Article (refereed) - postprint

Su, Chao; Song, Shuai; Lu, Yonglong; Wang, Pei; Meng, Jing; Lu, Xiaotian; Juergens, Monika D.; Khan, Kifayatullah; Baninla, Yvette; Liang, Ruoyu. 2018. **Multimedia fate and transport simulation of perfluorooctanoic acid/perfluorooctanoate in an urbanizing area.** *Science of the Total Environment*, 643. 90-97. https://doi.org/10.1016/j.scitotenv.2018.06.156

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

Chao Su [a, b], Shuai Song [a], Yonglong Lu [a, b*], Pei Wang [a], Jing Meng [a], Xiaotian Lu [a, b], Monika D. Jürgens [c], Kifayatullah Khan [a, d], Yvette Baninla [a, b], Ruoyu Liang [a, b]

[a] State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Center for Ecology & Hydrology, Wallingford, OX10 8BB, UK

[d] Department of Environmental and Conservation Sciences, University of Swat, Swat 19130, Pakistan

*Corresponding author:

Yonglong Lu

State Key Laboratory of Urban and Regional Ecology, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, 100085, Beijing, China.

Tel: 86-10-62915537

Fax: 86-10-62918177

E-mail: yllu@rcees.ac.cn

Abstract

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

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

1. Introduction

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

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

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

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

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

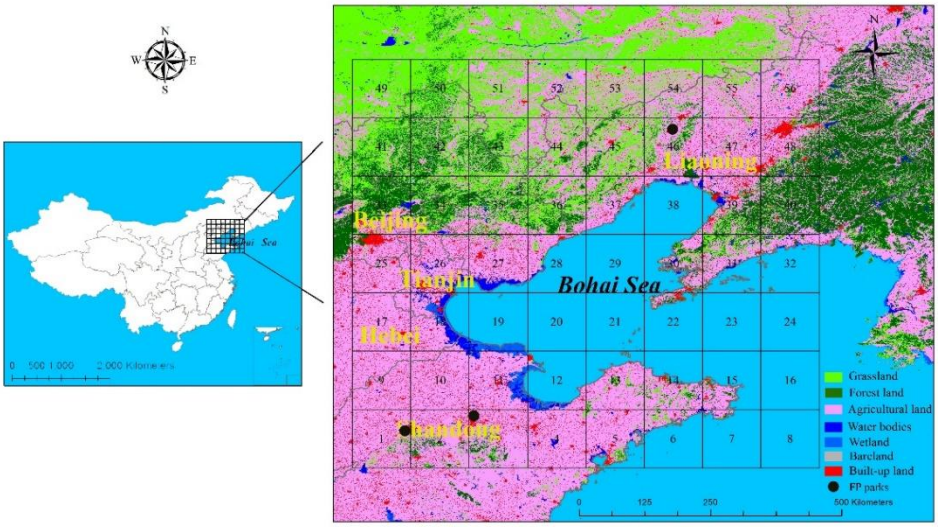
89 BETR-Urban-Rural model considering the effects of urbanization is more accurate to
90 model the concentrations of chemicals like PAHs and PFOS (Song et al., 2016; Su et
91 al., 2018a; Su et al., 2018b).

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

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

$$Ratio = 10^{(\mathrm{pH}-\mathrm{p}Ka)} \quad (1)$$

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

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

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

2.3 Parameterization

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

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

Table 1 Physical- chemical properties of PFAAs at 20 ℃*

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	-	-

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

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

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

2.4 Emission estimation methodology

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

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

3. Results and Discussion

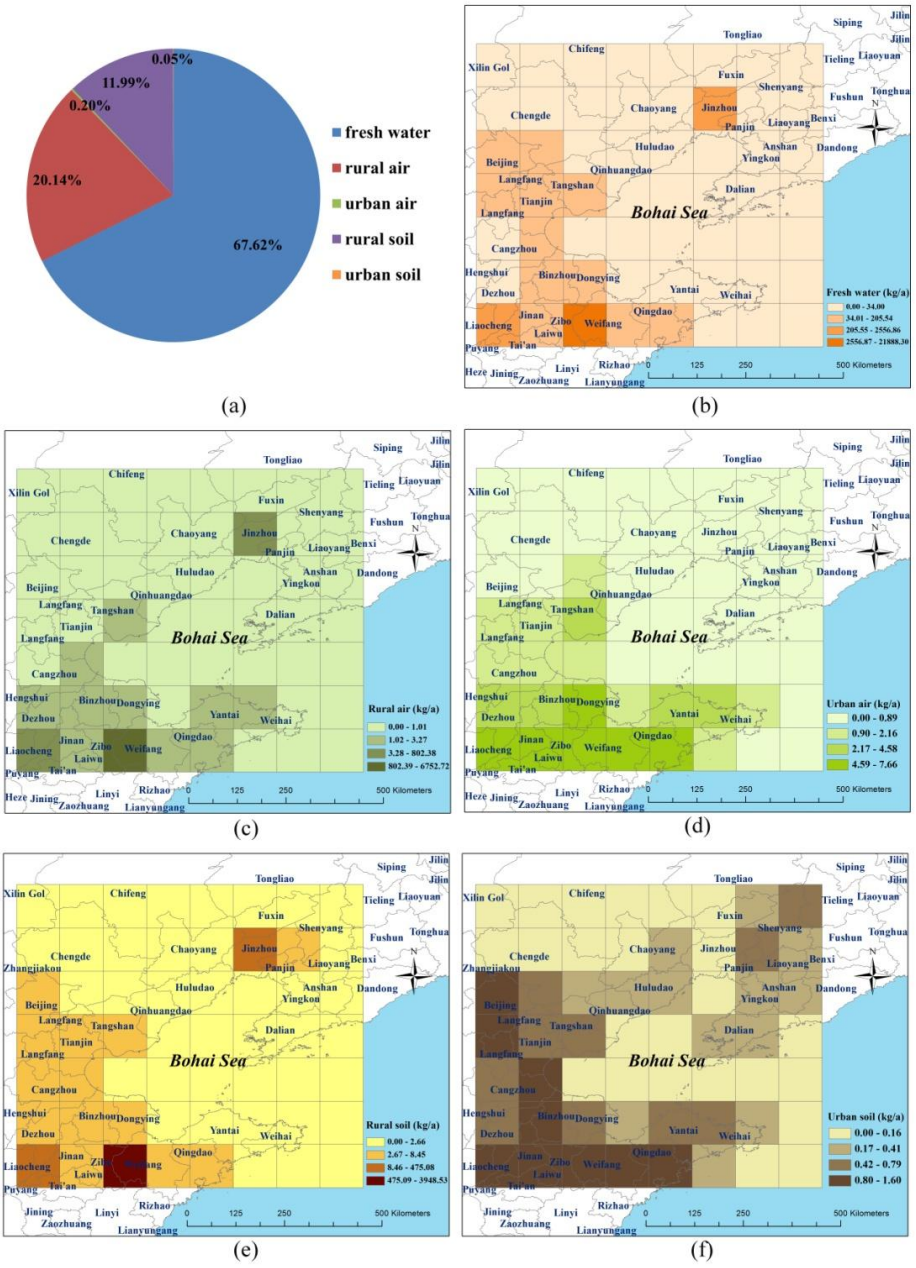
3.1 Emission estimation

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

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

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

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

3.2.2 Spatial distribution of PFOA/PFO concentrations in compartments

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

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

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

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

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

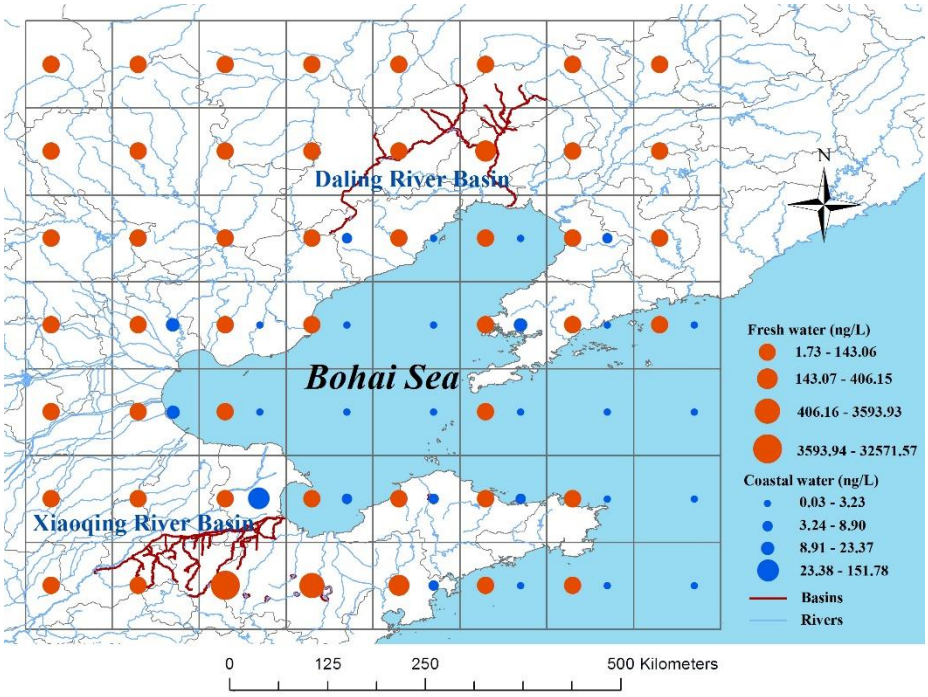


Fig. 3 Spatial distribution of PFOA/PFO concentrations in fresh water and coastal water.

3.3 Fate and transport processes of PFOA/PFO

In this section, we described the fate and transport behavior of PFOA/PFO in the Bohai Rim, and discussed the differences between PFOA/PFO and perfluorooctane sulfonates (PFOS, another one of PFAAs family). It included the fate of PFOA/PFO, contaminating sources of PFOA/PFO to fresh water, advection processes linking grid cells and degradation, and intermedia transfer process.

3.3.1 The fate of PFOA/PFO in the Bohai Rim

The fate of PFOA/PFO in the Bohai Rim was identified on the basis of predicted inventories in all compartments (Fig. 4). There were remarkable differences between PFOS and PFOA/PFO as both have different functional groups. Different from PFOS, water system was the predominant sink of PFOA/PFO, among which the coastal water,

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

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

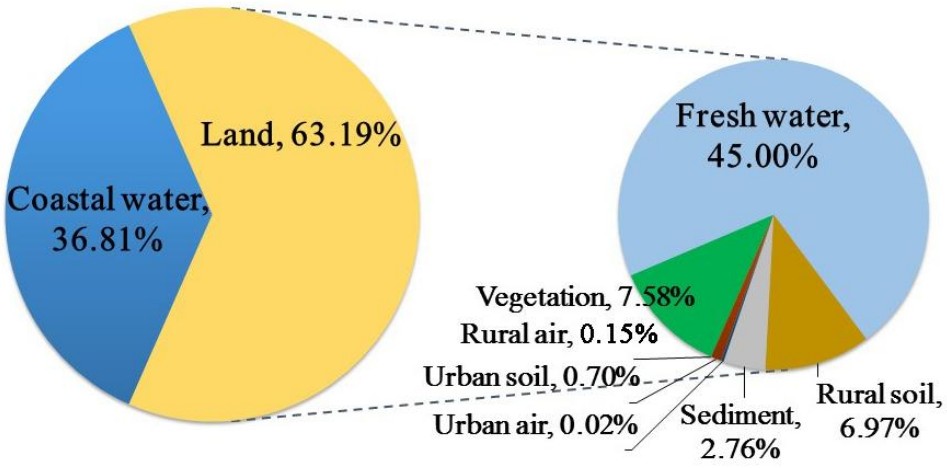


Fig. 4 The fate distribution of PFOA/PFO in the Bohai Rim

3.3.2 Sources of PFOA/PFO to fresh water

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

3.3.3 Advection and degradation processes of PFOA/PFO

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

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

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

3.3.4 Intermedia transport fluxes of PFOA/PFO

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

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

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

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

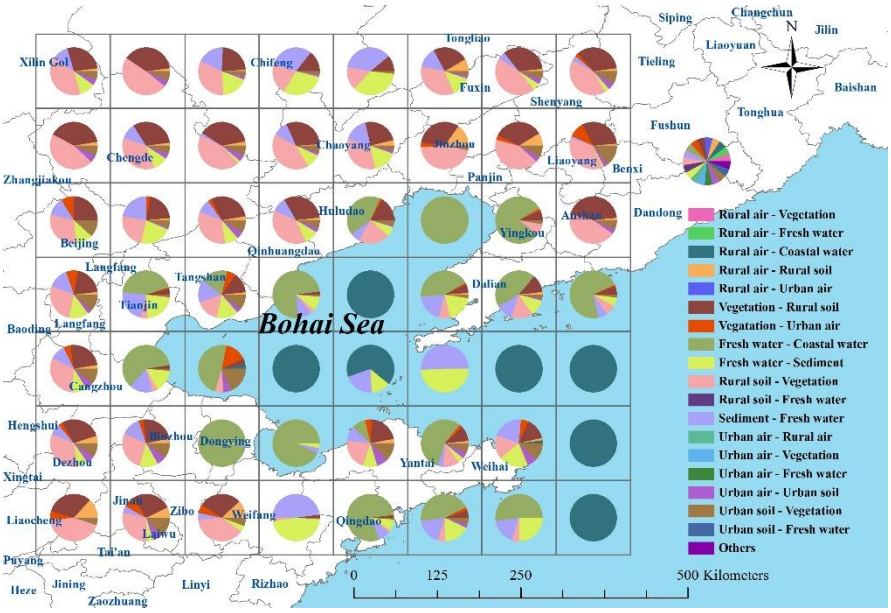


Fig. 5 Intermedia transport pathways of PFOA/PFO in the Bohai Rim. Note: Others included the transport pathways from urban soil to urban air, rural soil to rural air, coastal water to rural air, fresh water to urban air, fresh water to rural air, vegetation to urban soil, and vegetation to rural air because the flux for each process was too small. The size of the pies did not indicate the total transport flux of PFOA/PFO.

3.4 Sensitivity and uncertainty analysis

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

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

4. Conclusion

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

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

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

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

Acknowledgement

This study was supported by the National Key R & D Program of China (2017YFC0505704), and the National Natural Science Foundations of China under Grant No. 41420104004, No. 71761147001 and No. 41501539, the Chinese Academy of Sciences (KFZD-SW-322), and the Key Technology R&D Program of Tianjin (16YFXTSF00380).

References

Armitage, J., Cousins, I.T., Buck, R.C., Prevedouros, K., Russell, M.H., MacLeod, M., Korzeniowski, S.H., 2006. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. Environ. Sci. Technol. 40, 6969-6975.

Armitage, J.M., MacLeod, M., Cousins, I.T., 2009. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. Environ. Sci. Technol. 43, 1134-1140.

Bao, J., Liu, W., Liu, L., Jin, Y., Dai, J., Ran, X., Zhang, Z., Tsuda, S., 2010. Perfluorinated compounds in the environment and the blood of residents living near fluorochemical plants in Fuxin, China. Environ. Sci. Technol. 45, 8075-8080.

Blaine, A.C., Rich, C.D., Sedlacko, E.M., Hyland, K.C., Stushnoff, C., Dickenson,

458 E.R., Higgins, C.P., 2014. Perfluoroalkyl acid uptake in lettuce (Lactuca sativa) and
459 strawberry (Fragaria ananassa) irrigated with reclaimed water. Environ. Sci. Technol.
460 48, 14361-14368.
461 Barton, C. A., Kaiser, M. A., Russell, M. H., 2007. Partitioning and removal of
462 perfluorooctanoate during rain events: the importance of physical-chemical properties.
463 J. Environ. Monitor. 9, 839-846.
464 Burns, D.C., Ellis, D.A., Li, H., McMurdo, C.J., Webster, E., 2008. Experimental pKa
465 determination for perfluorooctanoic acid (PFOA) and the potential impact of pKa
466 concentration dependence on laboratory-measured partitioning phenomena and
467 environmental modeling. Environ. Sci. Technol. 42, 9283-9288.
468 Chen, H., 2009. Construction and situation of fluorine chemical industrial park in
469 China. Organo-Fluorine Industry 3, 59-64 (in Chinese).
470 Chen, H., Wang, X., Zhang, C., Sun, R., Han, J., Han, G., Yang, W., He, X., 2017.
471 Occurrence and inputs of perfluoroalkyl substances (PFASs) from rivers and drain
472 outlets to the Bohai Sea, China. Environ. Pollut. 221, 234-243.
473 Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in
474 wildlife. Environ. Sci. Technol. 35, 1339-1342.
475 Li, L., Zhai, Z., Liu, J., Hu, J., 2015. Estimating industrial and domestic
476 environmental releases of perfluorooctanoic acid and its salts in China from 2004 to
477 2012. Chemosphere 129, 100-109.
478 Liu, S., 2014. Simulation of spatial explicit multimedia fate of POPs in Bohai Rim.
479 Dissertation. University of Chinese Academy of Sciences, Beijing, China (in Chinese,
480 with English abstract).
481 Liu, S., Lu, Y., Wang, T., Xie, S., Jones, K.C., Sweetman, A.J., 2014. Using gridded
482 multimedia model to simulate spatial fate of Benzo [α] pyrene on regional scale.

Environ. Int. 63, 53-63.

Liu, S., Lu, Y., Xie, S., Wang, T., Jones, K.C., Sweetman, A.J., 2015. Exploring the fate, transport and risk of Perfluorooctane Sulfonate (PFOS) in a coastal region of China using a multimedia model. Environ. Int. 85, 15-26.

Liu, Z., Lu, Y., Shi, Y., Wang, P., Jones, K., Sweetman, A.J., Johnson, A.C., Zhang, M., Zhou, Y., Lu, X., Su, C., Sarvajayakesavaluc, S., Khan, K., 2017. Crop bioaccumulation and human exposure of perfluoroalkyl acids through multi-media transport from a mega fluorochemical industrial park, China. Environ. Int. 106, 37-47.

Liu, Z., Lu, Y., Wang, T., Wang, P., Li, Q., Johnson, A.C., Sarvajayakesavalu, S., Sweetman, A.J., 2016. Risk assessment and source identification of perfluoroalkyl acids in surface and ground water: spatial distribution around a mega-fluorochemical industrial park, China. Environ. Int. 91, 69-77.

Mackay, D., 2001. Multimedia environmental models: the fugacity approach. CRC press.

MacLeod, M., Woodfine, D.G., Mackay, D., McKone, T., Bennett, D., Maddalena, R., 2001. BETR North America: a regionally segmented multimedia contaminant fate model for North America. Environ. Sci. Pollut. Res. 8, 156-163.

Meng, J., Lu, Y., Wang, T., Wang, P., Giesy, J.P., Sweetman, A.J., Li, Q., 2017. Life cycle analysis of perfluorooctanoic acid (PFOA) and its salts in China. Environ. Sci. Pollut. Res. 24, 11254-11264.

Meng, J., Wang, T., Wang, P., Zhang, Y., Li, Q., Lu, Y., Giesy, J.P., 2015. Are levels of perfluoroalkyl substances in soil related to urbanization in rapidly developing coastal areas in North China? Environ. Pollut. 199, 102-109.

Paul, A.G., Jones, K.C., Sweetman, A.J., 2008. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ. Sci. Technol. 43,

386-392.

Pistocchi, A., Loos, R., 2009. A map of European emissions and concentrations of PFOS and PFOA. Environ. Sci. Technol. 43, 9237-9244.

Prevedouros, K., Jones, K., Sweetman, A., 2004a. European-scale modeling of concentrations and distribution of polybrominated diphenyl ethers in the pentabromodiphenyl ether product. Environ. Sci. Technol. 38, 5993-6001.

Prevedouros, K., MacLeod, M., Jones, K.C., Sweetman, A.J., 2004b. Modelling the fate of persistent organic pollutants in Europe: parameterisation of a gridded distribution model. Environ. Pollut. 128, 251-261.

Schwarzenbach, R.P., Gschwend, P., Imboden, D., 2003. Environmental Organic Chemistry, 2nd ed. John Wiley & Sons Inc: New York, 2003.

Shi, Y., Vestergren, R., Xu, L., Song, X., Niu, X., Zhang, C., Cai, Y., 2015. Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China. Environ. Pollut. 206, 104-112.

Song, S., Su, C., Lu, Y., Wang, T., Zhang, Y., Liu, S., 2016. Urban and rural transport of semivolatile organic compounds at regional scale: A multimedia model approach. J. Environ. Sci. 39, 228-241.

Su, C., Lu, Y., Wang, T., Lu, X., Song, S., Li, L., Khan, K., Wang, C., Liang, R., 2018a. Dynamic multimedia fate simulation of Perfluorooctane Sulfonate (PFOS) from 1981 to 2050 in the urbanizing Bohai Rim of China. Environ. Pollut. 235, 235-244.

Su, C., Song, S., Lu, Y., Liu, S., Giesy, J.P., Chen, D., Jenkins, A., Sweetman, A.J., Yvette, B., 2018b. Potential effects of changes in climate and emissions on distribution and fate of perfluorooctane sulfonate in the Bohai Rim, China. Sci. Total

533 Environ. 613, 352-360.
534 Su, H., Lu, Y., Wang, P., Shi, Y., Li, Q., Zhou, Y., Johnson, A.C., 2016. Perfluoroalkyl
535 acids (PFAAs) in indoor and outdoor dusts around a mega fluorochemical industrial
536 park in China: Implications for human exposure. Environ. Int. 94, 667-673.
537 Su, H., Shi, Y., Lu, Y., Wang, P., Zhang, M., Sweetman, A., Jones, K., Johnson, A.,
538 2017. Home produced eggs: An important pathway of human exposure to
539 perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA) around a
540 fluorochemical industrial park in China. Environ. Int. 101, 1-6.
541 Toose, L., Woodfine, D.G., MacLeod, M., Mackay, D., Gouin, J., 2004. BETR-World:
542 a geographically explicit model of chemical fate: application to transport of α-HCH to
543 the Arctic. Environ. Pollut. 128, 223-240.
544 Vaalgamaa, S., Vähätalo, A.V., Perkola, N., Huhtala, S., 2011. Photochemical
545 reactivity of perfluorooctanoic acid (PFOA) in conditions representing surface water.
546 Sci. Total Environ. 409, 3043-3048.
547 Wang, P., Lu, Y., Wang, T., Fu, Y., Zhu, Z., Liu, S., Xie, S., Xiao, Y., Giesy, J.P., 2014a.
548 Occurrence and transport of 17 perfluoroalkyl acids in 12 coastal rivers in south Bohai
549 coastal region of China with concentrated fluoropolymer facilities. Environ. Pollut.
550 190, 115-122.
551 Wang, P., Lu, Y., Wang, T., Meng, J., Li, Q., Zhu, Z., Sun, Y., Wang, R., Giesy, J.P.,
552 2016a. Shifts in production of perfluoroalkyl acids affect emissions and
553 concentrations in the environment of the Xiaoqing River Basin, China. J. Hazard.
554 Mater 307, 55-63.
555 Wang, P., Lu, Y., Wang, T., Zhu, Z., Li, Q., Meng, J., Su, H., Johnson, A.C., Sweetman,
556 A.J., 2016b. Coupled production and emission of short chain perfluoroalkyl acids
557 from a fast developing fluorochemical industry: Evidence from yearly and seasonal

monitoring in Daling River Basin, China. Environ. Pollut. 218, 1234-1244.

Wang, P., Lu, Y., Wang, T., Zhu, Z., Li, Q., Zhang, Y., Fu, Y., Xiao, Y., Giesy, J.P., 2015. Transport of short-chain perfluoroalkyl acids from concentrated fluoropolymer facilities to the Daling River estuary, China. Environ. Sci. Pollut. Res. 22, 9626-9636.

Wang, T., Khim, J.S., Chen, C., Naile, J.E., Lu, Y., Kannan, K., Park, J., Luo, W., Jiao, W., Hu, W., 2012. Perfluorinated compounds in surface waters from Northern China: comparison to level of industrialization. Environ. Int. 42, 37-46.

Wang, Y., Fu, J., Wang, T., Liang, Y., Pan, Y., Cai, Y., Jiang, G., 2010. Distribution of perfluorooctane sulfonate and other perfluorochemicals in the ambient environment around a manufacturing facility in China. Environ. Sci. Technol. 44, 8062-8067.

Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K., 2014b. Global emission inventories for C 4–C 14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. Environ. Int. 70, 62-75.

Yu, Q., Zhang, R., Deng, S., Huang, J., Yu, G., 2009. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: kinetic and isotherm study. Water Res. 43, 1150-1158.

Zhang, Q., Zhang, C., Zhou, Q., Chen, L., 2006. Quantitative Characterization of PFOS and PFOA in the Surface Water by SPE-HPLC/MS. Sichuan Environ. 4, 002 (in Chinese, with English abstract).

Zhu, Z., Wang, T., Meng, J., Wang, P., Li, Q., Lu, Y., 2015. Perfluoroalkyl substances in the Daling River with concentrated fluorine industries in China: seasonal variation, mass flow, and risk assessment. Environ. Sci. Pollut. Res. 22, 10009-10018.