.16	Thompson et al. (2011)
Roter Main River, Germany	2006	0.07–0.31	0.02–0.07	Becker et al. (2008)
Western Baltic Sea	2005	0.03–0.67	0.06–0.68	Theobald et al. (2012)
German Bight	2004	0.04–2.4	0.08–1.6	Theobald et al. (2012)
German Bight	2011	0.023–5.36	0.007–0.43	This study

nd: not detected.

in sediments from Laizhou Bay. The non-TOC-normalized PNECs for PFOS and PFOA were 4.9 ng/g and 86 ng/g in river sediment, and 0.49 ng/g and 8.6 ng/g in marine sediment, respectively (Zhao et al., 2013).

The RQ values calculated for the sediment samples have been shown in Fig. 4. For the river sediments, the RQ values ranged from 0.03 to 0.13 for PFOS, and from 0.0001 to 0.011 for PFOA, respectively. All the RQs were less than 1, indicating no significant risk to benthic organisms. For marine sediment, the RQs ranged from 0.05 to 11 for PFOS (mean 1.1), and from 0.001 to 0.05 for PFOA (mean 0.01), respectively. RQs were great than 1 in 32% of the marine sediment samples. The maximum RQ for PFOS was 11, presented in sample G20 collected near the mouth of the Ems, followed by a value of 1.6 at site G22, which is influenced by the Elbe. These results suggest that PFOS may present some level of risk to benthic organisms in the German Bight, while the risks associated with PFOA appear to be negligible, based on the relatively low RQ.

4. Conclusions

In surface sediments from German Bight, PFOS, PFOA, and PFDA exhibited higher concentrations than other PFAAs. PFBS did not contribute greatly to Σ PFAA concentrations, although it was the dominant compound in the water phase. Because of their stronger affinity to the sediment, longer-chained PFAAs ($C > 10$) were more frequently detected than shorter-chained compounds, and at the same time presented lower concentrations. At semi-enclosed coastal sites, PFAAs accumulated because of the weak exchange of water and sediment, whereas PFAAs can be transported from the estuaries to open areas due to

currents and the homogenization effect. The distributions of PFAAs were related to the TOC content of the sediment. After normalizing the concentrations by TOC content, the PFAAs presented a different distribution. Some sites showed elevated values, which revealed the real status of contamination. Comparison with the literature showed that PFOS concentrations were higher than most other values reported worldwide, whereas PFOA presented moderate levels. Compared with previous surveys of the study area, PFOS and PFOA concentrations presented declining trends. It therefore appears that the regulation of C_8 -PFAAs has had positive results in German Bight, although RQ suggests that PFOS in marine sediment may represent an environmental risk to benthic organisms in German Bight.

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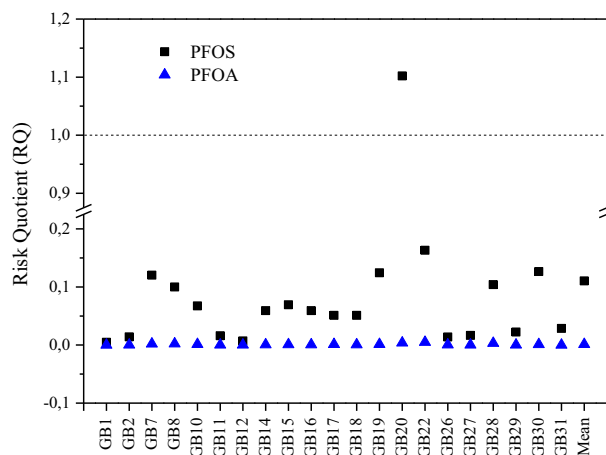


Fig. 4. Risk quotient (RQ) used for environmental risk assessment of PFOS and PFOA (RQ < 1 indicates no potential risk).

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