



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



Zhen Zhao<sup>a,b,c</sup>, Zhiyong Xie<sup>a,\*</sup>, Jianhui Tang<sup>c,\*</sup>, Gan Zhang<sup>b</sup>, Ralf Ebinghaus<sup>a</sup>

<sup>a</sup> Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of Coastal Research, Max-Planck Street 1, 21502 Geesthacht, Germany

<sup>b</sup> State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, CAS, Kehua Road 511, Guangzhou 510631, China

<sup>c</sup> Yantai Institute of Coastal Zone Research, CAS, Chunhui Road 17, Yantai 264003, China

### 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  $\Sigma$ PFAAs 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

\* Corresponding authors.

E-mail addresses: [zhiyong.xie@hzg.de](mailto:zhiyong.xie@hzg.de) (Z. Xie), [jhtang@yic.ac.cn](mailto:jhtang@yic.ac.cn) (J. Tang).

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 m<sup>3</sup>/s), Ems (85 m<sup>3</sup>/s), Weser (350 m<sup>3</sup>/s) and Elbe (750 m<sup>3</sup>/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. C<sub>4</sub>-, C<sub>6</sub>-, C<sub>8</sub>- and C<sub>10</sub>-PFSAs and C<sub>4</sub>-, C<sub>14</sub>-PFCAs, >99%) was purchased from Wellington Laboratories. The mass-labeled standards were obtained from the same company, which contained 9 compounds (i.e. <sup>13</sup>C-labeled C<sub>4</sub>-, C<sub>6</sub>-, C<sub>8</sub>-, C<sub>12</sub>-PFCAs, C<sub>8</sub>-PFSAs, and perfluorooctane sulfonamide (FOSA) and <sup>18</sup>O-labeled C<sub>6</sub>-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).

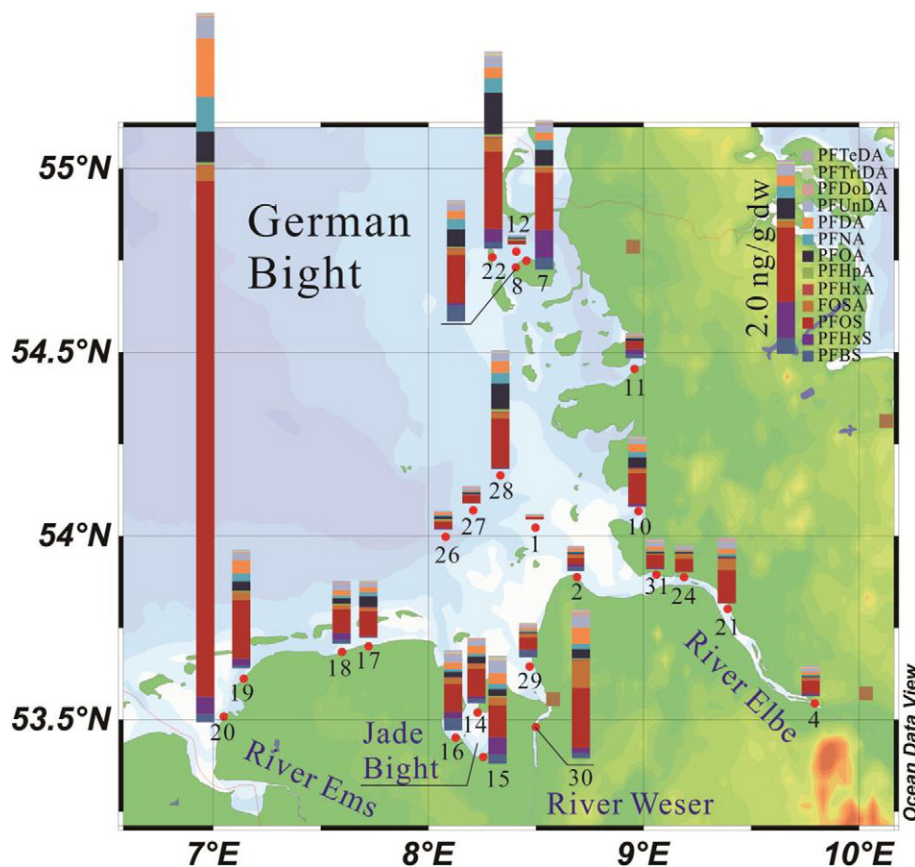


Fig. 1. Concentrations (ng/g dw) and spatial distribution of PFAAs in German Bight surface sediment.

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