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1 **Multimedia fate and transport simulation of Perfluorooctanoic**
2 **Acid/Perfluorooctanoate in an urbanizing area**

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23 **Abstract**

24 Strong global demand leads to significant production of fluoropolymers (FP) in China
25 which potentially release large quantities of Perfluorooctanoic Acid/
26 Perfluorooctanoate (collectively called PFOA/PFO) to the environment. Modelling
27 the fate and transport of PFOA/PFO provides an important input for human health
28 risk assessment. Considering the effects of urbanization and existing forms of
29 PFOA/PFO, this study used the modified multispecies Berkeley-Trent-Urban-Rural
30 model to simulate the transfer behavior of PFOA/PFO in the Bohai Rim, China.
31 Spatial distributions of PFOA/PFO emissions during the year 2012 for the study area
32 were illustrated. About two thirds of the total amount of PFOA/PFO was estimated to
33 be released into fresh water, and the total releases to rural areas were 160-fold higher
34 than those to urban areas due to the location of fluorochemical industrial parks. The
35 simulations predicted that hydrosphere was the fate of PFOA/PFO, followed by soil
36 and vegetation, which was consistent with field data. The highest PFOA/PFO
37 concentration was modeled in the Xiaoqing River basin with a value of 32.57 $\mu\text{g/L}$.
38 The PFOA/PFO concentrations in urban soils were generally higher than those in
39 rural soils except for grids 1, 3 and 46. In addition, it was estimated that the total flux
40 of PFOA/PFO entering into the Bohai Sea was 24.57 ton/year, 100-fold higher than
41 that of perfluorooctane sulfonates (PFOS).

42 **Keywords:** PFOA/PFO, multimedia model, hydrosphere, coastal region, China

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44

45 1. Introduction

46 Perfluorocarboxylates (PFCAs), belonging to the perfluoroalkyl acids (PFAAs)
47 family, are synthesized persistent perfluorochemicals which are frequently found in
48 the environment. Their specific structure makes them hydrophobic and resistant to
49 chemical degradation like oil, acid, heat or other forces (Armitage et al., 2009; Giesy
50 and Kannan, 2001; Su et al., 2016; Su et al., 2017; Vaalgamaa et al., 2011). They have
51 been widely used in various commercial and industrial applications, such as
52 electronics, food containers, polymers, carpets, caulks, fabric, shampoos, and
53 fire-fighting foams (Meng et al., 2017; Vaalgamaa et al., 2011; Wang et al., 2012).
54 Among PFCAs, the perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO)
55 (collectively referred as PFOA/PFO) have aroused a great concern because of their
56 frequent detection in the environment at the highest concentrations in recent years
57 (Wang et al., 2016a; Wang et al., 2012).

58 PFOA/PFO have the typical characteristics of persistent organic pollutants
59 (POPs), that is why the 3M company phased out the production in 2002. The U.S.
60 Environmental Protection Agency (USEPA) initiated the voluntary *2010/2015 PFOA*
61 *Stewardship Program* in 2006, and subsequently in the year 2015 the European
62 Council suggested that PFOA/PFO should be listed in the Stockholm Convention on
63 POPs (Meng et al., 2017). However, the industrial production of PFOA/PFO primarily
64 shifted from developed regions like North America and Europe to Asia (Armitage et
65 al., 2009; Paul et al., 2008; Wang et al., 2016a). Nowadays in Asia, China has become
66 the largest producer and contamination hotspot of PFOA/PFO, with frequent detection

67 at higher levels in various media around the fluorochemical manufacturing sites (Bao
68 et al., 2010; Li et al., 2015; Meng et al., 2017; Wang et al., 2016a; Wang et al., 2016b;
69 Wang et al., 2010; Wang et al., 2014b; Zhang et al., 2006).

70 The study area Bohai Rim is one of the most prosperous, urbanized and
71 industrialized regions in China (Liu et al., 2015). A variety of chemical production,
72 metal plating, printing, steel piping industries are widely distributed. Particularly,
73 there are some fluorochemical industrial parks located in the cities of Fuxin, Jinan and
74 Zibo of this region (Chen et al., 2017; Liu et al., 2017; Liu et al., 2016; Su et al., 2016;
75 Su et al., 2017; Wang et al., 2014a; Wang et al., 2016a; Wang et al., 2016b), which
76 released significant amount of PFOA/PFO into the surrounding environment.
77 Additionally, several studies have reported that PFOA is the predominant congener in
78 the ambient environment (soil, fresh water, sediment, dust, and dietary food like crops,
79 home produced eggs) of the Bohai region, posing potential health risks to local
80 residents (Liu et al., 2017; Su et al., 2016; Su et al., 2017; Wang et al., 2014a; Wang et
81 al., 2016a; Wang et al., 2016b; Wang et al., 2015). As it is difficult to monitor the
82 levels of PFOA/PFO in all environmental compartments on a large scale, therefore
83 using multimedia fate models may be a suitable technique to simulate concentrations
84 and the transport behavior of PFOA/PFO.

85 Earlier the Berkeley-Trent (BETR) model has been successfully used to simulate
86 the fate and distribution of various chemicals on both the global and regional scales
87 (Liu et al., 2014; Liu et al., 2015; Prevedouros et al., 2004a; Prevedouros et al., 2004b;
88 Toose et al., 2004). Furthermore, our previous studies have proved that the

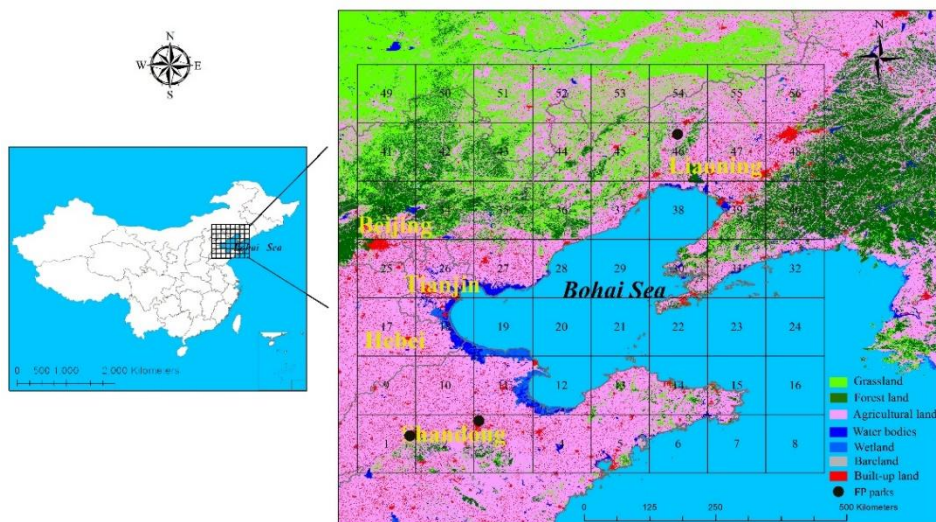
89 BETR-Urban-Rural model considering the effects of urbanization is more accurate to
90 model the concentrations of chemicals like PAHs and PFOS (Song et al., 2016; Su et
91 al., 2018a; Su et al., 2018b).

92 In this study, we applied the modified BETR-Urban-Rural model to simulate the
93 transport and fate of PFOA/PFO in the Bohai Rim, China. The main objectives of the
94 study are: 1) to estimate the spatial distribution of PFOA/PFO releases to all
95 environmental compartments in the Bohai Rim of China during the year 2012; 2) to
96 model the transport, fate and disposition of PFOA/PFO in the study area.

97 **2. Methods and Materials**

98 2.1 Study area

99 The study area Bohai Rim is geographically stretched between 36°N to 43°N
100 latitude and 116°E to 124°E longitude, and divided into 56 subsegments by 1°×1°
101 (Fig. 1). It is located in northern China, including five provinces namely Beijing city,
102 Tianjin city, parts of Shandong, Hebei, and Liaoning provinces. In the model, the 56
103 subsegments are linked by advection of air and water. Additionally, the role of the
104 upper air on transport is considered to be limited (Liu et al., 2014; Song et al., 2016;
105 Su et al., 2018a; Su et al., 2018b).



106

107

Fig. 1 Land use types of the study area with model segmentation.

108 2.2 Model description

109 The BETR-Urban-Rural model is based on the fugacity approach of the
 110 segmented multimedia BETR model (Liu et al., 2015; Liu, 2014; Mackay, 2001;
 111 MacLeod et al., 2001). The BETR-Urban-Rural model upgrades the BETR model by
 112 distinguishing the differences of POPs emissions and distributions between urban and
 113 rural areas. In this improved model, each segment contains 9 environmental
 114 compartments: upper air, lower rural air, lower urban air, vegetation, fresh water, fresh
 115 water sediment, rural soil, urban soil, and coastal water. Four kinds of processes are
 116 depicted in the model: 1) emissions to compartments, 2) intermedia transport, 3)
 117 advection by air or water, and 4) degradation (Fig. S1). More details about the
 118 BETR-Urban-Rural model structure and parameterization are available in our
 119 previous work (Song et al., 2016).

120 As both the anionic (PFO) and neutral (PFOA) forms of PFOA/PFO are usually
 121 present in the environment (Burns et al., 2008), the acid dissociation constant (pK_a) is

122 essential to understand and model the transport and fate of PFOA/PFO. Here, we
123 specify the physical-chemical properties of PFOA/PFO for both forms, where the pK_a ,
124 and environmental pH are used by applying the distribution ratio approach to describe
125 the exchange processes for PFO and PFOA simultaneously (Armitage et al., 2009;
126 Schwarzenbach et al., 2003). The more acidic the immediate aqueous environment is,
127 the greater the proportion of PFOA will be (Barton et al., 2007). Taking the organic
128 carbon partition coefficient (K_{oc}), and the air/water partition coefficient (K_{AW}) as
129 examples, the calculations are as follows (Eq. (1)-(3)) (Armitage et al., 2009).

$$130 \quad \text{Ratio} = 10^{(pH-pK_a)} \quad (1)$$

$$131 \quad D_{oc}^{PFOA/PFO} = \frac{1}{1+Ratio} K_{oc}^{PFOA} + \frac{Ratio}{1+Ratio} K_{oc}^{PFO} \quad (2)$$

$$132 \quad D_{AW}^{PFOA/PFO} = \frac{1}{1+Ratio} K_{AW}^{PFOA} \quad (3)$$

133 where pH means the pH value of the environmental media, $D_{oc}^{PFOA/PFO}$ is the
134 effective K_{oc} and $D_{AW}^{PFOA/PFO}$ is the effective K_{AW} for both forms of the compounds,
135 respectively. K_{oc}^{PFOA} and K_{oc}^{PFO} in the equations represent the partitioning
136 coefficients of the neutral and anionic PFOA/PFO forms, respectively (Armitage et al.,
137 2009). Therefore, in this study, the modified multispecies BETR-Urban-Rural model
138 was used to simulate the transport behavior and fate of PFOA/PFO on a steady
139 solution.

140 2.3 Parameterization

141 Emission rates of POPs, physical-chemical properties of POPs, environmental
142 parameters, and air/water flux matrixes of the study area were necessary to run the

143 model. The key physical-chemical properties of PFOA and PFO considered in the
 144 BETR-Urban-Rural model at 20 °C are listed in Table 1, including K_{oc} , K_{AW} , pK_a ,
 145 and degradation half-lives of the compartments. Here, we used the physical-chemical
 146 properties of ammonium perfluorooctanoate (APFO) to represent those of PFO
 147 because APFO is the most likely existing salt in the environment (Barton et al., 2007).
 148 For the pK_a of PFOA, we used the value 3.8 reported by Burns et al. (2008). When
 149 PFOA/PFO emitted to the environments, they were not expected to undergo either
 150 appreciable abiotic or biotic degradation, or volatilization (Armitage et al., 2006;
 151 Pistocchi and Loos, 2009). Their degradation rates were assumed to be about 0.01%
 152 per year for both PFOA and PFO for all compartments (Armitage et al., 2009) except
 153 for fresh water (3558 years) and coastal water (5990 years) (Vaalgamaa et al., 2011).

154 Table 1 Physical- chemical properties of PFAAs at 20 °C*

Properties	MW	M.P.	Solub	V.P.	Log(K_{oc})	Log(K_{AW})	pK_a
PFOA	414.1	53	3500	2.2	2.06	-2.4	3.8
PFO (APFO)	431.1	161	14200	-	2.00	-	-
PFOS	538.54	400	519	-	2.7	-	-

155 Notes: molar mass (MW, g/mol), melting point (M.P., °C), aqueous solubility (Solub,
 156 g/m^3), vapor pressure (V.P., Pa), K_{oc} (organic carbon partition coefficient, L/kg), K_{AW}
 157 (air/water partition coefficient). *(Barton et al., 2007; Burns et al., 2008; Liu et al.,
 158 2015; Su et al., 2018b; Yu et al., 2009).

159 Besides, the environmental parameters, and air/water flux matrices for the Bohai
 160 Rim for the year 2012 were collected using the methodology of (Liu et al., 2015).

161 Parameters like compartmental densities and scavenging ratios were obtained from
162 the literature or the model default set values. The spatially dependent parameters like
163 land cover information, temperature, precipitation were extracted from the remote
164 sensing and satellite data which were collected from National Geomatics Center of
165 China, and the National Aeronautics and Space Administration (NASA). The air and
166 water flow matrices were constructed through air and water flow rates. For all of the
167 above time-dependent parameters, the average annual values were used. Detailed
168 information about the data sources and parameterization methods are available in the
169 previous studies (Liu, 2014; Liu et al., 2014; Liu et al., 2015).

170 2.4 Emission estimation methodology

171 PFOA/PFO could be released into the environment during their whole lives,
172 from manufacturing to application, and to waste treatment. Meng et al. (2017)
173 conducted the material flow analysis for PFOA/PFO in China during 2012 using life
174 cycle assessment (LCA) method. Based on that methodology, we estimated the
175 emission of PFOA/PFO for the study area during each stage including production,
176 application, and waste disposal from both point sources and non-point sources. For
177 each stage, we estimated the direct emission of PFOA/PFO as well as the indirect
178 emission by transformation of precursors. And then we calculated the total emission
179 of PFOA/PFO to each compartment. Later on, the emission data of each compartment
180 were divided into each city based on the sources of PFOA/PFO. For example, the
181 distribution of releases into soil was estimated according to the production of

182 PFOA/PFO, fluoropolymer, perfluorooctane sulfonyl fluoride (POSF)-based products,
183 and application of FP, application in metal plating, application in manufacture of
184 aqueous firefighting foams (AFFFs), the number of fire, usage of pesticide,
185 wastewater discharge and generation of industrial solid waste in each city (Meng et al.,
186 2017). Finally, the data were distributed into each grid depending on the location of
187 emission sources (for industrial sources) and proportion of grid to the corresponding
188 city (for domestic sources).

189 **3. Results and Discussion**

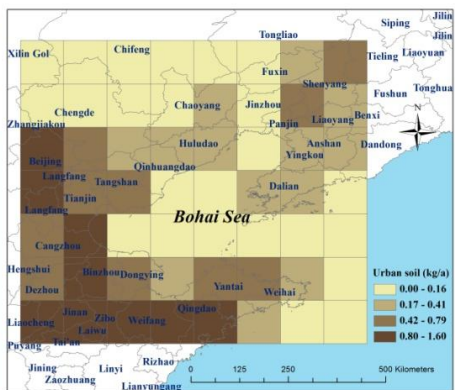
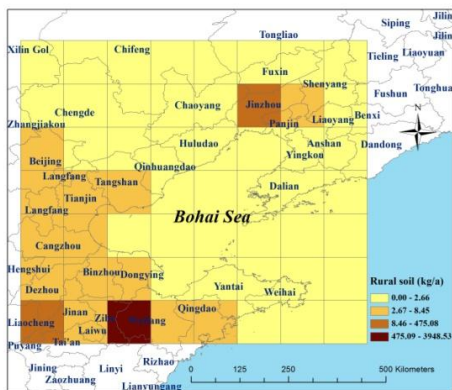
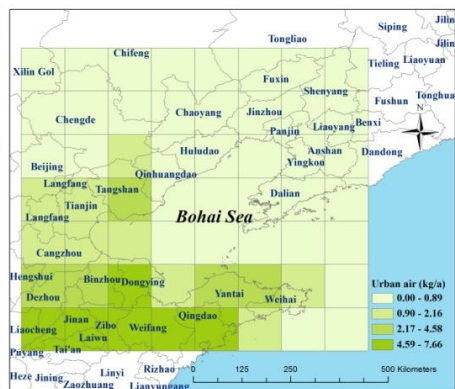
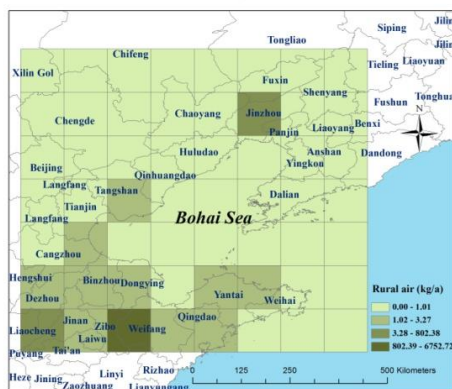
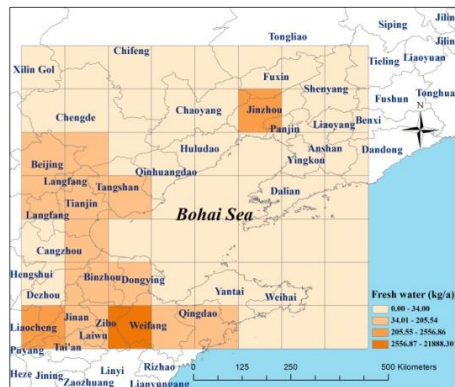
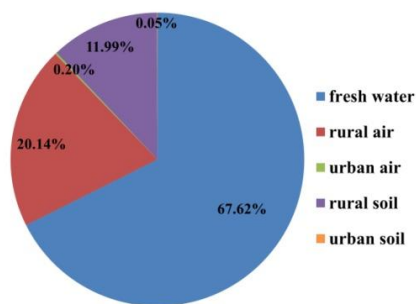
190 3.1 Emission estimation

191 We estimated the PFOA/PFO releases into fresh water, rural air, urban air, rural
192 soil, and urban soil for each grid. The estimated total emissions of PFOA/PFO and
193 their compartmental distributions are presented in Fig. 2.

194 In the Bohai Rim, using the LCA method it was estimated that the total releases
195 of PFOA/PFO to fresh water, rural air, urban air, rural soil and urban soil in 2012
196 were 28165.98 kg, 8388.53 kg, 82.46 kg, 4995.45 kg and 21.73 kg, respectively. The
197 total estimated emissions of PFOA/PFO in the rural areas were much higher than the
198 urban areas, among which from the industrial sources were found greater than those
199 from domestic sources. Among all the sources of PFOA/PFO, emissions along with
200 the production of FP made contributions of 88.6%, 96.7% and 87.8% for fresh water,
201 rural air and rural soil, respectively. There are three large fluorochemical industrial
202 parks producing FP located in the study area (Fig. 1) (Meng et al., 2017; Wang et al.,

203 2016a; Wang et al., 2015). One park located in Zibo city of Shandong province (grid 3)
204 was the largest manufacturer, and its releases to fresh water (Xiaoqing River), air, and
205 soil were up to 21.83 t, 6.75 t, and 3.94 t, respectively. Emissions of the other two
206 parks located in Jinan city and Fuxin city (grids 1 and 46, respectively) were
207 estimated to be the same, reaching 2.5 t, 0.80 t, 0.47 t to fresh water (Xiaoqing River
208 and Daling River, respectively), air, and soil, respectively. All the above releases were
209 from the production of FP and PFOA. It was thus clear that fresh water was the
210 primary compartment receiving PFOA/PFO, accounting for 67.62% of the total
211 releases (Fig. 2 (a)), followed by rural air (20.14%) and rural soil (11.99%). The
212 releases of PFOA/PFO to the urban air and soil were less than 1.00% of the total,
213 greatly different from PFOS (Liu et al., 2015).

214 For fresh water, rural air and soil, emissions to grid 3 (Zibo), grid 1 (Jinan), grid
215 46 (Fuxin) and their adjacent grids were significantly higher than the other regions.
216 However, for urban soil, no large differences were observed among grids, but the
217 emissions from Beijing, Tianjin, and some cities of Shandong province were higher.
218 For urban air, the emissions of Shandong province were relative higher, which may be
219 credited to the developed industrial application of FP.



220
 221 **Fig. 2** Compartmental distribution of PFOA/PFO releases (a) and spatial
 222 distribution of PFOA/PFO releases to compartments in the Bohai Rim, China: (b)
 223 fresh water, (c) rural air, (d) urban air, (e) rural soil, and (f) urban soil.

224 3.2 Model validation and output

225 3.2.1 Model validation

226 Concentrations of PFOA/PFO in all compartments were obtained from the model
227 simulation which was run to steady state solution by inputting emission and
228 environmental data. The model validation was assessed by comparing the modeled
229 PFOA/PFO concentrations in fresh water, sediment, urban soil and rural soil with
230 measured data from the published reports (Table 2). Available measured
231 concentrations of PFOA/PFO from 2011 to 2014 were collected. Generally, modeled
232 concentrations of PFOA/PFO compared favorably to measured concentrations, and
233 they had no significant differences ($P>0.05$). In most cases, the modeled
234 concentrations of PFOA/PFO were lower than the measured data since the modeled
235 concentrations represented the annual mean values in grids while the measured data
236 varied with sampling time and sites (Wang et al., 2016a). Reasonably the modeled
237 concentrations of PFOA/PFO in 2012 in fresh water and sediment were between the
238 measured values of 2011 and 2014 with a steady annual FP growth rate (Wang et al.,
239 2016a).

240 Table 2 Compilation of PFOA/PFO concentrations in fresh water, sediment, urban soil and rural soil of this study along with available reports

Location	Sampling Year	Sample Size	Range of Concentrations	Mean value of measured data	Corresponding Grids	Range of modeled Concentrations	Mean value of modeled data	References
Fresh water (ng/L)								
Daling River	2011	26	0.60-348	110.91 [*]	38, 45, 46, 54	15.71-359.47	113.86 [*]	(Wang et al., 2015)
Daling River	2012	19	0.58-675	199.98 [*]	38, 45, 46, 54	15.71-359.47	113.86 [*]	(Wang et al., 2016b)
Daling River	2013	18	n.d.-2280	271.25 ^a	38, 45, 46, 54	15.71-359.47	113.86 ^a	(Zhu et al., 2015)
Xiaoqing River	2014	36	21.60-341000	14386.07 ^a	1-3, 10-11	53.61-32571.57	6575.37 ^a	(Shi et al., 2015)
Fresh water sediment (ng/g)								
Daling River	2011	26	0.66-8.97	2.15 [*]	38, 45, 46, 54	0.02-1.93	0.56 [*]	(Wang et al., 2015)
Xiaoqing River	2014	33	0.16-98	20.04 ^a	1-3, 10-11	0.11-68.59	13.87 ^a	(Shi et al., 2015)
Urban soil (ng/g)								
Soil in South Bohai Coastal Region	2011	7	n.d.-0.93	0.26 [*]	3-5, 10, 11, 13, 14	0-0.60	0.10 [*]	(Meng et al., 2015)
Rural soil (ng/g)								
Soil in South Bohai Coastal Region	2011	33	n.d.-13.30	0.82 [*]	3-6, 10-13, 15	0-2.85	0.33 [*]	(Meng et al., 2015)

241 Note: ^{*} indicated that there were no significant differences between the mean values of measured and modeled data expressed by one-way
 242 analysis of variance (ANOVA) ($P>0.05$). ^a means that we could not find the original data from literatures to do the one-way ANOVA.

243 3.2.2 Spatial distribution of PFOA/PFO concentrations in compartments

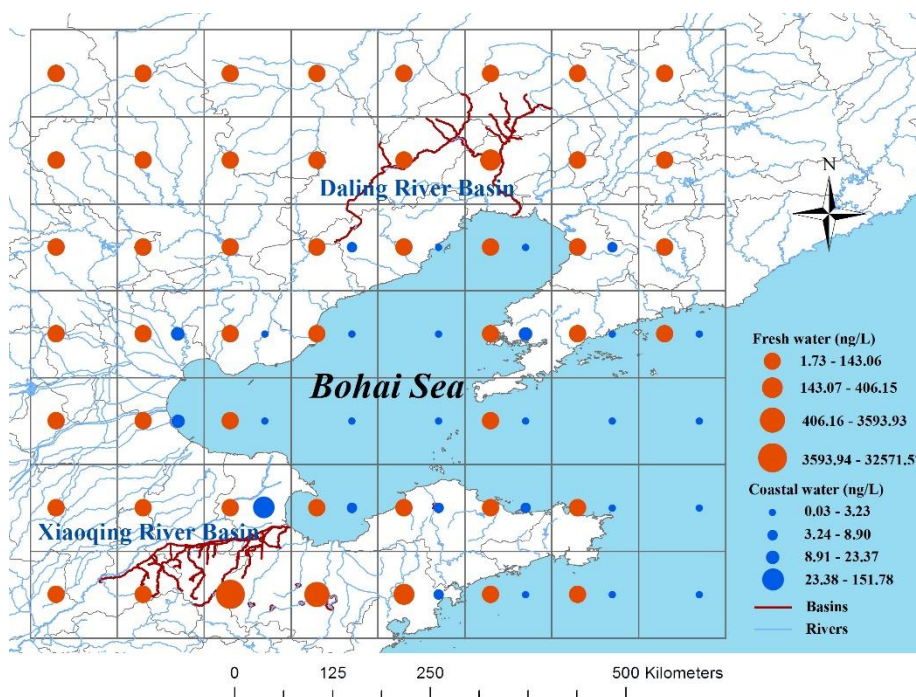
244 The modeled concentrations of PFOA/PFO were 1.73-32571.57 ng/L (median:
245 27.17 ng/L) for fresh water, 0-68.59 ng/g dw (median: 0.06 ng/g dw) for fresh water
246 sediment, 0-0.60 ng/g dw (median: 0.01 ng/g dw) for urban soil, 0-2.85 ng/g dw
247 (median: 0.01 ng/g dw) for rural soil, 0.01-80.43 ng/g dw (median: 0.09 ng/g dw) for
248 vegetation and 0.03-151.78 ng/L (median: 2.11 ng/L) for coastal water. Overall, the
249 PFOA/PFO concentrations were comparatively higher in fresh water and coastal water,
250 with large coefficients of variations (CVs) being 6.34, 6.65, 3.86, 5.13, 4.49 and 1.87
251 for each compartment, respectively. Since the PFOA/PFO concentrations were
252 comparatively higher in fresh water and coastal water, these compartments were
253 considered representatives to explore the spatial distribution of PFOA/PFO
254 concentrations (Fig. 3).

255 Fresh water was modeled to have the highest PFOA/PFO concentrations. The
256 highest PFOA/PFO concentration was modeled in Xiaoqing River basin, up to 32.57
257 $\mu\text{g/L}$ in grid 3 and 3.59 $\mu\text{g/L}$ in grid 4, followed by 0.36 $\mu\text{g/L}$ in grid 46 of Daling
258 River basin (Fig. 3). The industrial emissions from fluoropolymer parks in the Zibo
259 and Fuxin cites were credited the direct contributors. Although in the Xiaoqing River
260 basin, the grid 4 might have an overestimated concentration owing to the important
261 role of fresh water advection, where the fresh water fluxes represented mean values of
262 grids. Interestingly, the grid 1 containing the industrial source of Jinan City was not
263 predicted a notable concentration (53.61 ng/L), which mainly resulted from the fact
264 that the grid was near the boundary and the outflow flux was rather larger than inflow
265 flux. In addition, PFOA/PFO concentrations in coastal water were lower than those in
266 fresh water due to huge dilution of seawater. The maximum value in coastal water was

267 151.78 ng/L in grid 11, downstream of the Xiaoqing River, followed by grids 18 and
268 26 (Tianjin City) with concentrations of 23.37 ng/L and 13.34 ng/L, respectively (Fig.
269 3). It mainly resulted from the massive industrial and domestic emissions from Tianjin
270 City after Zibo, Jinan and Fuxin cities.

271 For most grids, PFOA/PFO concentrations were low in rural and urban soils
272 because of the big surface runoff from soil to fresh water despite the atmospheric
273 deposition. The PFOA/PFO concentrations in urban soils were generally higher than
274 those in rural soils except for grids 1, 3 and 46, where PFOA/PFO concentrations in
275 rural soils were about 2-fold higher than the urban soils. The modeled highest
276 PFOA/PFO concentration 3.02 ng/g in rural soil was observed in grid 3 (Zibo city),
277 followed by grid 46 (Fuxin city) and grid 1 (Jinan city), with values of 0.62 ng/g and
278 0.60 ng/g, respectively. In this study, the modeled PFOA/PFO concentrations in rural
279 soils were lower than the measured ones from sampling sites, since the volumes of
280 rural soils are large and the modeled concentrations represent the annual mean values
281 of grids.

282 The spatial distribution of PFOA/PFO concentrations in vegetation was
283 comparatively consistent with the distribution of releases to rural air and rural soil.
284 The highest concentration 80.43 ng/g was also modeled in grid 3, followed by 18.29
285 ng/g and 13.13 ng/g in grids 46 and 1, respectively. The intermedia transport flux
286 from rural air to vegetation as well as the root uptake from soil to vegetation might be
287 the main contributors.



288

289

Fig. 3 Spatial distribution of PFOA/PFO concentrations in fresh water and

290

coastal water.

291

3.3 Fate and transport processes of PFOA/PFO

292

In this section, we described the fate and transport behavior of PFOA/PFO in the

293

Bohai Rim, and discussed the differences between PFOA/PFO and perfluorooctane

294

sulfonates (PFOS, another one of PFAAs family). It included the fate of PFOA/PFO,

295

contaminating sources of PFOA/PFO to fresh water, advection processes linking grid

296

cells and degradation, and intermedia transfer process.

297

3.3.1 The fate of PFOA/PFO in the Bohai Rim

298

The fate of PFOA/PFO in the Bohai Rim was identified on the basis of predicted

299

inventories in all compartments (Fig. 4). There were remarkable differences between

300

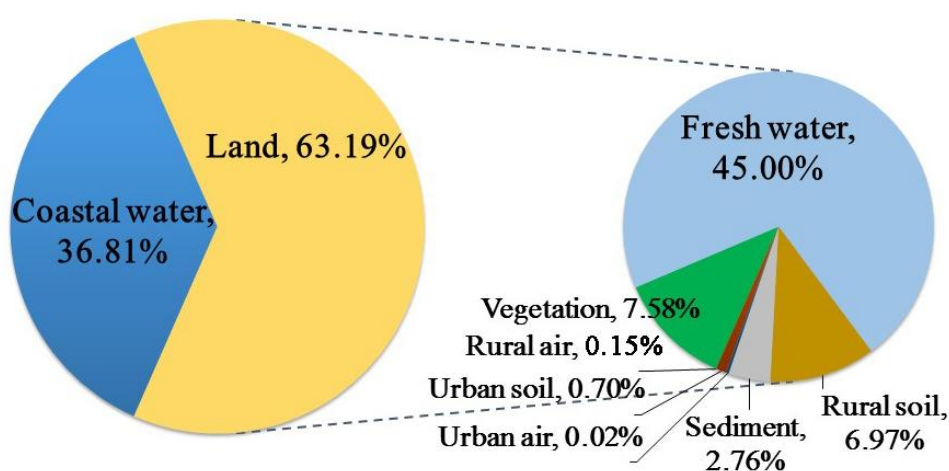
PFOS and PFOA/PFO as both have different functional groups. Different from PFOS,

301

water system was the predominant sink of PFOA/PFO, among which the coastal water,

302 fresh water and sediment accounted for about 42.11%, 41.23%, and 2.53% of the total
 303 amount of PFOA/PFO stored, respectively. After all, from the long term, coastal water
 304 may be the final fate of PFOA/PFO. Only 7.03% of the PFOA/PFO was modeled to
 305 be stored in soil (6.39% in rural soil and 0.64% in urban soil), whereas for PFOS, soil
 306 was predicted to be the predominant sink, taking up 53.00% of the total amount (Liu
 307 et al., 2015). A partial explanation for it may be the huge releases of PFOA/PFO to
 308 fresh water, and the relatively lower transport rate from fresh water to soil. Besides,
 309 the productive and application modes, distinct physical-chemical properties, and
 310 discharge ways of PFOA/PFO and PFOS also had important impacts on their sinks.

311 Besides hydrosphere and soil, vegetation was also an important sink of
 312 PFOA/PFO in which 6.94% of the total amount of PFOA/PFO was predicted to be
 313 stored. This is mainly because of the atmospheric deposition. And the PFAAs less
 314 than 8 carbon chain length are more inclined to accumulate in leaves via hydroponic
 315 solution (Blaine et al., 2014). Last but not least, the storage of PFOA/PFO in rural and
 316 urban air was less than 0.01% even though there was a large quantity of PFOA/PFO
 317 emitting to rural air. The major reason is that the inter-compartmental transfer fluxes
 318 from air to other compartments were larger than those from other compartments to air.



319

320 **Fig. 4** The fate distribution of PFOA/PFO in the Bohai Rim

321

322 3.3.2 Sources of PFOA/PFO to fresh water

323 As the fate of PFOA/PFO, we took fresh water as an example to explore the
324 possible sources of PFOA/PFO indicated by all transport fluxes entering into fresh
325 water (Fig. S3). The observations indicated that direct emission to fresh water, fresh
326 water inflow between grids, and transport from sediment to fresh water were the three
327 main sources of PFOA/PFO to fresh water. The average fluxes of these 3 sources
328 accounted for 47.18%, 41.45%, and 11.12% of the total fluxes, respectively, which
329 suggested that not only the direct releases from the pollution source but also the fresh
330 water advection between sub-regions could play important roles in PFOA/PFO
331 contamination in fresh water.

332

333 3.3.3 Advection and degradation processes of PFOA/PFO

334 Advection fluxes of PFOA/PFO in the study area indicated by inflow and
335 outflow fluxes of air, fresh water and coastal water between adjacent grids are shown
336 in Fig. S4. Obviously, for grids located beside the Bohai Sea, coastal water was the
337 predominant pathway for spatial transport of PFOA/PFO, whereas for other grids
338 fresh water advection was the primary pathway. In contrast, the effect of air
339 inflow/outflow was very small, which was similar to that of PFOS (Liu et al., 2015).
340 It was inferred that the dominant driving force for spatial distribution of PFOA/PFO
341 might be water.

342 In the model simulation, the degradation rates of PFOA/PFO were negligibly
343 small due to the extremely long half-lives in compartments (Table 1). Hence, the

344 primary removal way of PFOA/PFO from the environmental compartments was via
345 advection, including air/water outflows, vegetation growth dilution, leaching process
346 from soil, and sediment burial.

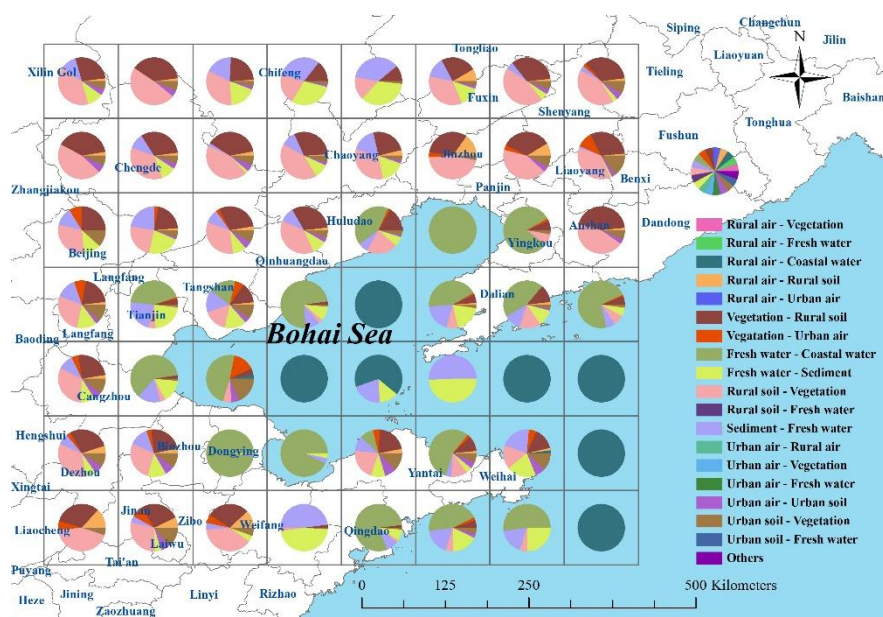
347 3.3.4 Intermedia transport fluxes of PFOA/PFO

348 As one of the behaviors in the BETR-Urban-Rural model, intermedia transport
349 fluxes of PFOA/PFO under steady state were discussed.

350 There were great differences among grids for intermedia transfer pathways
351 which could be broadly classified into three groups. For those grids in the Bohai Sea
352 completely, from rural air to coastal water was almost the unique transfer process of
353 PFOA/PFO while the transport flux from coastal water to rural air was negligibly
354 small (Fig. 5) due to its much lower saturated vapor pressure compared to PAHs
355 (Song et al., 2016). For the grids on the shore of the Bohai Sea, the runoff from fresh
356 water to coastal water was the predominant pathway, followed by fresh water to
357 sediment and sediment to fresh water (Fig. 5). Particularly for grid 26, there were
358 some differences between PFOS and PFOA/PFO, fluxes from fresh water to sediment
359 and sediment to fresh water were relatively larger for PFOS (Su et al., 2018b). For the
360 third group in which grids in the continent completely, pathway from rural soil to
361 vegetation was the primary way, followed by vegetation to rural soil and the mutual
362 transports between fresh water and sediment (Fig. 5). This is different from PAHs for
363 which mutual transports between air and soil for both urban and rural areas were the
364 main ways on land (Song et al., 2016).

365 In total, it was estimated that the flux of PFOA/PFO entering into the Bohai Sea
366 was 24.57 ton/year, which was about 100-fold greater than the quantity of PFOS into
367 the sea because of the agglomeration of fluorochemical industry in the study area.

368 Among all the sources to the Bohai Sea, the transfer flux from fresh water runoff to
 369 coastal water contributed 99.9%. Combining the emission estimation results in
 370 Section 3.1, it was inferred that the emission along with the production of FP in the
 371 Bohai Rim made the contribution of 88.4% to the contamination of the Bohai Sea.
 372 Such serious contamination of PFOA/PFO was largely caused by release of wastes
 373 from manufactures especially wastewater, which did not enter into municipal
 374 wastewater treatment plants (WWTPs) but would be treated in the WWTPs operated
 375 by the manufactures (Meng et al., 2017). Therefore, strengthening supervision and
 376 guidance, and implementing some mitigation measures during waste treatment is
 377 necessary and urgent.



378

379 **Fig. 5** Intermedia transport pathways of PFOA/PFO in the Bohai Rim. Note:

380 Others included the transport pathways from urban soil to urban air, rural soil to rural
 381 air, coastal water to rural air, fresh water to urban air, fresh water to rural air,
 382 vegetation to urban soil, and vegetation to rural air because the flux for each process
 383 was too small. The size of the pies did not indicate the total transport flux of
 384 PFOA/PFO.

385

386 3.4 Sensitivity and uncertainty analysis

387 Since fresh water was not only the predominant receiving compartment and sink
388 of PFOA/PFO, but also the driving force for PFOA/PFO transport, we conducted a
389 sensitivity analysis of all the parameters influencing the concentration of PFOA/PFO
390 in fresh water, taking grid 26 as an example. Each parameter was assumed to increase
391 by 0.1%, and the sensitivity coefficient (S) was calculated using Eq. (S1). The results
392 indicated that the fresh water flow rate (from 18 to 26) and emission to fresh water
393 were the most sensitive parameters, followed by total surface area, percentage of
394 surface area covered by fresh water, and PFOA/PFO reaction half-life in fresh water
395 (Table S1).

396 Additionally, ten sensitive parameters were selected to conduct the Monte Carlo
397 simulation using the Crystal Ball software to assess the uncertainty of the modeled
398 concentration of PFOA/PFO in fresh water in grid 26. The simulation was run 10,000
399 times repeatedly, and the estimated distribution of PFOA/PFO concentration in fresh
400 water was obtained (Fig. S5). The result showed that the estimated distribution of
401 PFOA/PFO concentration fitted well with a lognormal distribution, and the predicted
402 mean value of Monte Carlo was 71.38 ng/L, comparable to the modeled concentration
403 71.20 ng/L. However, the PFOA/PFO concentration in fresh water had a little higher
404 uncertainty with a CV of 1.33, which was due to the higher variability of PFOA/PFO
405 reaction half-life in fresh water.

406 4. Conclusion

407 China has become the main producer of PFOA/PFO in recent years along with
408 the phase out of 3M Company. The Bohai Rim is known as an economically
409 developed region as well as the contamination “hotspot” of PFOA/PFO in China. In

410 this study, the modified multispecies BETR-Urban-Rural model was applied to
411 explore the transport and fate of PFOA/PFO in the Bohai Rim. First, the estimated
412 total release of PFOA/PFO to each compartment revealed that fresh water was the
413 primary compartment receiving PFOA/PFO, and the total emission of PFOA/PFO to
414 rural area was significantly higher than urban area because of the available
415 fluorochemical industrial parks. Results of the simulations suggested that hydrosphere
416 was the predominant sink of PFOA/PFO, followed by soil and vegetation, which was
417 different from that of PFOS. The highest PFOA/PFO concentration was modeled in
418 the Xiaoqing River basin, followed by the Daling River basin, for which the direct
419 PFOA/PFO emission, fresh water inflow, and transport from sediment to fresh water
420 were the main three contributors. Furthermore, due to the hydrophilicity, coastal water
421 and fresh water transport were the predominant pathways of PFOA/PFO spatial
422 transfer. Additionally, it was estimated that the flux of PFOA/PFO entering into the
423 Bohai Sea was approximately 24.57 ton/year, which was 100-fold greater than the
424 quantity of PFOS into the sea.

425 Overall, it is important to pay more attention to monitor the levels of PFOA/PFO
426 and assess the risks of PFOA/PFO to ecosystems in fresh water and costal water. Also,
427 it is necessary to design more effective programs to mitigate risks by minimizing
428 releases from production, application and waste management due to the longer
429 half-lives of PFOA/PFO in compartments. Currently, vacuum distillation is the most
430 effective available technology to reduce release during the production of PFOA/PFO
431 (Meng et al., 2017). And, during the application of PFOA/PFO, there would be some
432 effective alternatives like low-carbon fluoride. Besides, FP manufactures should take
433 some waste treatment and recovery measures, and establish some industrial chains of
434 circular economy like Changshu Hi-tech Fluorochemical Industrial Park (Chen 2009).

435 In conclusion, control over reduction of PFOA/PFO should focus on reliable
436 alternatives and effective technologies during production and wastewater treatment,
437 and more efficient economic development modes.

438

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445

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