

1 Pollution pathways and release estimation of
2 perfluorooctane sulfonate (PFOS) and
3 perfluorooctanoic acid (PFOA) in central and
4 eastern China

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22 ABSTRACT: China has gradually become the most important manufacturing and
23 consumption centre of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid
24 (PFOA) and the world's major contamination hotspots. However, a systematic
25 analysis of pollution pathways for PFOS/PFOA into the different environmental
26 compartments and their quantification in China are less known. This paper provided a
27 comprehensive estimation on PFOS and PFOA release into the environment in the
28 central and eastern region of China, which accounted for vast majority of national
29 emission. About 80-90% of PFOS/PFOA contamination in the Chinese environment
30 was estimated to come from manufacturing and use facilities mostly via industrial
31 wastewater discharge. The other major contamination sources were screened to be
32 aqueous fire-fighting foams (AFFF), and pesticides including sulfluramid ~~the~~
33 ~~breakdown of the pesticide sulfluramid~~ for PFOS. For PFOA, following some way
34 behind industrial wastewater, were industrial exhaust gas, domestic wastewater and
35 landfill leachate as contamination sources. For surface water contamination, the major
36 pollution contributors after industrial wastewater were AFFF spill runoff for PFOS,
37 and domestic wastewater and precipitation-runoff for PFOA. The majority PFOS that
38 contaminated soil was associated with infiltration of AFFF and pesticides~~sulfluramid~~
39 ~~pesticide~~, while most PFOA in soil was attributed to atmospheric deposition and
40 landfill leachate. Where groundwater had become contaminated, surface water
41 seepage was estimated to contribute about 50% of PFOS and 40% of PFOA whilst the
42 remainder was mostly derived from soil leaching. A review of the available
43 monitoring data for PFOS/PFOA in the field confirmed industrial wastewater, landfill

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44 leachate and AFFF application as important sources. Higher concentrations of PFOA
45 than PFOS in precipitation also corroborated more PFOA release in the air
46 compartment. To reduce PFOS/PFOA contamination of the Chinese environment the
47 focus for control should be on industrial wastewater emissions.

48 KEYWORDS: PFOS/PFOA; pollution pathway; release estimation; environmental
49 risk; pollution hotspot

50 1. Introduction

51 Having excellent chemical stability, high surface activity, with water and oil
52 repellence (Giesy and Kannan, 2001; 2002), perfluoroalkyl acids (PFAAs) have been
53 widely used as surfactants and surface protectors, performance chemicals, lubricants
54 and pesticides. However, concerns have been raised due to their environmental
55 persistence, toxicity, long-range transport and bioaccumulation properties (Takagi et
56 al., 2011; Lescord et al., 2015; Liu et al., 2015b). These chemicals have been detected
57 in many components of the environment, and some of PFAAs are believed to be
58 ubiquitously present in both the natural environment and the biota~~Continuous release~~
59 ~~of these substances has resulted in them becoming ubiquitous in the environment~~
60 (Post et al., 2013; Miralles-Marco and Harrad, 2015). They are transported in surface
61 water and air (Wang et al., 2015) leading to their deposition in oceans, soil and
62 groundwater (Sharma et al., 2015; Zhao et al., 2016; Armitage et al.,
63 2006)~~(Prevedouros et al., 2006; Sharma et al., 2015).~~

64 Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are two of

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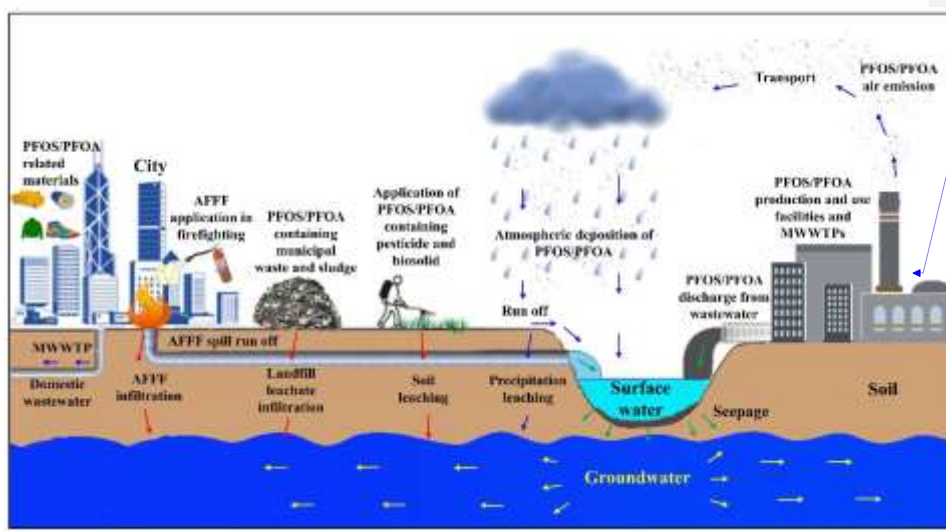
65 the most frequently detected PFAAs in the environment (Wang et al., 2015). Due to
66 their adverse environmental impacts and potential health risks, PFOS have been listed
67 in a series of national and multilateral regulation agreements including the Stockholm
68 Convention in 2009 (UNEP, 2009; USEPA, 2009); while 2010/2015 PFOA
69 Stewardship Program was implemented to reduce PFOA emission (USEPA, 2006).
70 Although production and application of PFOS and PFOA have been discontinued in
71 Europe and America (USEPA; 2009), they have continued to increase in China due to
72 on-going domestic and international demands (Wang et al., 2016). After a decade of
73 continuous expansion, China's annual production capacity of PFOS and PFOA
74 plateaued at approximately 220-240 t/yr by 2011 and 150 t/yr by 2013, respectively
75 (Liu et al., 2008; Li et al., 2015). The widespread contamination and the associated
76 risks to environment and human health remain a concern for the scientific community
77 and government regulators.

78 PFOS and PFOA can be released to the surrounding environment during
79 manufacturing and application of PFOS/PFOA-containing products (Wang et al.,
80 2014a). Local PFOS contamination is usually associated with discharge from
81 industries such as metal plating, textile treatment and PFOS manufacturing, whilst hot
82 spots of PFOA contamination are derived from production and fluoropolymer (FP)
83 manufacturing and processing ([Lim et al., 2011](#); [Prevedouros et al., 2006](#))(~~[Xie et al.,](#)~~
84 ~~[2013b](#)~~; ~~[Li et al., 2015](#)~~). The occurrence of PFOS/PFOA pollution hotspots in soil,
85 water and air associated with manufacturing facilities have been increasingly reported
86 in China (Chen et al., 2009; Wang et al., 2015). However, the broader picture of

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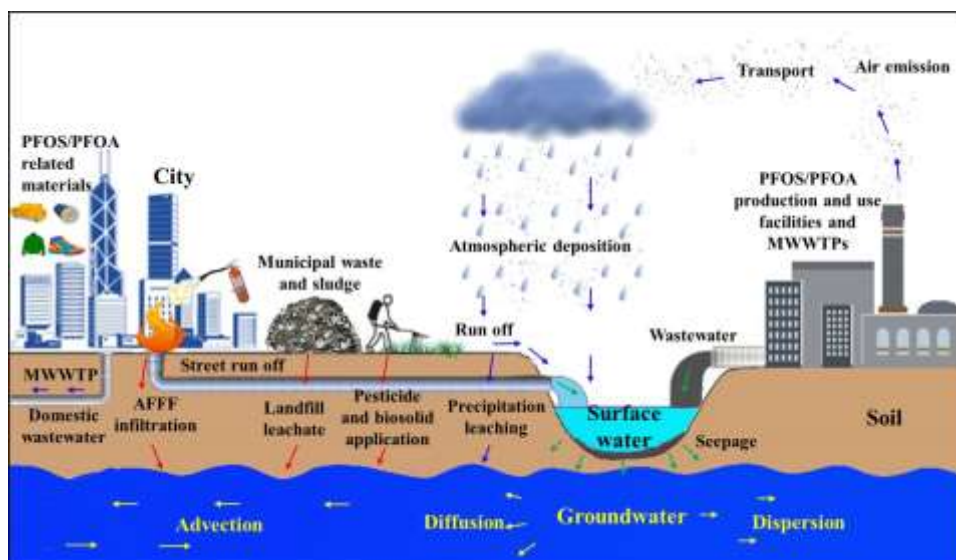
87 pollution pathways for PFOS/PFOA into different environmental compartments and
88 their quantification across China are less well known. The purpose of this study was
89 to provide a comprehensive estimation of PFOS and PFOA release into the Chinese
90 environment.

91 2. Identification of sources and pollution pathways



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94 Fig.1 Schematic diagram of sources and pollution pathways for PFOS/PFOA.

95 There are two major sources of PFOS/PFOA pollution in China, that from the
96 domestic source and that from the industrial source (a major component in China)
97 (Fig. 1). The initial recipients for this release are soil and surface water. Industrial
98 emission of PFOS/PFOA mainly includes two pollution pathways: (i) PFOS/PFOA
99 discharged into surface waters via industrial wastewater (Wang et al., 2012); and (ii)
100 PFOS/PFOA emission to air followed by deposition to surface water and terrestrial
101 surfaces. Given their mobile characteristics, those in deposited into the terrestrial
102 environment will ultimately run off into surface water or infiltrate deeper into soil
103 (Xiao et al., 2012a; Shan et al., 2015). ~~The PFOS/PFOA in domestic products~~ can be
104 released into surface water through municipal wastewater treatment plants
105 (MWWTPs) (Zhang et al., 2013). In certain cases, the concentrations of PFAAs
106 especially for PFOA increase from the influent to the effluent of MWWTPs,
107 suggesting the biodegradation of precursors during the biological wastewater
108 treatment (Xiao et al., 2012b). Those that do not escape directly may be trapped in
109 biosolids in the MWWTPs or enter landfill with the disposal of unwanted products. In
110 both cases further leaching into soils and surface/groundwater are possible. Other
111 sources include the dispersion of aqueous fire-fighting foam (AFFF), and in
112 agriculture from the natural breakdown of the pesticides including sulfluramid ~~the~~
113 ~~natural breakdown of the pesticide sulfluramid~~ both of which can be released into soil
114 (Chen et al., 2012; Zhang et al., 2013; Löfstedt Gilljam et al., 2015; Yan et al., 2015).
115 Both PFOS and PFOA can enter into groundwater mainly through surface water

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116 seepage and soil leaching (Xiao et al., 2015; Liu et al., 2016).

117 **4.3. Estimation methods of environmental releases**

118 The production process commonly used by Chinese PFOS and PFOA manufacturers
119 is electrochemical fluorination (ECF), which was previously used by global producers.
120 The ratio of linear to branched perfluorinated C chains is roughly 70% to 80% linear
121 and 20% to 30% branched in the case of the synthesis of PFOS and PFOA (Buck et al.,
122 2011). Considering a large part of PFOS/PFOA produced in China meets the domestic
123 demands, the release estimation took into account both the linear and branched
124 isomers of PFOS/PFOA. After a decade of substantial increase in production and use
125 of PFOS and PFOA in China there has been a plateau over the period of 2010 to 2013
126 (Wang et al., 2015; Li et al., 2015). The vast majority of PFOS ~~(98%)~~ and PFOA
127 ~~(87%)~~ were emitted in the central and eastern region of China, which are developed
128 industrial and commercial areas are centred. The first step was to collect and further
129 process emission data for PFOS and PFOA from the central and eastern region of
130 China in 2010-2013. The next step was to estimate environmental release for transport
131 processes~~process~~ such as atmospheric deposition, runoff, soil leaching and surface
132 water seepage. The presence of PFOS/PFOA in different environmental compartments,
133 following the release from different routes was then calculated.

134 In the present study, main precursors of PFOS/PFOA were considered as possible
135 when collecting and further processing the emission data for PFOS and PFOA. PFOS
136 precursors mainly included perfluorooctane sulfonamides (FOSAs) and

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137 perfluorooctane sulfonamidoethanol (FOSEs) while PFOA precursors primarily
138 referred to fluorotelomer alcohols (FTOHs), FOSAs and FOSEs (Buck et al., 2011).
139 Some precursors such as FTOHs, FOSAs and FOSEs are industrial products, and may
140 be released to the environment during the process of manufacturing and using. FOSAs
141 and FOSEs are produced based on perfluorooctane sulfonyl fluoride (POSF); while
142 FTOHs is manufactured based on fluorotelomer (FT) (Prevedouros et al., 2006). In
143 addition, these precursors were also released as impurities or by-products when
144 manufacturing other FT-based or POSF-based products including PFOS and PFOA
145 (Lim et al., 2011; Wang et al., 2014a). Environmental release data of these precursors
146 we collected or calculated were based on the production or use amount and
147 corresponding emission factors and/or content as impurities in a certain industrial or
148 use process (Xie et al., 2013b; Li et al., 2015). Then, these precursors were uniformly
149 converted to PFOS/PFOA equivalents through respective transformation factors,
150 which meant the degradation yields of PFOS/PFOA by weight from PFOS/PFOA
151 precursors.

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152 *3.1 Contamination of surface water and soil*

153 *3.1.1 Wastewater and sewage sludge discharge*

154 For industrial wastewater, the release estimation of PFOS/PFOA were based on the
155 production or use amount of PFOS/PFOA-related chemicals and the emission factors
156 to water in a certain industry. According to the above method, ~~Consideration of the~~
157 ~~emission data suggested~~ the release of PFOS and PFOA through industrial

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158 wastewater discharge ~~have been were~~ estimated to be 58 t/yr and 27.3 t/yr,
159 respectively (Xie et al., 2013b; Li et al., 2015). The starting point for an estimation
160 of PFOS/PFOA release through domestic wastewater discharge was the assumption
161 that PFOS, PFOA and precursors would enter the drain/sewer system ~~and further~~
162 WWTPs following cleaning, wiping and washing of the products in the domestic
163 indoor environment ~~(Xie et al., 2013a)~~. Regional emission of PFOS/PFOA from
164 local WWTPs have been found to be estimated from corresponding statistical data on
165 population density (PD) and per capita disposable income (PCDI) (Xie et al., 2013a;
166 Li et al., 2015). Based on the estimation equations and regional statistical data,
167 release of PFOS/PFOA via MWWTP emission (E_{MWWTP}) was calculated in this
168 study (detailed description and data in Supplementary Material and Table S1). Total
169 discharge amount of FOSA and N-Ethyl perfluorooctane sulfonamidoacetic acid
170 (EtFOSAA), which passed the WWTPs without degradation, were averagely ~5% of
171 those for PFOS and ~2% of those for PFOA, based on monitoring data from 28
172 MWWTPs in 11 cities of central and eastern China (Zhang et al., 2013). The release
173 of these precursors from MWWTPs were also calculated according to the above
174 proportions and the estimated release of PFOS/PFOA, and then further converted to
175 PFOS and PFOA equivalents through respective transformation factors (detailed
176 description in Supplementary Material).~~The detailed description of estimation~~
177 ~~methods for MWWTP emission (E_{MWWTP}) and supporting data was contained in the~~
178 ~~Supplementary Material and Table S1. Degradation of PFOS/PFOA precursors, for~~
179 ~~example Σ FOSA (N-alkyl substituted perfluorooctane sulfonamides) was also~~

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180 ~~considered in MWWTP emission.~~ Mass flow of PFOS/PFOA in wastewater and
181 sewage sludge from 43 MWWTPs ~~in in these regions~~~~the central and eastern region~~
182 ~~of China~~ was also collected to calculate emission proportion through domestic
183 wastewater ($P_{MWWTP\ water}$) and through sewage sludge ($P_{MWWTP\ sludge}$) (reviewed
184 in Table S2). Eq. (1) was used to estimate the release of PFOS/PFOA (W_{MWWTP}) in
185 domestic wastewater to surface water.

$$186 \quad W_{MWWTP} = E_{MWWTP} \times P_{MWWTP\ water} \quad (1)$$

187 In China, approximately 8.5 million tons dry weight of municipal sewage sludge
188 (biosolid) are generated each year (Zhang et al., 2013). It is calculated that the
189 biosolids would contain average concentrations of 18 ng/g for PFOS and 8.3 ng/g for
190 PFOA. About 48% of these biosolids were applied to land via agriculture and urban
191 greening ($P_{Biosolid\ application}$) as a soil amendment while 35% of them were disposed
192 as landfill ($P_{Biosolid\ landfill}$) (Chen et al., 2012). No further treatment occurs for these
193 PFOS/PFOA in biosolids in landfill or applied to the local soil compartment
194 (Lindstrom et al., 2011). ~~Eqs. (2) and (3)~~ were used to estimate the release and
195 leaching of PFOS/PFOA into soil from biosolid application to the land
196 ($S_{Biosolid\ application}$) and landfill ($S_{Biosolid\ landfill}$).

$$197 \quad S_{Biosolid\ application} = E_{MWWTP} \times P_{MWWTP\ biosolid} \times P_{Biosolid\ application} \quad (2)$$

$$198 \quad S_{Biosolid\ landfill} = E_{MWWTP} \times P_{MWWTP\ biosolid} \times P_{Biosolid\ landfill} \quad (3)$$

199 3.1.2 Aqueous Fire-fighting Foam(AFFF) runoff and infiltration

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200 Perfluorooctane sulfonyl fluoride (POSF)-based AFFF, mainly produced by
201 consuming the PFOS-salts, is the predominant type of foam in China and is also
202 known to contain PFOA impurities (Lim et al., 2011; Andreas and Leo, 2009). During
203 the application of AFFF, PFOS is directly released to the environment as main
204 ingredients, while PFOA is released in the form of impurities. Due to unavailability of
205 PFOS/PFOA precursors content, these substances was not taken into account for my
206 calculation present in the foam formulation. The concentration ratio of PFOS:PFOA
207 in POSF-based AFFF, produced by similar process to those in China, has been
208 estimated to be 10:1 or even lower (Andreas and Leo, 2009). Emission of PFOS in
209 AFFF application to the environment was estimated to be 7 t/yr (Xie et al., 2013b).
210 According to the PFOS:PFOA ratio (10:1) in POSF-based AFFF, a more modest
211 emission of PFOA was estimated at 0.7 t/yr. When estimating the environmental
212 release of PFOS/PFOA in AFFF, fire training and fire intervention are both considered
213 in the present study (Zhang et al., 2012). The environmental release of PFOS/PFOA
214 during AFFF application was estimated based on a commonly used scenario (Brooke
215 et al., 2004), that there is no containment of this fire-fighting foam after discharge,
216 which is the case in China, and 50% of the release goes to surface water without
217 treatment and 50% to soil which could ultimately, if present, lead to groundwater.
218 ~~According to the assumed PFOS:PFOA ratio (10:1) in AFFF (Andreas and Leo,~~
219 ~~2009), a more modest emission of PFOA was estimated at 0.7 t/yr. This ratio was~~
220 ~~informed by data on consumption of PFOS (100 t/a) and PFOA (9t/a) in AFFF~~
221 ~~production in China (Mei, 2007; Yu, 2010). Based on the assumption that there is no~~

222 ~~containment of this fire-fighting foam after discharge, an arbitrary value of 50%~~
223 ~~release was presumed to go to surface water and 50% to soil which could ultimately,~~
224 ~~if present, lead to groundwater (Brooke et al., 2004).~~ Therefore, the release of PFOS
225 in AFFF application to both surface water and soil were 3.5t/yr respectively, while
226 those of PFOA were 0.35t/yr respectively.

227 3.1.3 Atmospheric deposition, runoff and infiltration

228 The air emission of PFOS from production and metal plating was estimated to be 1.3
229 t/yr. For PFOA emissions to the atmosphere were estimated at 7.3 t/yr according to
230 previous calculations of total environmental emission (40t) (Xie et al., 2013b; Li et al.,
231 2015). Except for small amount of PFOS/PFOA precursors, most airborne
232 PFOS/PFOA were combined with particulate matters, ~~which was easily deposited to~~
233 ~~land and ocean (Harada et al., 2006; Barton et al., 2006).~~ Liu et al. (2015b) estimated
234 that ~65% of PFOS generated from air emission can deposit to the local region and
235 the remaining will transport to a longer distance.~~Based on the assumption that the~~
236 ~~precursors were instantly degraded to PFOS, about 65% of PFOS from air emission~~
237 ~~would reach to land in a typical region, the Bohai Rim, which were simulated by the~~
238 ~~Berkeley-Trent model (Liu et al., 2015b).~~ Although higher proportion of airborne
239 PFOS/PFOA would be deposited to land in some inland regions, the proportion (65%)
240 were conservatively used due to shortage of detailed information about atmospheric
241 transport. Air emission of PFOS/PFOA was assumed to be evenly deposited to a large
242 surrounding expanse of terrestrial surface and surface water.

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243 The maximum mass fractions of airborne PFOS and PFOA were observed in
244 particulate matter of $<0.3\mu\text{m}$ and $<10\mu\text{m}$, respectively, most of which would be
245 removed by wet precipitation (Barton et al., 2006; Harada et al., 2006). Removal by
246 precipitation was also expected to take out both the smallest size particles ($<1\mu\text{m}$) as
247 well as the coarser size particles ($<10\mu\text{m}$) (Taniyasu et al., 2013; Dreyer et al., 2015).
248 In general, 80%-90% of atmospheric particulate matter were presumed to be captured
249 in wet deposition while dry deposition would only account for 10%-20% (Dai, 2006;
250 Shan et al., 2015). In this study, proportions of wet deposition ($P_{wet\ deposition}$) was
251 conservatively estimated to be 80% and the remaining 20% ($P_{dry\ deposition}$) were
252 attributed to dry deposition. The proportion of exposed surface water, both rivers and
253 lakes, in the provinces of central and eastern China were calculated to be 5.7% for
254 average percentage of surface water area ($P_{Surface\ water}$) (IGSNRR, 2014). Eq. (4)
255 can be used to calculate the contamination of surface water by PFOS/PFOA
256 ($W_{deposition}$) via air emission and subsequent direct deposition, where E_{air}
257 represented air emission of PFOS/PFOA and P_{Land} represented the proportion of
258 airborne PFOS/PFOA deposited to the land.

$$259 \quad W_{deposition} = E_{air} \times P_{Land} \times P_{Surface\ water} \quad (4)$$

260 What is the fate of the PFOS/PFOA that is deposited on the terrestrial environment?
261 With the exception of direct deposition to surface water, most PFOS/PFOA arriving
262 through dry deposition would reach soil and vegetation, and those present in
263 vegetation would also reach the soil through litter fall and precipitation washout. Both

264 the EU system for the evaluation of substances model and the Berkeley-Trent model
 265 estimate that less than 0.3% of PFOS in soil would be entrained in runoff and be
 266 transported to surface water, which was ~~an negligible proportion negligible~~ (Brooke et
 267 al., 2004; Liu et al., 2015b). Due to similar physicochemical properties (e.g. $\log K_{oc}$)
 268 between PFOS and PFOA, ~~this study assumed that PFOS and PFOA in soil entrained~~
 269 ~~by runoff to surface water could be negligible and these substances carried by runoff~~
 270 ~~to surface water came from precipitation~~~~this study assumed that all PFOS/PFOA~~
 271 ~~would behave in the same way~~. Based on annual precipitation and runoff, an average
 272 runoff coefficient (C_{runoff}) in eastern and central China was calculated to be 0.34,
 273 which was approximate to the median of runoff coefficients (0-0.8) for natural surface
 274 (IGSNRR, 2014). The PFOS/PFOA not captured in runoff, would enter deeper within
 275 soil through infiltration. ~~Eqs. (5) and (6)~~ can be used to calculate the release of
 276 PFOS/PFOA through runoff to surface water (W_{runoff}) and through atmosphere
 277 deposition to soil ($S_{precipitation}$).

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$$278 \quad W_{runoff} = E_{air} \times P_{Land} \times P_{wet\ deposition} \times (1 - P_{surface\ water}) \times C_{runoff} \quad (5)$$

$$279 \quad S_{deposition} =$$

$$280 \quad E_{air} \times P_{Land} \times (1 - P_{surface\ water}) \times [P_{dry\ deposition} + P_{wet\ deposition} \times (1 -$$

$$281 \quad C_{runoff})] \quad (6)$$

282 3.1.4 Landfill leachate infiltration

283 In China, most landfills are not adequately lined to prevent leachate migration. The
 284 total leakage of PFAAs from landfill leachate ($E_{landfill}$) to local soil and groundwater

285 in China was estimated to be 3.1 t/yr with approximately 81% of the national leakage
286 coming from the central and eastern regions (NBS, 2014). Based on the
287 concentrations of individual PFAA found in landfill leachate (Yan et al., 2015), the
288 percentage of PFOS and PFOA in landfill that could enter the leachate ($P_{landfill}$) were
289 estimated to be 3.3% and 60%, respectively. Eq. (7) can be used to estimate the
290 amount of PFOS/PFOA released from landfill to soil ($S_{landfill}$). As landfill in China
291 mainly consists of biosolids and municipal solid waste (MSW), PFOS/PFOA (S_{MSW})
292 derived from MSW can be estimated by total release in landfill leachate ($S_{landfill}$)
293 and those derived from biosolid landfill ($S_{Biosolid\ landfill}$) (Eq. 8).

$$294 \quad S_{landfill} = E_{landfill} \times P_{Landfill,central\ and\ eastern\ China} \times P_{landfill} \quad (7)$$

$$295 \quad S_{MSW} = S_{landfill} - S_{Biosolid\ landfill} \quad (8)$$

296 3.1.5 Pesticide infiltration

297 In China, sulfluramid is the predominant PFOS/PFOA-related pesticide, which was
298 used to estimate PFOS/PFOA release from pesticide in this study (Zhang et al., 2012).
299 The main active ingredient in sulfluramid is N-ethyl perfluorooctane sulphonamide
300 (Et-FOSA) (Löfstedt Gilljam et al., 2015), which would ultimately transform to PFOS
301 and PFOA through photolysis, oxidation, biotransformation, and so forth (Tomy et al.,
302 2004; Martin et al., 2006; Plumlee et al., 2009). Furthermore, PFOS and PFOA were
303 also released to the environment as impurities in sulfluramid.~~The pesticide~~
304 ~~sulfluramid, which is still licensed for use in China, contains PFOS/PFOA precursors~~
305 ~~(eg. n-ethyl perfluorooctane sulfonamide) which can be transformed back into these~~

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306 ~~molecules (Löfstedt Gilljam et al., 2015).~~ For sulfluramid containing pesticides, the
 307 vast majority are released into the terrestrial environment during application. The
 308 environmental release of PFOS has been estimated to be 2.6 t/a by Zhang et al. (2012),
 309 while those of PFOA was calculated to be 1.4 t/a based on the annual consumptions of
 310 Et-FOSA for sulfluramid, emission factors in use process, transformation rate to
 311 PFOA and PFOA content as impurities in sulfluramid (detailed description in
 312 Supplementary Material). The use amount of sulfluramid in the central and eastern
 313 region of China accounted for 96% of total national use amount
 314 ($P_{Pesticide,central\ and\ eastern\ China}$) (Zhang et al., 2012).~~In China, environmental~~
 315 ~~releases of PFOS/PFOA ($E_{pesticide}$) have been estimated to be 2.6 t/a and 1.4 t/a,~~
 316 ~~respectively (detailed description in Supplementary Material) (Zhang et al., 2012).~~
 317 ~~The proportion of sulfluramid used in the central and eastern region of China~~
 318 ~~($P_{Pesticide,central\ and\ eastern\ China}$) has been estimated to be 96% (Zhang et al., 2012).~~
 319 According to emission factors for pesticides used in personal/domestic situations from
 320 the Technical Guidance Documents (TGD) (European Commission, 2003), 90% of
 321 sulfluramid (P_{soil}) would release to local soil during use, the proportion of sulfluramid
 322 (P_{soil}) which is released to local soil was estimated to be 90%. Infiltration. The release
 323 of PFOS/PFOA ($S_{pesticide}$) from pesticide application to soil can be estimated by Eq.
 324 (9).

$$325 \quad S_{pesticide} = E_{pesticide} \times P_{Pesticide,central\ and\ eastern\ China} \times P_{soil} \quad (9)$$

326 *3.2 Groundwater contamination*

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327 3.2.1 Surface water seepage

328 Contaminated surface water seepage is a major pollution pathway of PFOS/PFOA in
329 groundwater (Lin et al., 2015; Liu et al., 2016). Official data concerning total
330 groundwater recharge ($V_{total\ recharge}$), recharge from surface water
331 ($P_{surface\ water\ recharge}$) and total surface water volume ($V_{surface\ water}$) in central and
332 eastern region of China were used to calculate seepage rates of PFOS/PFOA from
333 surface waters ($SR_{surface\ water}$) (Table S4) (MWR, 2011; 2013) [Eq.(10)]. Using a
334 multimedia fate model for PFOS in the Bohai Rim of China, the proportion adsorbed
335 by sediment was calculated to be about 5% of total release in surface
336 water ($P_{Sediment\ absorption}$) (Liu et al., 2015b). **Due to a similar $\log K_{oc}$ between**
337 **PFOS (2.4-4.7) and PFOA (1.3-4.5), this proportion was used to estimate the amount**
338 **adsorbed by sediment (Higgins and Luthy, 2006; Johnson et al., 2007; Ferrey et al.,**
339 **2009; Ahrens et al., 2011; Li et al., 2012).** Eq.(11) was used to estimate the release of
340 PFOS/PFOA through surface water seepage to groundwater ($G_{seepage}$).

341
$$SR_{surface\ water} = \frac{V_{total\ recharge} \times P_{surface\ water\ recharge}}{V_{surface\ water}} \quad (10)$$

342
$$G_{seepage} = E_{surface\ water} \times (1 - P_{Sediment\ absorption}) \times SR_{surface\ water} \quad (11)$$

343 3.2.2 Soil leaching into groundwater

344 Due to their relatively high solubility in water and low $\log K_{oc}$ ($\log K_{oc}$ of 3.0 and
345 2.8), the potential for PFOS/PFOA in soil (E_{soil}) to be leached into groundwater by
346 precipitation or irrigation is ~~found assumed~~ to be high (Zareitalabad et al., 2013; Xiao

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347 et al., 2015). In the present study, the high leaching potential was mainly attributed to
348 ~~The assumption was also based on~~ the fact that relatively high irrigation intensity and
349 precipitation occurred in central and eastern China (NBS, 2014), which had a big
350 contribution to soil leaching of PFOS/PFOA. The leaching percentage of PFOS/PFOA
351 ($P_{leaching}$) in soil was estimated to be 90% based on a dissipation model, which was
352 based on results observed during leaching experiments (Gellrich et al., 2012;
353 Zareitalabad et al., 2013). According to a long-term pilot study, only 0.001% of PFOA
354 and 0.004% of PFOS in soil could be accumulated by vegetation (winter rye, canola,
355 winter wheat and winter barley), which was negligible in this estimation (Stahl et al.,
356 2013). As the main grain producing areas, large areas of the same or similar crops are
357 planted in the central and eastern regions of China (NBS, 2014). Therefore, Eq. (12)
358 was used to estimate release of PFOS/PFOA through soil leaching into groundwater
359 ($G_{soil\ leaching}$).

$$360 \quad G_{soil\ leaching} = E_{soil} \times P_{leaching} \quad (12)$$

361 **4. Results and discussion**

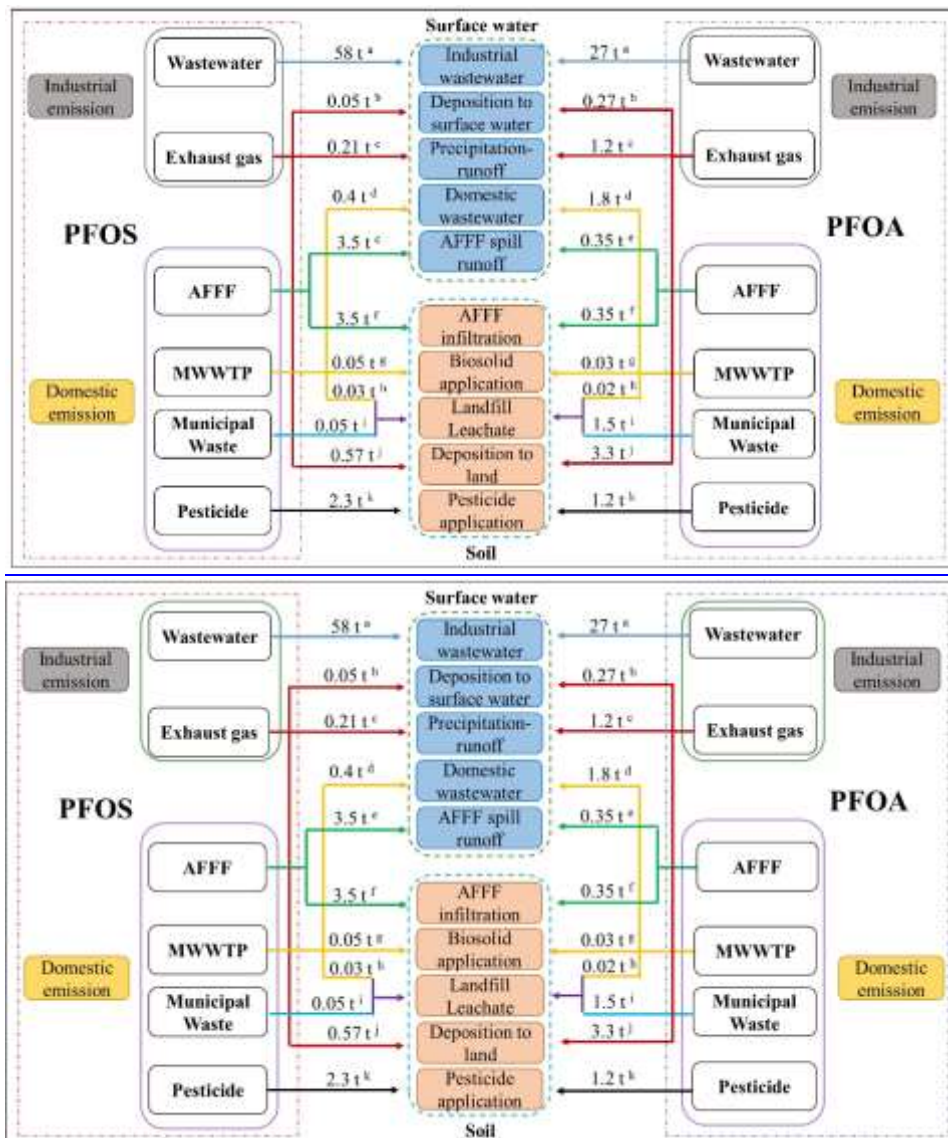
362 *4.1 Major sources screening and release comparison*

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365 Fig.2 Environment release of PFOA and PFOS in different pollution pathways.

366 **Note:** a was calculated by data from Xie et al. (2013b) and Li et al. (2015); b, c and j were
 367 calculated by Eq. (4, 5, 6) and data from Xie et al. (2013b), Li et al. (2015), Dai (2006), IGSNNR
 368 (2014) and Liu et al. (2015b) ; d, g and h were calculated by Eq. (1, 2, 3, S1, S2, S3, S4) and data
 369 from Zhang et al. (2013), Chen et al. (2012) and references listed in Table S1; e and f were

370 calculated by data from Xie et al. (2013b), Andreas and Leo (2009) and Brooke et al. (2004); i
371 was calculated by Eq. (7, 8) and data from Yan et al. (2015) and (NBS, 2014); k was calculated by
372 Eq. (9, S5) and data from Zhang et al. (2012) and European Commission (2003).

373 Overall about 70t of PFOS and 40t of PFOA were estimated to be released into the
374 environment in central and eastern China (Fig. 2). The most important observation
375 here is that this contamination was dominated by industrial emissions which
376 contributed 86% of PFOS and 87% of PFOA to this environmental release. This
377 clearly shows the unique challenge faced by China. The vast majority of this
378 industrial emission was in wastewater discharged to surface water. Although not
379 important in terms of quantity of release, it can be observed that the release of PFOS
380 to the air compartment from industrial emission (1.3 t/yr and 1.9% of the total
381 environmental emission) was significantly lower than for PFOA (7.3 t/yr and 18% of
382 the total emission). This is linked to the ~~facts assumption~~ that only two PFOS-related
383 industrial processes, which are PFOS production and metal plating, contribute to air
384 emissions of PFOS (Paul et al., 2008) whilst each main PFOA-related industrial
385 processes, which included PFOA production, FP manufacturing and processing, use of
386 aqueous fluoropolymer dispersions (AFDs) and industrial processes of POSF- and
387 FT-based products, contributed air emission of PFOA, and the total release is
388 considerable~~PFOA production and nearly all related industrial processes make~~
389 ~~considerable emissions of PFOA into the atmosphere~~ (Wang et al., 2014a; b).

390 Overall, domestic emissions are a much less important source of contamination in

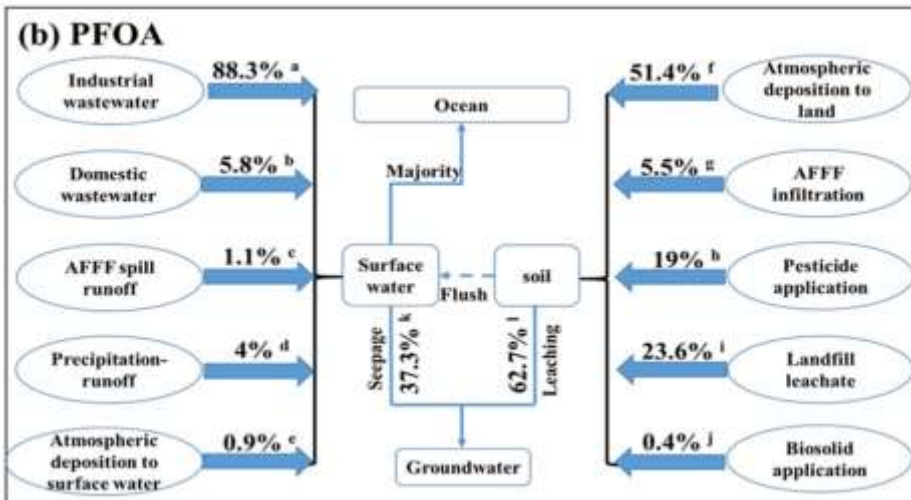
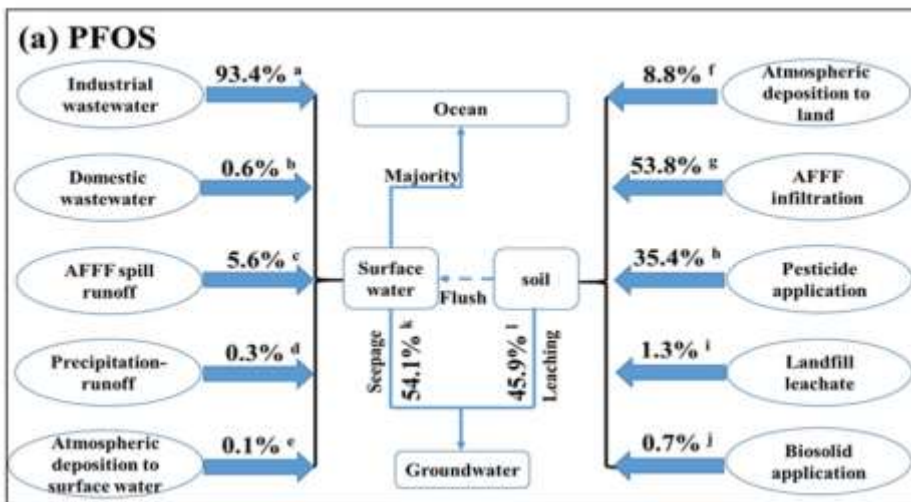
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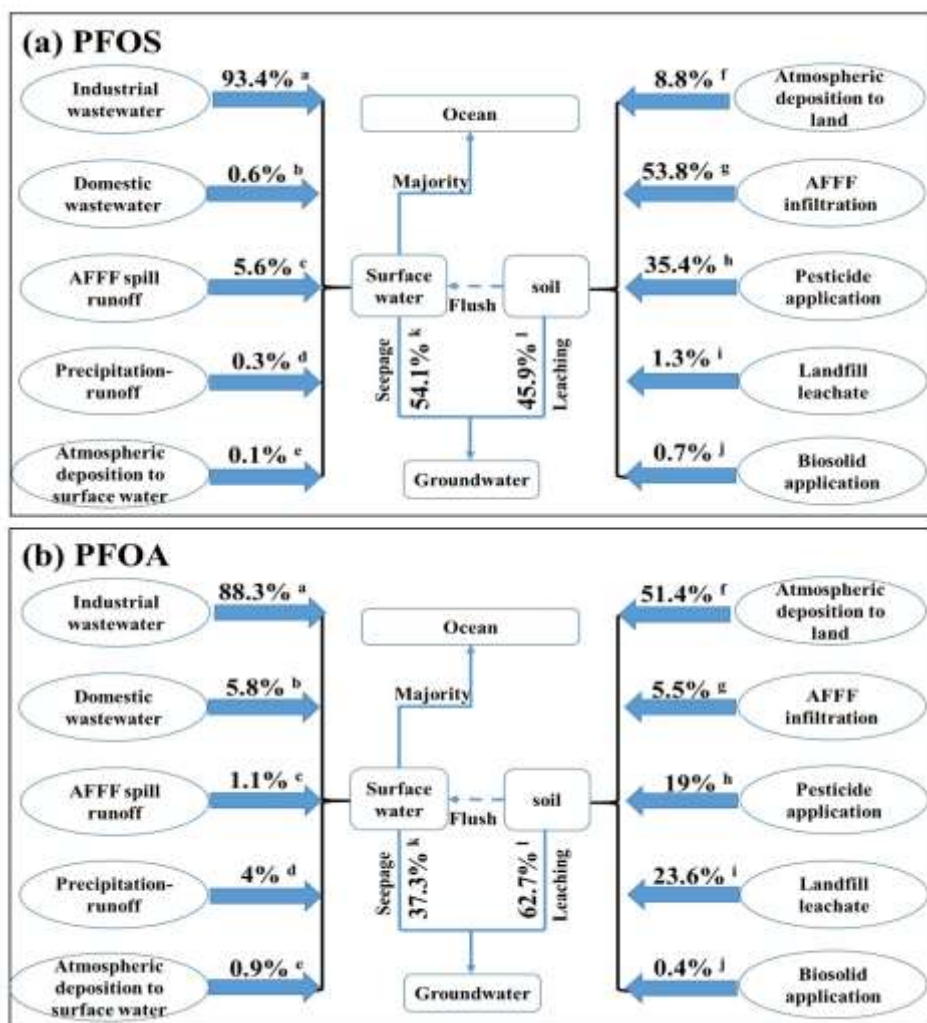
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391 central and eastern China in terms of quantity (Fig. 2). The higher emissions of PFOS
392 compared to PFOA were linked to its use in AFFF and in ~~sulfluramid~~ pesticides. The
393 release of PFOA in domestic wastewater was about 4 times of those of PFOS.
394 However, the emission proportion of PFOA (3.2%) derived from sewage sludge
395 (biosolid) was much lower than those of PFOS (21%). This is linked to the slightly
396 higher $\log K_{oc}$ of PFOS compared to PFOA (Higgins and Luthy, 2006). Release of
397 PFOA in landfill leachate derived from municipal solid waste (mainly consisting of
398 domestic garbage) was two orders of magnitude higher than that of PFOS. The higher
399 PFOA releases from domestic wastewater and garbage were considered to be linked to
400 its higher relative use in the home following the gradual phase-out of PFOS-based
401 chemicals by the Chinese government (Wang et al., 2009).

402 *4.2 Contribution estimation of PFOS and PFOA in different pathways*





404

405 Fig. 3 Contribution of PFOS (a) and PFOA (b) in different pathways.

406 **Note:** a was calculated by data from Xie et al. (2013b) and Li et al. (2015); b and j were calculated
 407 by Eq. (1, 2, S1, S2, S3, S4) and data from Zhang et al. (2013), Chen et al. (2012) and references
 408 listed in Table S1; c and g were calculated by data from Xie et al. (2013b), Andreas and Leo
 409 (2009) and Brooke et al. (2004); d, e and f were calculated by Eq. (4, 5, 6) and data from Xie et al.
 410 (2013b), Li et al. (2015), Dai (2006), IGSNNR (2014) and Liu et al. (2015b); h was calculated by
 411 Eq. (9, S5) and data from Zhang et al. (2012) and European Commission (2003); i was were

412 calculated by Eq. (3, 7) and data from Yan et al. (2015) and (NBS, 2014); k was calculated by Eq.
413 (10, 11) and data from MWR (2011; 2013) and Liu et al. (2015b); l was calculated by Eq.(12) and
414 data from Gellrich et al. (2012) and Zareitalabad et al. (2013).

415 In China, from all sources about 62 t/yr of PFOS were estimated to be released into
416 surface water. Industrial wastewater was the dominant pollution pathway of PFOS in
417 surface water and contributed about 93% (Fig. 3). Due to the relatively high content
418 of PFOS (0.4-0.6% by weight) in AFFF, this was the second most important source.
419 The release of PFOS to soil was estimated at 7 t/yr in central and eastern China. The
420 majority of soil contamination ~~coming came~~ from the use of AFFF and ~~sulfluramid~~
421 **pesticide**. Total contribution from other pollution pathways was less than 11%.

422 Like PFOS, the major release to surface water from PFOA came from industry (Fig
423 3). However, a larger proportion of PFOA emission came from MWWTP discharge
424 (5.8%) and precipitation-runoff (4%). About 6 t/yr of PFOA was released into soil and
425 much of this was attributed to atmospheric deposition. Landfill leachate and pesticide
426 application were next in proportion as sources of soil contamination.

427 Because of their persistence and mobility, groundwater and ocean were the
428 predominant ultimate sinks of PFOS/PFOA. The majority of PFOS/PFOA in surface
429 water will eventually flow into the ocean (Liu et al., 2015b). Surface water seepage
430 and soil leaching contributed almost all of the PFOS/PFOA in groundwater. Due to
431 absorption and retardation by soil particles, the leaching of PFOS/PFOA would occur
432 in a relatively long and slow process of several years depending on groundwater depth

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433 (Xiao et al., 2015). Therefore, transport of PFOS/PFOA through surface water
434 seepage was transient and fast, whilst the movement of PFOS/PFOA through soil
435 leaching was expected to be long lasting and slow.

436 4.3 Uncertainty analysis and study limitation

437 Some uncertainty analysis and study limitations were discussed in this release
438 estimation. As emerging pollutants, sufficiently detailed information on PFOS/PFOA
439 consumption are still lack, and emission data of PFOS and PFOA are only available
440 for major sources. In fact, other industrial sources including paper making, oil
441 exploitation, cleaning products and domestic sources such as traffic, outdoor
442 commercial activities and sulfotine pesticide may also contribute small quantities of
443 PFOS and PFOA in the environment. Therefore, environmental release of PFOS and
444 PFOA in central and eastern China might be underestimated. Some emission data of
445 PFOS/PFOA impurities may be conservative compared to the actual values, due to
446 application of emission factors for the developed countries, which have enforced more
447 strict emission regulations.

448 ~~Due to shortage of sufficient data on PFOS/PFOA transport, only the major~~
449 ~~pollution pathways were discussed in this study.~~ Actually, plant bioaccumulation,
450 runoff scouring, and diffusion between different environmental media, which
451 contributed very small quantities of PFOS and PFOA, are also potential pollution
452 pathways in the environment. Less consideration of these factors may lead some
453 uncertainties for release estimation. In addition, some detailed information on

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454 PFOS/PFOA emission at subregional levels cannot be available. Thus, some transport
455 parameters of PFOS/PFOA in the processes such as runoff, surface water seepage and
456 sediment adsorption had to be conservatively homogenized to roughly estimate
457 environmental release within a large scope. Although the variation of these parameters
458 in these subregions were limited, the estimates may also lead some disparities
459 compared to the actual values.

460 To the best of our knowledge, there are no precise data on degradation rates of the
461 precursors, or the extent to which PFOS/PFOA may be produced, so the estimated
462 release in this study could merely reflect the worst case in which all precursors would
463 transform to PFOS/PFOA instantly.~~In addition, it is unclear about the degradation~~
464 ~~rates of airborne PFOS/PFOA precursors, so the estimated release in this study could~~
465 ~~merely reflect the worst case in which all precursors would convert to PFOS/PFOA.~~
466 In fact, the transformation process of some precursors may be very slow, which may
467 lead underestimation of PFOS/PFOA generated by precursors in the different studied
468 media. Although degradation of Σ FOSA were considered in release estimation from
469 MWWTP, there is a shortage of information on other precursors such as FTOHs as
470 another source for PFOS/PFOA in MWWTP emission. Furthermore, the lack of
471 discharge load of PFOS/PFOA precursors in landfill leachate and AFFF, although
472 their release contribution may be very low, led another underestimation of
473 PFOS/PFOA release to the environment.

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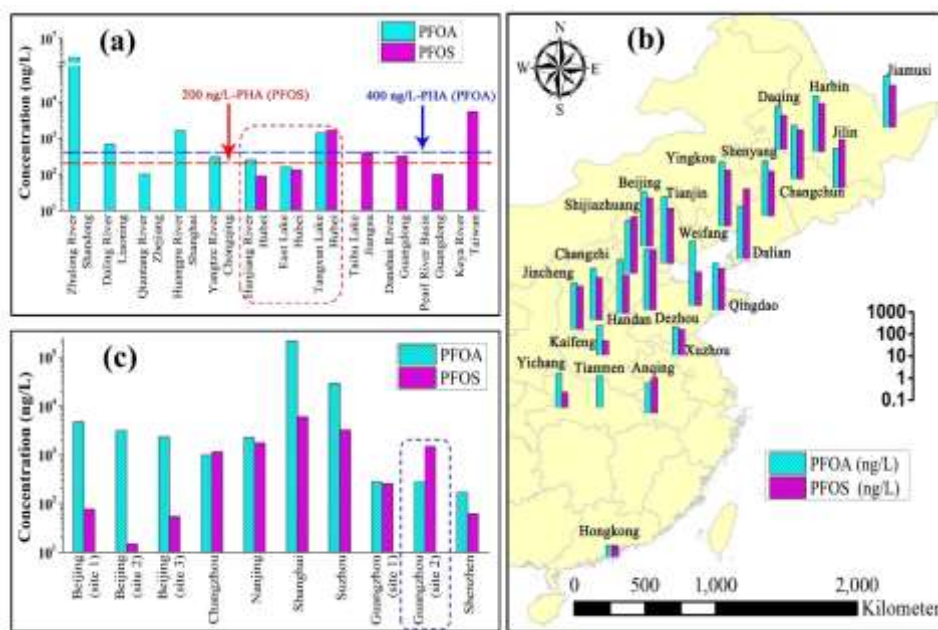
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474 Compared to those (65%) in coast regions, the proportions of airborne PFOS/PFOA

475 deposited to land are much higher in inland regions. Use of the conservative value
 476 may cause a release underestimation (0-35%) of PFOS/PFOA through pollution
 477 pathways associated with air emission. However, the release underestimation does not
 478 significantly change the contribution structure of PFOS/PFOA from these pathways in
 479 soil and surface water, for the total air emission of PFOS was relatively small while
 480 that of PFOA was very large. Despite the above mentioned uncertainties, this study
 481 seemed to provide a reasonable approach to estimate contribution of air emission to
 482 PFOS/PFOA in soil and surface water.

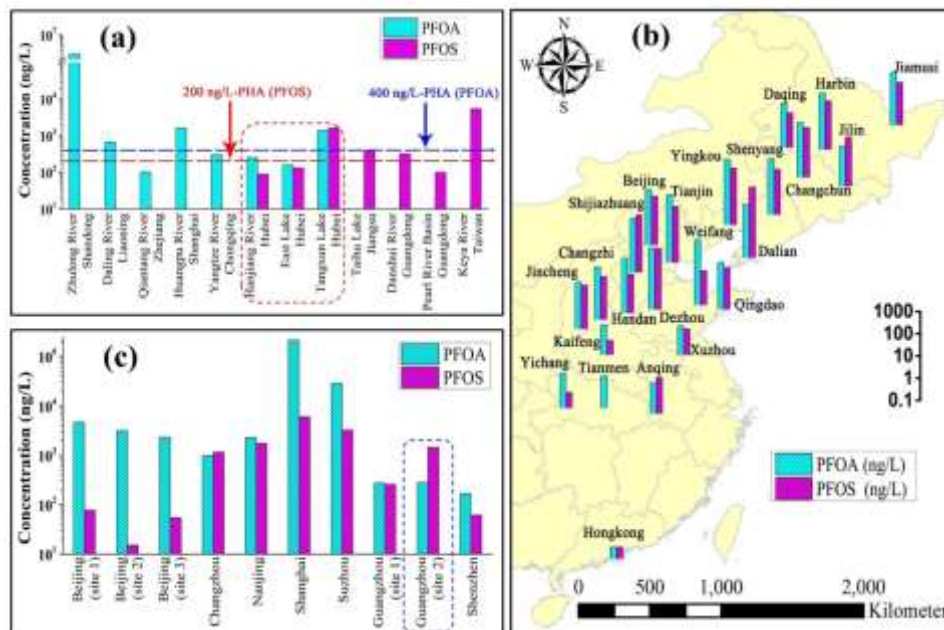
483 4.4 Confirmation of field monitoring data for the release estimations
 484 Corroboration of monitoring data for the release estimations

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487 Fig.4 Occurrence of PFOS and PFOA in surface water(a), precipitation(b) and landfill
 488 leachate(c).

489 **Note:** Monitoring data were reviewed from Liu et al. (2009), Shan et al. (2015), Yi et al. (2012),
 490 Yan et al. (2015), Zhang et al. (2014), Wu et al. (2012) and other references listed in Table S5.

491 It has been demonstrated that the emissions from industry appear to be the most
 492 important for pollution in China (Fig. 2 and 3). Evidence already exists for industrial
 493 wastewater discharge leading to hotspots of PFOS/PFOA in the most developed
 494 regions of China (Fig. 4a). Some of these polluted sites have levels comparable or
 495 even much higher than health risk assessment thresholds for drinking water, such as
 496 the provisional health advisory (PHA) set by the USEPA (Fig.4a) (USEPA, 2014).
 497 After receiving effluent from PFOS/PFOA-related facilities, the concentrations of
 498 PFOA in adjacent river and groundwater were up to 1.7 mg/L and 240 µg/L in Zibo

499 City (Liu et al., 2016); while PFOS levels were 5.4 µg/L and 61 ng/L respectively in
500 nearby surface water and groundwater in Taiwan (Lin et al., 2009). Wastewater
501 discharge from numerous PFOS and PFOA related facilities led to high concentrations
502 of these two substances in the surface water in Hubei Province (Wang et al., 2013;
503 Zhou et al., 2013).

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504 Compared with industrial wastewater release, PFOS and PFOA levels caused by
505 domestic wastewater discharge were, as expected, generally low. According to data
506 from 43 MWWTPs in central and eastern China, the average concentrations of PFOS
507 and PFOA in MWWTP effluent were 9.7 ng/L and 33 ng/L, respectively (reviewed in
508 Table S3). PFOS/PFOA slightly increase in concentration through the MWWTP
509 activated sludge system, probably due to precursor degradation (Dinglasan et al., 2004;
510 Rhoads et al., 2008). In general, the baseline concentrations of PFOS/PFOA in major
511 rivers and lakes were far below assessment threshold of aquatic ecological risk (Fig.
512 S1) (Giesy et al., 2010).

513 Monitoring data of PFOS/PFOA in wet deposition support the release estimations
514 assumptions that were made for the air compartment (Fig. 4b). In particular, in most
515 monitoring sites, PFOA in precipitation showed higher concentrations than PFOS.
516 Due to the limited transport of particle-borne PFOS/PFOA, some high concentrations
517 of PFOS/PFOA in precipitation occurred near industrial sources. The highest
518 concentrations of PFOS and PFOA in precipitation were up to 545ng/L and 107ng/L,
519 respectively (Liu et al., 2009; Shan et al., 2015).

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520 AFFF application and landfill leachate were also prone to cause local risk hotspots.
521 In fire accidents or drills, instantaneous release of hundreds or even thousands liters of
522 AFFF caused 511 ng/g of PFOS and 418 ng/g of PFOA in local soil (Yi et al., 2012).
523 In China, a landfill was reported to lose average 7.6×10^4 m³/yr of leachate with high
524 concentrations of PFOS (1.2-6µg/L) and PFOA (0.3-214µg/L) to local soil and
525 groundwater (Fig. 4c) (Zhang et al., 2014; Yan et al., 2015). Some sites of soil and
526 landfill leachate in Guangzhou showed higher concentrations of PFOS than PFOA,
527 which may be due to waste from the local semiconductor industry (Wu et al., 2012).
528 Except for these hotspots, the concentrations of PFOS/PFOA in soil in most areas
529 were at relatively low levels, far below a residential soil screening level by the
530 USEPA (USEPA, 2014) (Fig.S2).

531 **4.5. Conclusion and observations**

532 Overall, the results of this study indicated that:

- 533 ● About 80-90% of PFOS/PFOA contamination in the Chinese environment was
534 estimated to come from manufacturing and use facilities mostly via industrial
535 wastewater discharge.
- 536 ● For PFOS the next most important contamination sources was the use of AFFF
537 and ~~sulfuramid~~ pesticides, while domestic wastewater and industrial exhaust gas
538 losses were much less important.
- 539 ● For PFOA the most important losses after industrial wastewater were deemed to

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540 be from domestic wastewater, industrial exhaust gas and landfill.

541 ● Industrial wastewater, landfill leachate and AFFF application often cause local
542 risk hotspots of PFOS/PFOA in the Chinese environment.

543 ● The most beneficial way to reduce environmental contamination by PFOS/PFOA
544 in China would be to focus on controlling release from industrial wastewater.
545 Besides, local pollution hotspots caused by AFFF application and landfill leachate
546 should also be paid attention.

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