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Perfluoroalkyl and polyfluoroalkyl substances in the lower atmospheres and surface waters of the Chinese Bohai Sea, Yellow Sea, and Yangtze River Estuary

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Highlights

- PFASs were investigated in the low atmosphere and surface water;
- 8:2 FTOH and PFOA were the predominant compounds in the air and water, respectively;
- Distribution of PFASs were influenced by sources, geographical condition, and marine current;
- High levels of PFOA were found in the Bohai Sea;
- Total inventories of PFOA and PFOS were 646 kg and 7.6 kg, respectively.

Abstract

30 Polyfluoroalkyl and perfluoroalkyl substances (PFASs), in the form of polyfluoroalkyl
31 substances in the gas phase in air and perfluoroalkyl substances in the dissolved phase in
32 surface water, were investigated during a sampling campaign in the Bohai Sea, Yellow Sea,
33 and Yangtze River Estuary in May 2012. In the gas phase, concentrations of neutral Σ PFASs
34 ranged from 76–551 pg/m³. Higher concentrations were found in the South Yellow Sea.
35 Accounting for 92%–95% of Σ PFASs, 8:2 fluorotelomer alcohol (FTOH) was the
36 predominant compound. Air mass back trajectory analysis indicated that neutral Σ PFASs
37 came mainly from the coast of the Yellow Sea, including the Shandong, Jiangsu, and
38 Zhejiang provinces of China, and the coastal region of South Korea. In the dissolved phase in
39 surface water, concentrations of ionic Σ PFASs ranged from 1.6–118 ng/L, with the Bohai Sea
40 having higher concentrations than both the Yellow Sea and the Yangtze River Estuary.
41 Releases from industrial and domestic activities as well as the semiclosed geographical
42 conditions increased the level of Σ PFASs in the Bohai Sea. The spatial distributions of
43 perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFASs) were
44 significantly different. The Laizhou Bay, which is part of the Bohai Sea, was the major source
45 region of PFCAs and the Yangtze River Estuary was the major source of PFASs. The
46 inventories of ionic Σ PFASs were estimated as 438, 318, and 94 kg in the Bohai Sea, Yellow
47 Sea, and Yangtze River Estuary, respectively.

48 **Keywords: PFASs, air and water, environmental concentrations, surface water**
49 **inventory**

50 **1. Introduction**

51 Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been widely used for more than
52 60 years because of their lipophilic and hydrophilic characteristics. PFASs have been found in
53 various environmental compartments worldwide. Some longer-chained PFASs ($C \geq 8$) are
54 bioaccumulative and toxic, and thus are listed in national and international regulations. After
55 perfluorooctanesulfonic acid (PFOS), a PFAS, and related compounds were added to the

56 Stockholm Convention's Annex B, their production and use significantly decreased. Major
57 global manufacturers of perfluorooctanoic acid (PFOA), another PFAS, and its precursors
58 promised to stop their production of such voluntarily in 2015. However, the release of PFASs
59 continue by other means, for example, the production of irreplaceable homologues, the
60 consumption of stockpiles, and emission from previously-sold commercial products(Kwok et
61 al., 2015; Müller et al., 2011), can all lead to high levels in some regions.

62 The ionic PFASs are resistant to photolysis, pyrolysis, and biotransformation, thus making
63 them highly persistent in the environment. They have high water solubility because of their
64 carboxylic or sulfonic acid groups, and can be transported a long distance via water. In
65 addition, the terminal fluorine functional group makes ionic PFASs hydrophobic. Thus, open
66 sea surface water is presumed an important sink of ionic PFAS homologues(Armitage et al.,
67 2009). Neutral PFASs, such as fluorotelomer alcohols (FTOHs), are volatile and distributed
68 mainly in air rather than particle phase(Ahrens et al., 2011; Dreyer et al., 2009). After
69 oxidation by radicals and oxides, neutral PFASs in the air transform to ionic PFASs and then
70 reach the earth's surface through dry/wet deposition which was considered as the indirect
71 sources. However, the direct sources are confirmed as the main contributors of PFASs
72 worldwide pollution.

73 Several studies have reported on the pollution from PFASs, especially PFOA and PFOS,
74 along the Chinese coastline. The composition of ionic PFASs in surface water was
75 significantly different geographically. In the Pearl River Estuary and South China Sea, PFOS
76 usually occurred at higher concentrations than other homologues did (Kwok et al., 2015),
77 whereas, for the rest of the Chinese coast and seas, PFOA was the predominant pollutant, as
78 reported in most studies (Wang et al., 2012; Wang et al., 2015b). The industrial production
79 and use of such were the reasons for the high levels detected in some hotspots, for example,
80 the rivers upstream to the Liaodong (Fuxin City) (Bao et al., 2010) and Laizhou (Weifang
81 City) Bays (Heydebreck et al., 2015) which are part of Bohai Sea, and the direct release of

82 ionic PFASs was suggested as the major source of this. To our best knowledge, only one
83 study has focused on neutral PFASs in the Chinese atmosphere. Lai et al. (2016) found that
84 FTOH was the predominant neutral PFAS group in atmosphere of northern South China Sea,
85 and the sources were the long-range transport from East Asia cities. Additionally, Li et al.
86 (2012) reported that 8:2 FTOH was the predominant PFAS in the Chinese terrestrial
87 atmosphere, with the coastal regions having higher levels than the inner land did, which is
88 related to the fluorine industry and urbanization. Modeling studies have speculated low
89 contribution from indirect sources of ionic PFASs on the earth's surface. However, studies
90 concerning air and water simultaneously are rare, which leads to uncertainty when
91 determining the source, behavior, and fate of PFASs in the coastal sea.

92 The Chinese Bohai and Yellow Sea have a combined total area over 470 000 km².
93 Hundreds of rivers in China as well as in the Korean Peninsula discharge industrial and
94 domestic wastewater into this region. In the semiclosed Bohai Sea, high concentrations of
95 PFOA and PFOS were detected in the rivers discharging water into the sea, which creates the
96 potential to elevate the levels in marine water (Sun et al., 2011; Wang et al., 2014a). Along
97 the Yellow Sea coast, for instance, Liaoning (where Fuxin City located), Shandong (where
98 Weifang City located), Zhejiang, and Jiangsu Province, the fluorochemical industries are
99 considered point sources of PFASs. Moreover, most rapidly developing cities are located
100 along the Bohai and Yellow Sea coast, for example Tianjin and Qingdao City (Shandong
101 Province) and are regarded as nonpoint sources. Yangtze River is the longest river in China.
102 The provinces and cities in middle and down streams of Yangtze River, for example, Hubei,
103 Jiangxi, Zhejiang Province, and Shanghai City, have been reported large volume of PFOS
104 release(Xie et al., 2013) and high PFASs concentrations in aquatic system(Chen et al., 2015b;
105 Pan et al., 2014b). Gao et al. (2014) investigated PFASs in marine sediments from the Bohai,
106 Yellow, as well as East China Seas and a general decreasing trend was found from the coast
107 to the open sea. PFASs in the sediment might migrate from the water by partition and

108 adsorption or from organisms' bodies, which finally settle in the sediment. Unfortunately, to
109 our best knowledge, no studies have focused on the PFASs pollution in the air and water of
110 the Bohai Sea, Yellow Sea and Yangtze River Estuary.

111 In light of this, this study revealed the pollution characteristics of PFASs in the lower
112 atmospheres and surface waters of the Bohai Sea, Yellow Sea, and Yangtze River Estuary.
113 The large geographical scale of this study was beneficial to elaborate comprehensively on the
114 source and transport of such pollutants. To our best knowledge, this is the first time PFASs
115 pollution in the air and water have been investigated simultaneously, enabling insight into the
116 source, behavior, and fate of PFASs in the Bohai Sea, Yellow Sea and Yangtze River Estuary.

117 **2. Material and methods**

118 **2.1 Standards and reagents**

119 Twenty-nine neutral and ionic PFASs were analyzed, i.e., 6:2, 8:2, 10:2, and 12:2 FTOHs;
120 6:2 and 8:2 fluorotelomer acrylates (FTACs); N-methyl perfluorobutane sulfonamide
121 (MeFBSA); N-methyl perfluorooctane sulfonamide (MeFOSA); N-ethyl perfluorooctane
122 sulfonamide (EtFOSA); N-methyl perfluorobutane sulfonamidoethanol (MeFBSE); N-methyl
123 perfluorooctane sulfonamidoethanol (MeFOSE); and N-ethyl perfluorooctane
124 sulfonamidoethanol (EtFOSE) were measured in the air samples and C₄–C₆, C₈, and C₁₀
125 perfluoroalkane sulfonic acids (PFASs); C₄–C₁₄ perfluoroalkyl carboxylic acids (PFCAs); and
126 perfluorooctanesulfonamide (FOSA) were measured in the surface water samples. Sixteen
127 mass-labeled analytes were used as the Internal Standards (IS) including ¹³C-labeled
128 perfluoroalkane sulfonamides (FASAs), perfluoroalkane sulfonamidoethanols (FASEs), and
129 ²H-labeled FTOHs for the air samples (ISI) and ¹³C-labeled ionic PFCAs and FOSAs and ¹⁸O-
130 labeled perfluorohexanesulfonate (PFHxS) for the water samples (ISII) (**Table S1**). For the air
131 samples, 9:1 FTOH was employed as the injection standard (InjS)I and 2H-perfluoro-[1,2-
132 ¹³C₂]-2-decenoic acid (8:2 FTUCA) was employed as the InjSII for the water samples. FTACs
133 and 9:1 FTOH were purchased from Fluorochemo Ltd. (United Kingdom). The other

134 standards were purchased from Wellington Laboratory Inc (Canada). **Table S1** lists the
135 information about the target compounds and standards in detail. Methanol, acetone,
136 dichloromethane (DCM), and *n*-hexane were all residue grade and purchased from Merck
137 (Darmstadt, Germany). Ammonium hydroxide (NH₄OH) (25%) was also purchased from
138 Merck (Darmstadt, Germany). Ultrapure Millipore water was produced by a Milli-Q® Plus
139 185 system (Zug, Germany).

140 **2.2 Sample collection**

141 Air and surface water samples were collected from May 2–20, 2012 from the research vessel
142 *Dongfanghong-2*. The sampling area covered the Bohai Sea, Yellow Sea, and the Yangtze
143 River Estuary in China. Information about the sampling stations is summarized in **Tables S2**
144 **and S3**.

145 Fifteen air samples were taken using a high-volume air sampler, which was placed in the
146 front of the ship's upper deck. Each sample was collected as a 24-hour nonstop air mass. A
147 glass fiber filter (GF/F, diameter 12 cm, pore size 0.7 μm) trapped airborne particles and a
148 self-packed polyurethane(PUF)/XAD-2 glass column trapped the gaseous phase. Before
149 sampling, the filters were baked at 450 °C for 12 h and the columns were Soxhlet extracted
150 for 16 h using acetone to remove any contaminants. After sampling, the filters and columns
151 were stored at -20 °C until further treatment in a clean lab.

152 Using a stainless basket, 72 surface water samples (depth: 0–30 cm) were collected from 67
153 sampling sites (including 5 duplicated samples) and stored in 1-L polypropylene (PP) bottles.
154 A glass fiber filter (GF/C, Ø47 mm, pore size 1.2 μm) was used for filtration. The dissolved
155 phase was spiked first by 1 ng ISII and then solid-phase-extracted (SPE) onboard using Oasis
156 WAX cartridges (Waters, 150 mg, 6 cc, 30 μm) at a speed of 2 drops per second via gravity.
157 The filters were baked at 450 °C for 4 h before use, and the cartridges were preconditioned
158 with 10 mL methanol before water loading. The sample-loaded filters and cartridges were
159 stored at -20 °C before further treatment in a clean lab.

160 **2.3 Extraction**

161
162 Sample extractions were performed in a clean lab (Class 10 000) with Teflon-free materials.
163 The air columns were Soxhlet extracted by DCM for 16 h after being spiked with 2.5 ng ISI.
164 The extracts were rotary evaporated to 1–2 mL using *n*-hexane as the keeper. After removing
165 the residual water by passing the extract through 3 g prebaked Na₂SO₄, the extracts were
166 concentrated down to 150 µL under gentle nitrogen flow (>99.999%). Before instrument
167 analysis, the concentrated extracts were spiked with 1 ng InjSI. Because PFASs were not
168 expected in the particles, the filters were not analyzed in this study. The WAX cartridges were
169 first washed with 15 mL Millipore water to remove the salt, and then dried using a vacuum
170 pump. The cartridges were eluted using 10 mL methanol with 0.1% NH₄OH. The eluents
171 were concentrated down to 150 µL. The eluents were spiked with 1 ng InjSII before
172 instrumental analysis.

173 **2.4 Instrumental analysis**

174 For volatile PFASs in the air samples, quantification was performed by gas chromatography
175 (6890, Agilent Technologies, Waldbronn, Germany)/mass spectrometry (Agilent
176 Technologies) (GC/MS) with positive chemical ionization (PCI) in selected ion-monitoring
177 (SIM) mode. For ionic PFASs in the water samples, the quantification was performed using a
178 high performance liquid chromatography-negative electrospray ionization-tandem mass
179 spectrometry system (HPLC-(-)ESI-MS/MS) that consisted of an HP 1100 HPLC system
180 (Agilent Technologies) coupled to an API 3000 triple-quadrupole mass spectrometer (Applied
181 Biosystems/MDS SCIEX). The characteristic ions for GC/MS and precursor/product ions for
182 HPLC-MS/MS are listed in [Table S1](#). More details of the instrumental analyses can be found
183 elsewhere(Ahrens et al., 2009).

184 **2.5 Quality assurance and quality control**

185 The instrumental detection limit (IDL) was defined using a signal-to-noise ratio of 3. The
186 method detection limit (MDL) was determined using a signal-to-noise ratio of 10 for the
187 analytes not detected in the blank samples, and for the analytes detected in the blank samples,
188 the MDLs were extrapolated under 98% confidence intervals of the concentrations in the
189 blank samples and their standard deviations. Six field blank and eight laboratory blank
190 samples were prepared. Only PFOA was found in all the blank samples, with an average
191 concentration of 33 pg/L and standard variation of 9.6 pg/L. The IDLs and MDLs for
192 individual compounds are shown in **Table S4**. Concentrations of PFASs in duplicated samples
193 showed deviation within $\pm 25\%$. Recoveries for individual ISs are listed in **Table S5**. The
194 average recoveries ranged from $38\% \pm 10\%$ for $^{13}\text{C}_8\text{-FOSA}$ to $119\% \pm 36\%$ for $^{13}\text{C}_4\text{-PFBA}$.
195 Concentrations were all corrected by the corresponding recoveries.

196 **2.6 Air Mass Back Trajectories**

197 Using NOAA's HYSPLIT model (with 50 m as the arrival height
198 (http://www.arl.noaa.gov/HYSPLIT_info.php)), 120-h back trajectory analysis of air masses
199 occurred. Air mass back trajectories for individual air samples are presented in **Figure S2**.

200 **3 Results and discussion**

201 **3.1 Concentrations and composition of PFASs in air and surface** 202 **water**

203 **3.1.1 Neutral PFASs in air**

204 In the gas phase, 10 neutral PFASs were detected, i.e., 6:2, 8:2, 10:2, and 12:2 FTOH; 8:2
205 FTAC; MeFOSA; EtFOSA; MeFBSA; EtFOSE; and MeFBSE. The concentrations of
206 individual PFASs and neutral Σ PFASs are presented in **Table S6**. Σ PFASs concentrations
207 ranged from 76 to 551 pg/m^3 . Σ FTOHs concentrations (73 to 540 pg/m^3) were one to three
208 orders of magnitude higher than Σ FTACs (<0.20 to 1.4 pg/m^3), Σ FASAs (1.3 to 11 pg/m^3),
209 and Σ FASEs (0.14 to 1.5 pg/m^3). The predominant compound was 8:2 FTOH, with
210 concentrations ranging from 55 to 430 pg/m^3 , accounting for 92% to 99% of Σ PFASs.

211 Concentrations of other FTOH homologues declined in the following order: 10:2 FTOH > 12:2
212 FTOH > 6:2 FTOH, which were consistent with those in the atmosphere above the Japan Sea
213 and North Pacific Ocean (Cai et al., 2012a). The ratios of 6:2 to 8:2 and 10:2 to 8:2 FTOHs
214 ranged from 0.01 to 0.04 and 0.08 to 0.33, respectively, and no significant differences in these
215 were found among the locations. The 6:2 to 8:2 FTOH ratios were similar to impregnating
216 agents (0.02); however, the 10:2 to 8:2 FTOH ratios were much lower than the products (0.6).
217 One possible reason for the lower 10:2 to 8:2 FTOH ratio might be the higher affinity to
218 particles because of the longer chain in the 10:2 FTOH (Wang et al., 2014b). Because particle
219 analysis was not performed in this study, this speculation could not be confirmed; therefore,
220 more research should be conducted to explain this comprehensively. The mean concentration
221 of FASAs was 4.4 pg/m³, which was significantly higher than that of FASEs (mean 0.6
222 pg/m³). FASAs last longer in air than FASEs do and have the potential to be transported
223 longer distances than FASEs (D'Eon et al., 2006). MeFBSA and MeFBSE were detected in all
224 samples, at higher concentrations than MeFOSA and Me/EtFOSE were, which could be
225 attributed to the replacement of C₈-PFASs. In the air samples from the Bohai and Yellow
226 Seas, only 8:2 FTAC was detected at low levels (<0.20–1.4 pg/m³) in the gas phase. FTACs
227 have a relatively shorter lifetime in the atmosphere and may not be transported over long
228 ranges (Butt et al., 2009)

229 **3.1.2 Ionic PFASs in surface water**

230 In the water dissolved phase, 10 PFASs were detected, i.e., C₄–C₁₀ PFCAs and C₄, C₆, and
231 C₈ PFASs, with detection frequencies from 3 to 100%. Individual and ionic Σ PFASs
232 concentrations are shown in **Table S7**. In the Bohai Sea, Σ PFASs concentrations ranged from
233 3.9 to 118 ng/L (mean 31 ng/L, median 15 ng/L). In the Yellow Sea and Yangtze River
234 Estuary, significant lower Σ PFASs concentrations than in the Bohai Sea were found, ranging
235 from 1.6 to 17 ng/L (mean 5.4 ng/L, median 3.9 ng/L) and from 1.7 to 12 ng/L (mean 4.9
236 ng/L, median 3.3 ng/L), respectively. The two highest concentrations of 108 ng/L and 118

237 ng/L were detected at sites W65 and W66 in the Laizhou Bay, Bohai Sea, where industrial
238 discharge from adjacent rivers might be major sources (Wang et al., 2014a). Excluding these
239 two sites, concentrations were all below 61 ng/L, indicating less discharge volume and a
240 strong dilution effect.

241 \sum PFACs concentrations (1.4 to 117 ng/L) were dramatically higher than \sum PFASAs (0.1 to
242 1.3 ng/L) in the studied region. PFOA was the predominant compound, which accounted for
243 51% to 90% of the \sum PFASs concentrations. The higher concentrations of PFOA in the Bohai
244 Sea (mean 26 ng/L) than in the Yellow Sea (median 3.8 ng/L) and the Yangtze River Estuary
245 (mean 2.9 ng/L) were mainly due to the large inputs from the Laizhou Bay coast (Heydebreck
246 et al., 2015) and the weak water exchange capacity of the Bohai Sea. The contribution of
247 PFBA to \sum PFASs varied from 1% to 10% and its concentrations were comparable in the
248 studied region (with a mean of 0.67 ng/L in the Bohai Sea, 0.22 ng/L in the Yellow Sea, and
249 0.23 ng/L in the Yangtze River Estuary). PFBA was introduced a substitute after PFOA was
250 voluntarily phased-out. In China, relatively high concentrations of PFBA (up to 6280 ng/L)
251 have been reported in an inland aquatic system (Tangxun Lake) (Zhou et al., 2013). However,
252 the concentration of PFBA in the current study was relatively low (mean of 0.23 ng/L).
253 Another substitute, PFHxA, had comparable contributions as PFBA did, with a range from
254 3% to 12% and concentrations ranging from 0.2 to 4.1 ng/L (Bohai Sea: 1.4 ng/L, Yellow Sea:
255 0.40 ng/L, and Yangtze River Estuary: 0.55 ng/L). The low levels of alternative homologues
256 (PFBA and PFHxA) and high levels of legacy ones (PFOA) indicate that manufactory
257 structure had not been changed in the coastal region of North China until 2012. Other PFCA
258 homologues contributed little to the \sum PFCA concentrations. PFPA and PFHpA had average
259 compositions of 7% and 4%, respectively. Longer-chained PFCA (C>8) were not detected in
260 most of the surface water samples. Gao et al. (2014) reported high detection frequency of
261 PFDA and PFUnDA in sediment and attributed the degradation of precursors as the cause. In
262 the surface waters, PFDA and PFUnDA concentrations were below the detection limit (0.02

263 ng/L). Because the longer-chained PFASs have a higher affinity for organic matter and
264 particles, they might be transported by suspended matter from the sea surface to the sediment.
265 PFOS accounted for 4% of \sum PFASs concentrations, which was significantly lower than that
266 of PFOA. The concentrations ranged from <0.03 to 0.1 ng/L (mean: 0.07 ng/L). Similar
267 composition patterns of PFOA and PFOS were reported for the Bohai Bay (Wang et al.,
268 2015a) and south Bohai coastal rivers (Wang et al., 2014a). PFBS, which was a substitute of
269 PFOS, occurred at concentrations from <0.04 to 0.9 ng/L. FOSA, a neutral PFAS, was
270 detected in 36% of the water samples in concentrations ranging from <0.03 to 0.36 ng/L
271 (mean: 0.10 ng/L). FOSA is an intermediate of the (bio)transformation of Et-FOSA(E) to
272 PFOS. The occurrence of FOSA indicated the (bio)degradation from precursors to PFOS in
273 coastal water.

274 **3.2 Distributions, sources, and transportation of PFASs**

275 The spatial distribution of neutral PFASs in marine boundary air is presented in [Figure 1](#)
276 and the air mass back trajectories for each air sample are shown in [Figure S2](#). Samples
277 collected in the South Yellow Sea (A1–A6) had higher \sum PFASs concentrations (76 to 511
278 pg/m^3 , mean: 302 pg/m^3) than those from the North Yellow and Bohai Seas (A8–A14) (85 to
279 223 pg/m^3 , 146 pg/m^3). Air masses of A1–A3 were mainly from the coast around the Yellow
280 Sea with \sum PFASs concentrations ranging from 192 to 296 pg/m^3 . Li et al. (2012) reported
281 comparable \sum PFASs concentrations in Yellow Sea coastal cities of China (from 113 to 306
282 pg/m^3). The mean concentration of \sum FTOHs and \sum FASEs+FASAs in Korean outdoor air
283 were 19731 and 260 pg/m^3 , respectively (Kim et al., 2012), which suggested attribution to one
284 significant source. Concentrations of \sum PFASs in samples A4–A6 ranged from 374 to 551
285 pg/m^3 with the air masses coming from the Shandong, Zhejiang, and Jiangsu coastal regions,
286 which are the most industrialized and urbanized regions of China. In spite of the air masses
287 coming mainly from the south Yellow Sea, the \sum PFASs concentration for site A8 was
288 comparable with those for A1–A3, suggesting good mixture and weak degradation/deposition

289 in the south Yellow Sea atmosphere. Air masses for sites A9–A11, from the Korea Peninsula
290 coast and Japan Sea, had lower \sum PFASs concentrations (170 to 220 pg/m^3) than those from
291 the south Yellow Sea (A1–A8, 192 to 511 pg/m^3). Cai et al. (2012) reported a neutral PFASs
292 concentration in the gas phase of 346 pg/m^3 in the Japan Sea, which supported the conclusion
293 of long-range transport of modeling. Samples A12–A16 represented continental air from
294 Mongolia and Russia and their \sum PFAS concentrations (85 to 98 pg/m^3) were lower than the
295 Asian background sites (110 to 140 pg/m^3) (Li et al., 2011b).

296 The results of Pearson relationship tests are listed in **Table S8**. Concentrations of FTOH
297 homologues were significantly related, indicating similar sources. MeFBSA was highly
298 correlated with FTOHs, suggesting the application of C_4 precursors. Interestingly, FOSE/As
299 were not related to each other as much as other PFASs were. The global regulation of C_8
300 compounds might lead to complex sources other than mainly C_8 pollution. Moreover, the
301 legacy precursors have different particle affinities and undergo different degradation
302 pathways, which might be the reasons for weak relationships between each other.

303 The spatial distributions of \sum PFASs in surface water are presented in **Figure 2**. PFOA,
304 which showed a similar distribution pattern, was discussed together with \sum PFASs (**Figure S3**).
305 Relatively high concentrations of \sum PFASs/PFOA were distributed at the mouth of Laizhou
306 Bay (W63–67, transect LZ), the southern part of Bohai Sea. The west part (W63 and W64) of
307 the Laizhou Bay mouth had lower concentrations than the east part did (W65–67). The west
308 part is influenced mainly by the Yellow River, which has suffered from decreasing water
309 discharge and serious pollution in recent years (Gao et al., 2008; He et al., 2006). The east
310 part is the gateway through which coastal water as well as adjacent river water move out of
311 the Laizhou Bay. Wang et al. (2014) investigated PFASs concentrations in surface water from
312 nine rivers emptying into the Laizhou Bay in 2011. In the Xiaoqing River, \sum PFASs
313 concentrations reached 5.07 $\mu\text{g}/\text{L}$. PFOA contributed about 90% of the \sum PFASs, which was
314 similar to the current study. Three years later, Heydebreck et al. (2015) reported extremely

315 high concentrations of PFOA, up to 579 $\mu\text{g/L}$, in the same river. Both groups stated that
316 wastewater from the fluoropolymer industry was the major source of PFOA, making the
317 Xiaoqing River a hotspot. Although there were biases because of different sampling locations
318 and measurement methods, the increasing trend was confirmed considering the lack of
319 regulation of PFOA in China.

320 In the Bohai Bay, the western part of Bohai Sea, from W55 to W57 (transect B),
321 concentrations of $\sum\text{PFASs}$ increased from north (9.4 ng/L at W57) to south (23.5 ng/L at
322 W55), with an inverse trend in salinity (31.2 PSU at W57 and 30.5 at W55). Similar trends
323 were found in 2011–2013 by Wang et al. (2015). Considering significant relationship between
324 the freshwater ratio (FWR) and the PFASs concentrations as well as the semiclosed
325 geographical conditions, the freshwater input might be the major source. Correspondingly,
326 relatively higher concentrations of PFASs were reported in the Haihe River (Li et al., 2011a),
327 the Yellow River Delta (Wang et al., 2015a), and the Yellow River Estuary (W63). For the
328 Liaodong Bay (the northern part of Bohai Sea) transect (W51, W52, W53, W58, and W59,
329 transect LD), comparable concentrations around 6 ng/L were found, except for site W59.
330 Coastal water in the Liaodong Bay may be trapped for some time before it is exchanged with
331 the open sea. It took at least three years for pollutants in the Liaodong Bay to reach half their
332 original concentrations (Wei et al., 2002). Before transportation through the mouth of the bay,
333 pollutants from direct sources might have been diluted well and therefore diffused.

334 Bohai Strait is the gateway for water exchange between the Bohai Sea and the Yellow Sea.
335 Bohai Sea surface water runs through the southern strait and Yellow Sea surface water runs
336 through the northern strait. For the Bohai Strait sampling transect (W48–50, transect BS), an
337 increasing trend of $\sum\text{PFASs}$ concentrations was found from north to south (from 3.06 to 10.5
338 ng/L), indicating the diffusion of PFASs from the Bohai Sea to the Yellow Sea.

339 In the Chinese Yellow Sea, $\sum\text{PFASs}$ concentrations were higher near the coast than in open
340 waters. No point sources of PFASs were found along the Yellow Sea coast. Ju et al. (2008)

341 and Chen et al. (2012) investigated PFOA and PFOS along the Dalian coast. Concentrations
342 of PFOA (0.17 to 95.7 ng/g) were significantly higher than of PFOS (<0.10 to 2.3 ng/g). On
343 the other side of the Yellow Sea coast, Σ PFASs of around 10 ng/L suggested normal levels
344 for the Korean coast (Naile et al., 2010). The marine current in the Yellow Sea was weak and
345 the Lagrangian residual current was mostly wind-driven. The Yellow Sea coastal current
346 transports water from north to south, which was conducive for pollutants from the Shandong
347 Peninsula to dilute and diffuse. The warm Yellow Sea current delivers water from south to
348 north and pollutants from the South Korean coast could be carried into the Bohai Sea.

349 The distribution of PFBA in Bohai and Yellow Sea was similar to PFOA as well as other
350 PFCAAs (Figure 3), whereas, one significant difference was comparable concentrations in the
351 Yangtze River Estuary to Shandong Peninsula. For PFSAAs, the Yangtze River Estuary was
352 the major source. In previous studies, concentrations of PFOS up to 703.3 ng/L were reported
353 by Pan et al. (2010) for the Yangtze River Delta. Xie et al. (2013) and Wang et al. (2015)
354 investigated the industrial and domestic emission of PFOS in China in 2010. The emission
355 density around the Yangtze River Delta was higher than for the coasts of the Bohai and
356 Yellow Seas. Moreover, the provinces that the Yangtze River runs through, for instance,
357 Hubei and Jiangxi, had higher emission volumes than other central areas of China, which
358 could elevate the PFOS concentrations for the Yangtze River Estuary. FOSA presented a
359 unique distribution pattern (Figure S3). The coasts of Qingdao City, China and South Korea
360 were the major sources of FOSA in the Yellow Sea water. FOSA is the product of neutral
361 PFASs and one precursor of PFOS. The occurrence of FOSA in this surface water suggested
362 indirect sources of ionic PFASs in the Bohai and Yellow Seas.

363 **3.3 Comparison of PFASs concentrations in air and surface water**

364
365 The neutral PFASs concentrations are presented in Table S9. Concentrations of 8:2 FTOH in
366 the air above the Bohai and Yellow Seas were comparable with those detected in urban and

367 rural areas on the Chinese continent (14.4 to 498 pg/m³) (Li et al., 2011b). Other FTOH
368 congeners (6:2, 10:2, and 12:2 FTOH) had higher concentrations in the continental air than in
369 the sea air. Comparing with other coastal regions worldwide, 8:2 FTOH/ Σ FTOHs
370 concentrations in the air above the Bohai and Yellow Seas were significantly higher than
371 those of the air above the South China Sea (12.5 to 75.5 pg/m³/17.8 to 106 pg/m³) (Lai et al.,
372 2016), German coast (4.5 to 85 pg/m³/7.3 to 146 pg/m³) (Wang et al., 2014b), Japanese coast (<
373 0.4 to 5.0 pg/m³) (Piekarz et al., 2007), and east coast of the USA (1.65 to 91.3/5.46 to 156
374 pg/m³) (Shoeib et al., 2010). Concentrations of MeFBSA/E in the air were higher than those
375 in the air above the North Atlantic Ocean (0.09 to 0.57 pg/m³/0.11 to 0.44 pg/m³), but lower
376 than those in Chinese continental air (3.11 to 64.9 pg/m³/nd to 2.19 pg/m³), North Sea coastal
377 air (nd to 4.6 pg/m³/0.1 to 3.9 pg/m³), and western Antarctic Peninsula coastal air (0.2 to 14.1
378 pg/m³/0.4 to 5.4 pg/m³). As for FASA/E, concentrations in air from the Bohai and Yellow
379 Seas were comparable with those reported at Büsum on the German coast (0.4 to 13 pg/m³/0.5
380 to 3.6 pg/m³) for samples collected in 2011–2012 (Wang et al., 2014b). In most of the
381 northern hemisphere, including the Arctic region (Ahrens et al., 2011), North Atlantic Ocean
382 coast of Europe (Jahnke et al., 2007), Japan Sea to the Arctic Ocean (Cai et al., 2012a), and
383 east coast of the USA (Shoeib et al., 2010), concentrations of FASEs were higher than those
384 in the air of the Bohai and Yellow Seas, whereas concentrations of FASAs had an inverse
385 pattern.

386 **Table S10** presents the PFOA and PFOS concentrations in coastal and marine surface
387 waters of China. The concentrations of PFOA (2.3 ng/L to 106 ng/L) in the Bohai Sea water
388 in the current study were comparable with those for the Dalian Coast (1.5 ng/L to 95.7 ng/L)
389 (Chen et al., 2012) and the north coast of the Bohai Sea (2.58 ng/L to 81.7 ng/L) (Wang et al.,
390 2011), but were higher than those found by Wang et al. (2015a) for the Bohai Bay (5.1 to 40.3
391 ng/L). The PFOA concentrations in the Yellow Sea (0.89 ng/L to 14 ng/L) and Yangtze River
392 Estuary (0.98 ng/L to 6.9 ng/L) were comparable with those for coastal areas of Hong Kong

393 (0.67 ng/L to 5.5 ng/L), but higher than those for the east and south Chinese coasts (0.04 ng/L
394 to 1.5 ng/L) (Cai et al., 2012b) and the South China Sea (0.16 ng/L to 0.42 ng/L) (Yamashita
395 et al., 2005). Compared to other coastal areas globally, the PFOA concentrations in Bohai Sea
396 water were similar to those in Tokyo Bay water (2.7 ng/L to 63 ng/L), which is a semiclosed
397 bay in Japan (Sakurai et al., 2010) and the estuarine and coastal areas of South Korea (2.95
398 ng/L to 68.5 ng/L) (Naile et al., 2010). The concentrations of PFOA in the waters of the
399 Yellow Sea and Yangtze River Estuary were similar to those in the Baltic Sea (0.25 ng/L to
400 4.45 ng/L) (Ahrens et al., 2010), but higher than those in the waters of the North Sea (<0.2
401 ng/L to 2.43 ng/L), coastal Norway (0.07 ng/L to 0.35 ng/L) (Ahrens et al., 2010), and
402 Catalanian coast, Spain (0.07 ng/L to 1.86 ng/L) (Sánchez-Avila et al., 2010).

403 The PFOS concentrations in the waters of the Bohai Sea (<0.03 ng/L to 0.12 ng/L), Yellow
404 Sea (<0.03 ng/L to 0.11 ng/L), and Yangtze River Estuary (<0.03 ng/L to 0.20 ng/L) were
405 comparable with those for the Dalian coast, China (0.1 ng/L to 0.2 ng/L) (Chen et al., 2012),
406 east to south Chinese coasts (0.02 ng/L to 0.07 ng/L) (Cai et al., 2012b), and South China Sea
407 (0.008 ng/L to 0.11 ng/L) (Yamashita et al., 2005), but lower than those Wang et al. (2015a)
408 found in the semiclosed Bohai Bay (2.2 to 15.8 ng/L) (Wang et al., 2015a) (Wang et al.,
409 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a)
410 (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et
411 al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a)
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413 al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al., 2015a) (Wang et al.,
414 2015a). Compared with other coastal areas worldwide, the PFOS concentrations in this study
415 were lower than those found in Asian and European coastal areas, i.e., the coastal area of
416 Hong Kong, China (0.07 ng/L to 2.6 ng/L) (Yamashita et al., 2005), coastal area of Japan
417 (<2.5 ng/L to 59 ng/L) (Taniyasu et al., 2003), North Sea (0.2 ng/L to 2.68 ng/L), and
418 Catalanian coast, Spain (0.05 ng/L to 3.93 ng/L) (Sánchez-Avila et al., 2010), but were at

419 similar levels to waters of the European coast of Atlantic Ocean (0.061 ng/L to 0.192 ng/L)
420 (Benskin et al., 2012) and the east coast of the United States (0.046 ng/L to 0.191 ng/L)
421 (Benskin et al., 2012).

422 Kwok et al. (2015) investigated the PFOA and PFOS levels in the South China Sea in the
423 same year (2012) as the current study. Concentrations of PFOA in the South China Sea in
424 2012 were significantly lower than those in the Bohai Sea, Yellow Sea, and Yangtze River
425 Estuary were. In contrast, the PFOS concentrations in the South China Sea were higher than
426 those were for the seas focused on in this study. Additionally, the PFOS concentrations were
427 higher than the PFOA concentrations in the South China Sea, and the same compositional
428 pattern occurred in the surface river waters from the Pearl River or Pearl River Estuary (Liu et
429 al., 2015; Pan et al., 2014a; So et al., 2007; Zhang et al., 2013). However, an inverse pattern
430 occurred in the Bohai Sea, Yellow Sea, and Yangtze River Estuary, as well as most other
431 rivers studied in China. One reason for this is that studies on PFOA and PFOS in Chinese
432 surface waters were conducted mainly after 2002, the year in which the production of PFOS
433 and related compounds in North American and European countries dramatically decreased
434 because of the voluntarily phased-out. Although the manufacturing of PFOS in China
435 increased from 2002, the volume was much lower than it was globally before 2002 (MEP,
436 2008). Moreover, the introduction of a shorter-chained substitute led to higher concentrations
437 of PFBS than of PFOS in industrial parks (Chen et al., 2015a; Jin et al., 2015) as well as inland
438 lakes (for instance, the Tangxun Lake). Differing from PFOS, the voluntary phase-out of
439 PFOA was much later (2015), and until recently, no global legislation had been proposed, as
440 it was for PFOS. Only one study involved collecting river samples from the Hun River in
441 Liaoning Province in 2002, which had significantly higher concentrations of PFOS (0.2 to
442 44.6 ng/L) than PFOA (<0.1 to 1.6 ng/L) (Jin et al., 2009).

443 **3.4 Inventories of PFOA and PFOS in the Chinese Bohai Sea, Yellow** 444 **Sea, and Yangtze River Estuary**

445 To estimate the inventory of PFASs in the Chinese Bohai Sea, Yellow Sea, and the Yangtze
446 River Estuary surface water, the boundary of the studied region was defined following the
447 distribution results generated by the Ocean Data View (Germany) software. The study area
448 was divided into 62 blocks depending on sampling site locations. Each sampling site was set
449 in the center of a block and the concentration at the sampling site was used as the
450 concentration for the whole block. The inventory (I) was calculated according to the
451 following equation:

$$452 \quad I = \sum_{i=1}^{62} C_i A_i D$$

453 where C_i is the concentration in each block; A_i is the area of each block; D is the disturbed
454 depth, which in this study was assumed as 30 cm, the height of the bucket; and I is the sum of
455 the inventory of all 62 blocks. The inventories of PFASs are presented in [Table S11](#). The
456 studied region covered about 35.3 km². The inventories of PFOA and PFOS were 646 kg and
457 7.6 kg, respectively, which suggested a larger release volume of PFOA than of PFOS.
458 Compared with the release of PFOS studied by Xie et al. (2013) and Wang et al. (2015b) the
459 inventories of PFOS in the surface waters in the current study were comparable to the
460 domestic release in Qingdao City, China and far lower than the industrial release from the
461 Chinese coast. More PFOS might be stored in deeper water, surface runoff, groundwater, near
462 shore water, and other aquatic mediums. The inventory of PFBS was 23 kg, which was
463 significantly higher than that of PFOS, indicating a shift from C₈-PFSA to C₄-PFSA
464 homologues. The inventories of shorter-chained PFCAs (C₄–C₇) were similar, but one order
465 of magnitude lower than those for PFOA were.

466 Riverine input might be the major contributor of PFASs in marine waters. In 2007, 2008,
467 and 2011, Wang et al. (2012) and Wang et al. (2014a) investigated 22 main rivers that deliver
468 water into the Bohai Sea. The calculated input masses of PFOA and PFOS were 4160 kg/a

469 and 171 kg/a, respectively. The PFOA volume was 24 times higher than that of PFOS was. In
470 this study, the inventory of PFOA (374 kg) was 311 times higher than it was for PFOS (1.2 kg)
471 in the Bohai Sea. PFOS might undergo different processes from PFOA during diffusion and
472 transportation from estuaries to the sea. For example, due to the sulfonate group (Higgins and
473 Luthy, 2006), PFOS has a stronger affinity for particles and organic matter than PFOA does.
474 PFOS in water might easily adsorb to sediment or accumulate in biota. Moreover, relatively
475 high concentrations of 8:2 FTOH in the air suggested larger input volumes of PFOA than
476 PFOS from indirect sources. Assuming the yield of PFOA from 8:2 FTOH was about 1.5%,
477 the indirect sources contributed PFOA from about 0.83 to 6.4 pg/m³. More studies should be
478 conducted to explain the sources and transportation of PFASs systematically.

479 **4. Conclusion**

480 In May 2012, 12 neutral PFASs and 17 ionic PFASs were investigated in air and surface
481 water of the Bohai Sea, Yellow Sea, and Yangtze River Estuary. Concentrations of neutral
482 PFASs in the gas phase were consistent with those reported in urban and rural regions of
483 China. Compared to other studies about marine air, Chinese seas in this study had high
484 concentrations. The air mass back trajectory analysis suggested complex sources. Air masses
485 with higher concentrations mainly came from the coast of the Yellow Sea including the
486 Chinese and South Korean sides, whereas air masses with lower concentrations mainly came
487 from the Yellow Sea and Japan Sea, northeastern China, Mongolia, and Russia. PFOA was
488 the predominant ionic congener, accounting for 51%–90% of ionic \sum PFASs. The spatial
489 distribution indicated that the major source of PFCAs was located around the Laizhou Bay,
490 whereas for PFSAs, the Yangtze River Estuary had higher concentrations than other areas.
491 The semiclosed geographical conditions influenced the diffusion, dilution, and exchange of
492 PFASs in the Bohai Sea. The direct release from industrial and domestic activities were the
493 main sources because the degradation from neutral PFASs was supposed to be slow and small.
494 The inventories of PFOS and PFOA in the studied region were estimated to be 7.6 kg and 646

495 kg, respectively. Because of the lack of study, the PFOA inventory could not be compared
496 with the release. More systematical study should be conducted to illustrate whether the
497 surface water is the sink of PFOS and PFOA.

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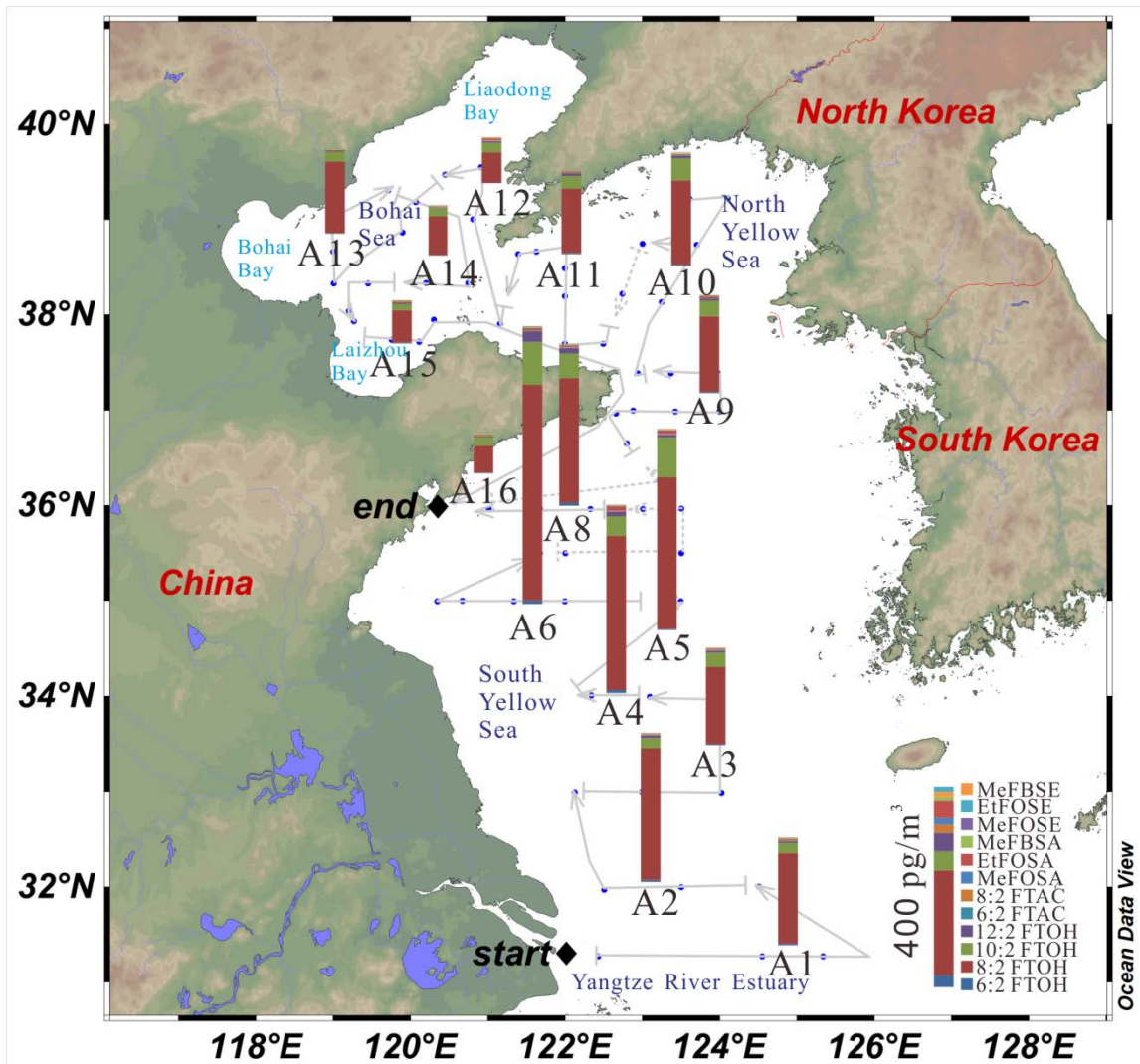
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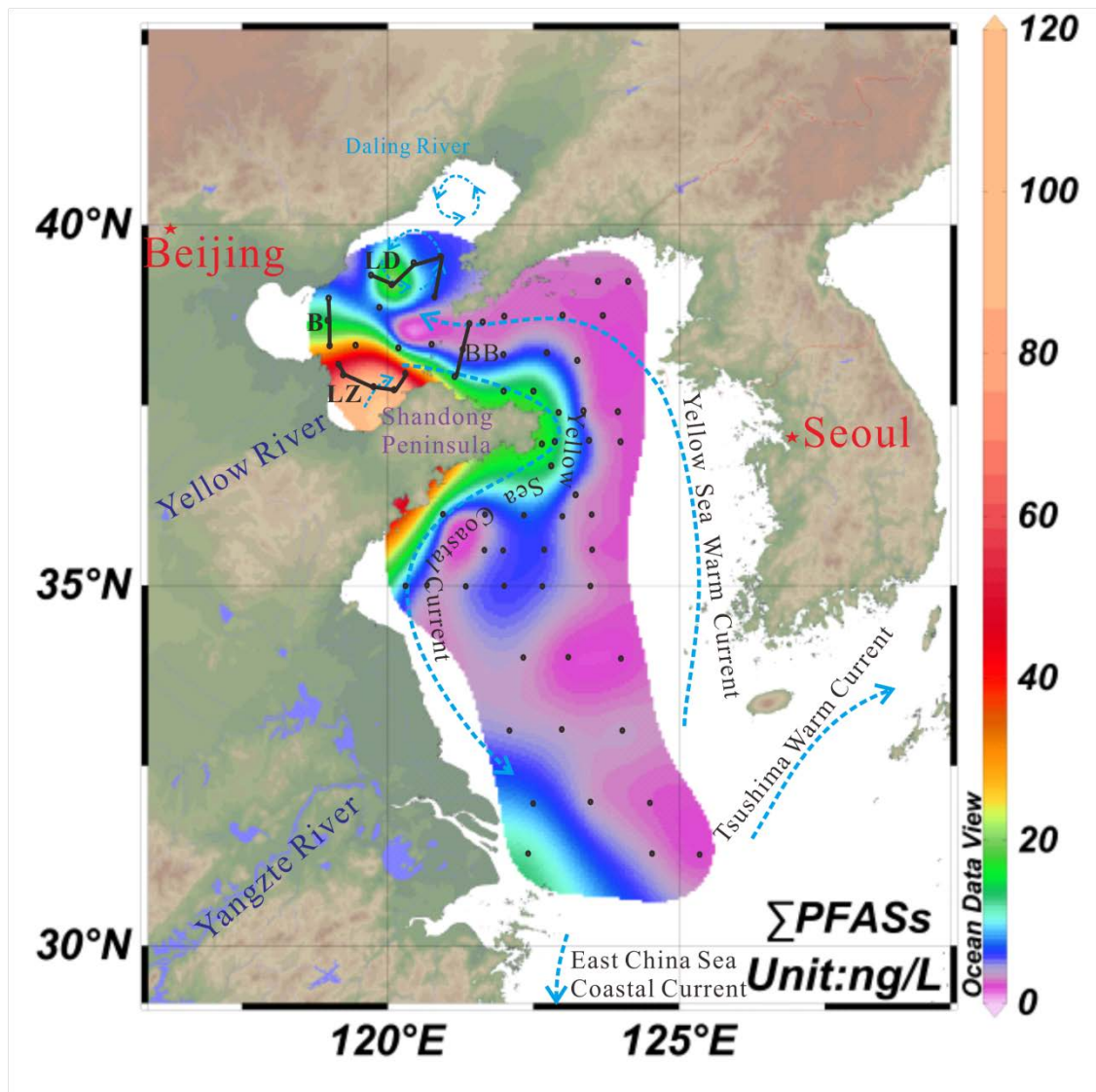
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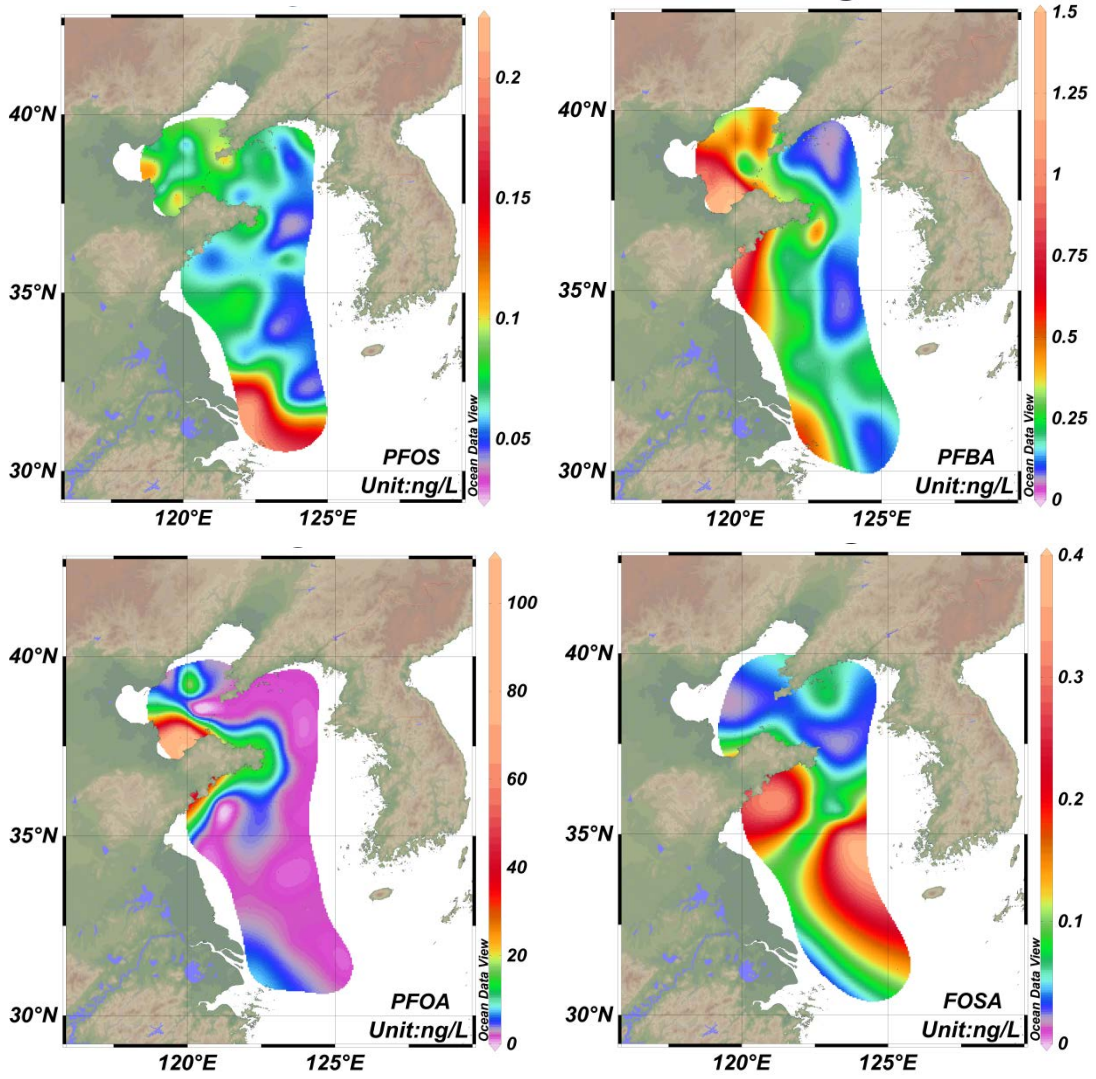
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Figure 1. Concentrations (pg/m^3) and distribution of neutral PFASs in air. Gray solid (air samples collected) and dotted (without air samples) lines show the sampling routes during the cruises from start (Shanghai) to end (Qingdao).



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Figure 2. Concentrations (ng/L) and distributions of ionic Σ PFASs in the surface waters of the Bohai Sea, Yellow Sea, and Yangtze River Estuary. Blue dotted lines with arrows indicate the direction of the marine current. Black dots represent the sampling sites. Black solid lines show the sampling transects.



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Figure 3 Concentrations (ng/L) and distributions of PFOS, PFBA, PFOA, and FOSA in the surface waters of the Bohai Sea, Yellow Sea, and Yangtze River Estuary.