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

Zhaoyang Liu [a,b], Yonglong Lu [a,*], Pei Wang [a], Tieyu Wang [a], Shijie Liu [c], Andrew C. Johnson [d], Andrew J. Sweetman [d,e], Baninla Yvette [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] *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China*

[d] *Centre for Ecology & Hydrology, Maclean Building, Crowmarsh Gifford Wallingford, Oxon,OX 10 8BB, UK*

[e] *Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK*

Corresponding author:

*Yonglong Lu

Tel: 86-10-62917903

Fax: 86-10-62918177

E-mail: yllu@rcees.ac.cn

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

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

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

1. Introduction

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

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

the most frequently detected PFAAs in the environment (Wang et al., 2015). Due to

their adverse environmental impacts and potential health risks, PFOS have been listed

in a series of national and multilateral regulation agreements including the Stockholm

Convention in 2009 (UNEP, 2009; USEPA, 2009); while 2010/2015 PFOA

Stewardship Program was implemented to reduce PFOA emission (USEPA, 2006).

Although production and application of PFOS and PFOA have been discontinued in

Europe and America (USEPA; 2009), they have continued to increase in China due to

on-going domestic and international demands (Wang et al., 2016). After a decade of

continuous expansion, China's annual production capacity of PFOS and PFOA

plateaued at approximately 220-240 t/yr by 2011 and 150 t/yr by 2013, respectively

(Liu et al., 2008; Li et al., 2015). The widespread contamination and the associated

risks to environment and human health remain a concern for the scientific community

and government regulators.

PFOS and PFOA can be released to the surrounding environment during

manufacturing and application of PFOS/PFOA-containing products (Wang et al.,

2014a). Local PFOS contamination is usually associated with discharge from

industries such as metal plating, textile treatment and PFOS manufacturing, whilst hot

spots of PFOA contamination are derived from production and fluoropolymer (FP)

manufacturing and processing (Lim et al., 2011; Prevedouros et al., 2006)(Xie et al., 2013b; Li et al., 2015). The occurrence of PFOS/PFOA pollution hotspots in soil,

water and air associated with manufacturing facilities have been increasingly reported

in China (Chen et al., 2009; Wang et al., 2015). However, the broader picture of
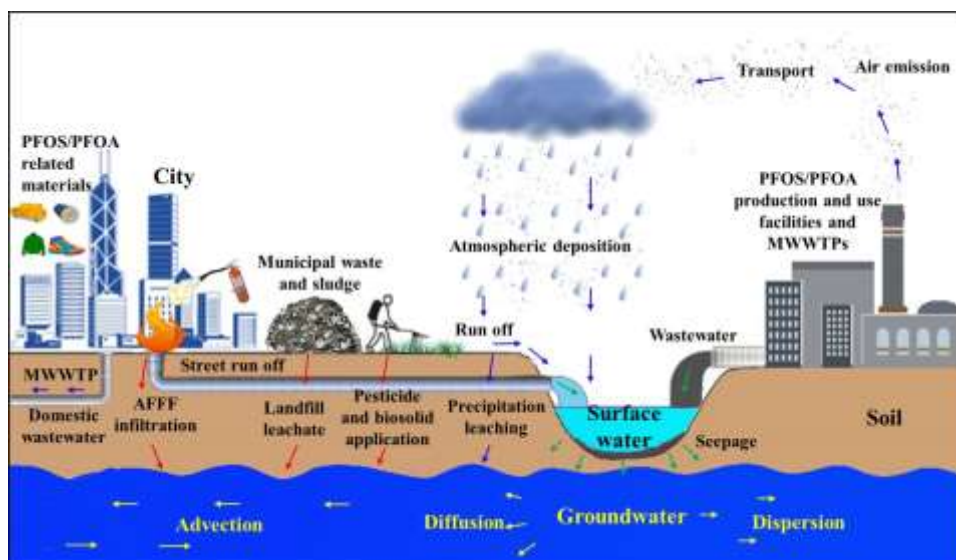
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87 pollution pathways for PFOS/PFOA into different environmental compartments and

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**
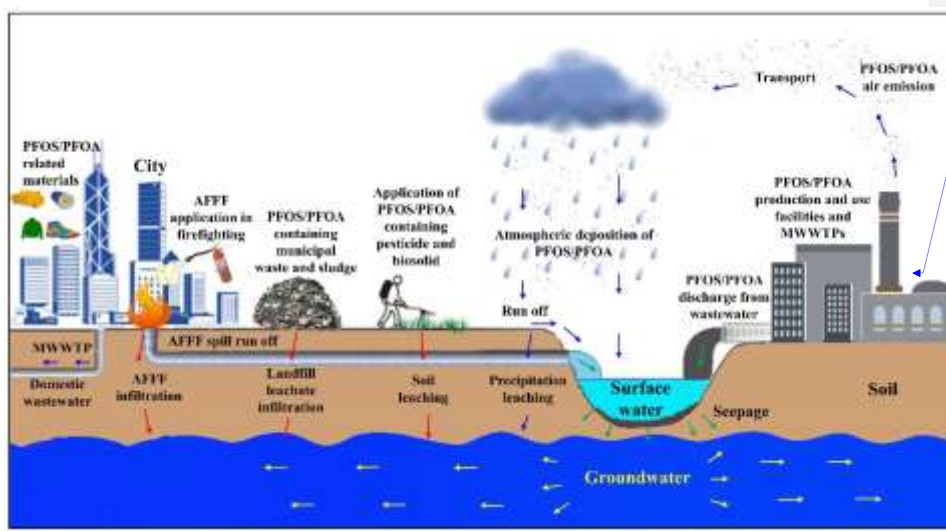
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93

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

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

4.3. Estimation methods of environmental releases

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

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

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

3.1 Contamination of surface water and soil

3.1.1 Wastewater and sewage sludge discharge

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

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

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

$$W_{MWWTP} = E_{MWWTP} \times P_{MWWTP\ water} \tag{1}$$

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

$$S_{Biosolid\ application} = E_{MWWTP} \times P_{MWWTP\ biosolid} \times P_{Biosolid\ application} \tag{2}$$

$$S_{Biosolid\ landfill} = E_{MWWTP} \times P_{MWWTP\ biosolid} \times P_{Biosolid\ landfill} \tag{3}$$

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

Perfluorooctane sulfonyl fluoride (POSF)-based AFFF, mainly produced by consuming the PFOS-salts, is the predominant type of foam in China and is also known to contain PFOA impurities (Lim et al., 2011; Andreas and Leo, 2009). During the application of AFFF, PFOS is directly released to the environment as main ingredients, while PFOA is released in the form of impurities. Due to unavailability of PFOS/PFOA precursors content, these substances was not taken into account for my calculation present in the foam formulation. The concentration ratio of PFOS:PFOA in POSF-based AFFF, produced by similar process to those in China, has been estimated to be 10:1 or even lower (Andreas and Leo, 2009). Emission of PFOS in AFFF application to the environment was estimated to be 7 t/yr (Xie et al., 2013b). According to the PFOS:PFOA ratio (10:1) in POSF-based AFFF, a more modest emission of PFOA was estimated at 0.7 t/yr. When estimating the environmental release of PFOS/PFOA in AFFF, fire training and fire intervention are both considered in the present study (Zhang et al., 2012). The environmental release of PFOS/PFOA during AFFF application was estimated based on a commonly used scenario (Brooke et al., 2004), that there is no containment of this fire-fighting foam after discharge, which is the case in China, and 50% of the release goes to surface water without treatment and 50% to soil which could ultimately, if present, lead to groundwater. According to the assumed PFOS:PFOA ratio (10:1) in AFFF (Andreas and Leo, 2009), a more modest emission of PFOA was estimated at 0.7 t/yr. This ratio was informed by data on consumption of PFOS (100 t/a) and PFOA (9t/a) in AFFF 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 asumption 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 <0.3μm and <10μm, 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 (<1μm) as

247   well as the coarser size particles (<10μm) (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 ($P_{wet\,depostion}$) was

251   conservatively estimated to be 80% and the remaining 20% ($P_{dry\,depostion}$) 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 ($P_{Surface\,water}$) (IGSNNR, 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
$$W_{deposition} = E_{air} \times P_{Land} \times P_{Surface\,water} \qquad\qquad (4)$$

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   (IGSNNR, 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 ($S_{precipitation}$).

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

279     $S_{deposition} =$

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

281     $C_{runoff})]$ (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

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

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

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

3.1.5 Pesticide infiltration

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

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molecules (Löfstedt Gilljam et al., 2015). For sulfluramid containing pesticides, the vast majority are released into the terrestrial environment during application. The environmental release of PFOS has been estimated to be 2.6 t/a by Zhang et al. (2012), while those of PFOA was calculated to be 1.4 t/a based on the annual consumptions of Et-FOSA for sulfluramid, emission factors in use process, transformation rate to PFOA and PFOA content as impurities in sulfluramid (detailed description in Supplementary Material). The use amount of sulfluramid in the central and eastern region of China accounted for 96% of total national use amount ($P_{Pesticide,central\ and\ eastern\ China}$) (Zhang et al., 2012). In China, environmental releases of PFOS/PFOA ($E_{pesticide}$) have been estimated to be 2.6 t/a and 1.4 t/a, respectively (detailed description in Supplementary Material) (Zhang et al., 2012). The proportion of sulfluramid used in the central and eastern region of China ($P_{Pesticide,central\ and\ eastern\ China}$) has been estimated to be 96% (Zhang et al., 2012).

According to emission factors for pesticides used in personal/domestic situations from the Technical Guidance Documents (TGD) (European Commission, 2003), 90% of sulfluramid (P_{soil}) would release to local soil during use. the proportion of sulfluramid (P_{soil}) which is released to local soil was estimated to be 90%. Infiltration The release of PFOS/PFOA ($S_{pesticide}$) from pesticide application to soil can be estimated by Eq. (9).

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

3.2 Groundwater contamination

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

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

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

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

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

4. Results and discussion

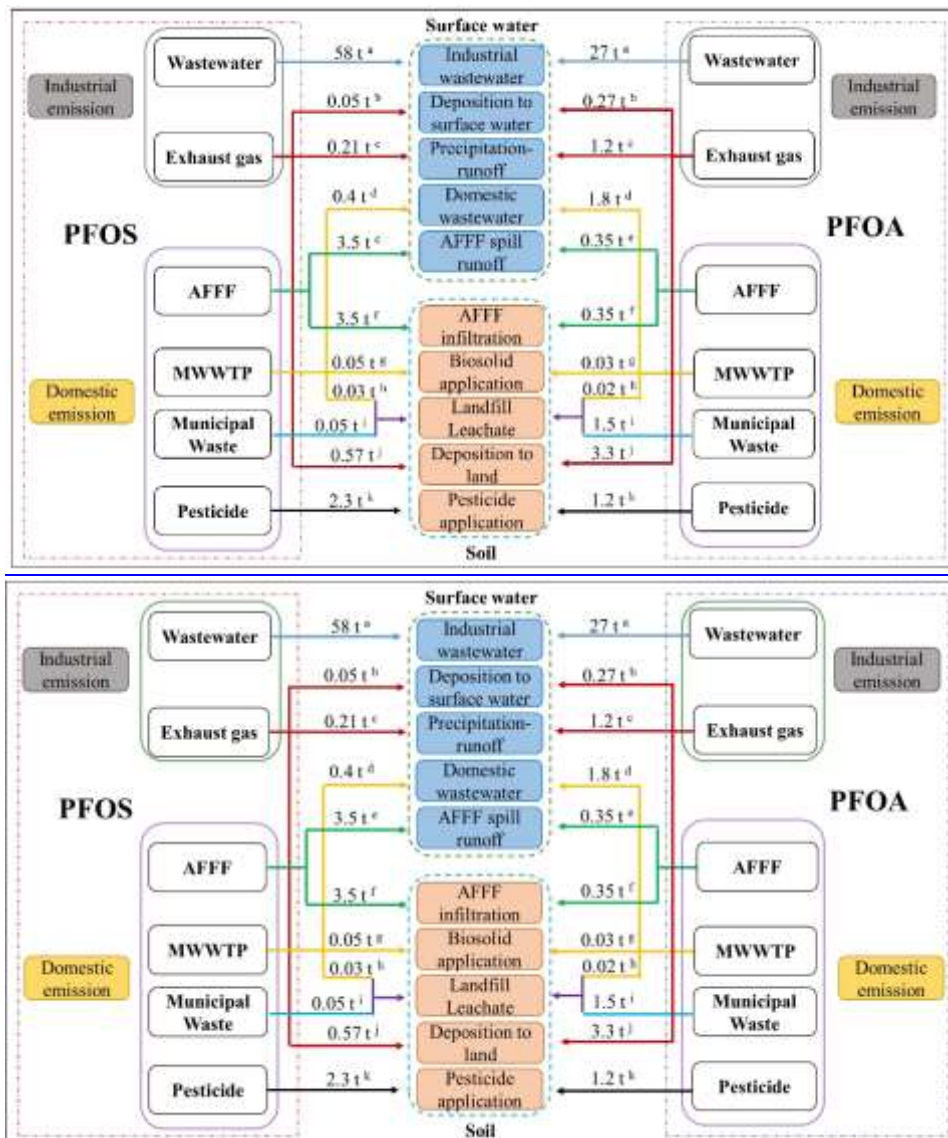*4.1 Major sources screening and release comparison*

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

Note: a was calculated by data from Xie et al. (2013b) and Li et al. (2015); b, c and j were

calculated by Eq. (4, 5, 6) and data from Xie et al. (2013b), Li et al. (2015), Dai (2006), IGSNNR

(2014) and Liu et al. (2015b) ; d, g and h were calculated by Eq. (1, 2, 3, S1, S2, S3, S4) and data

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 considerablePFOA production and nearly all related industrial processes make

389 considerable emissions of PFOA into the atmosphere (Wang et al., 2014a; b).

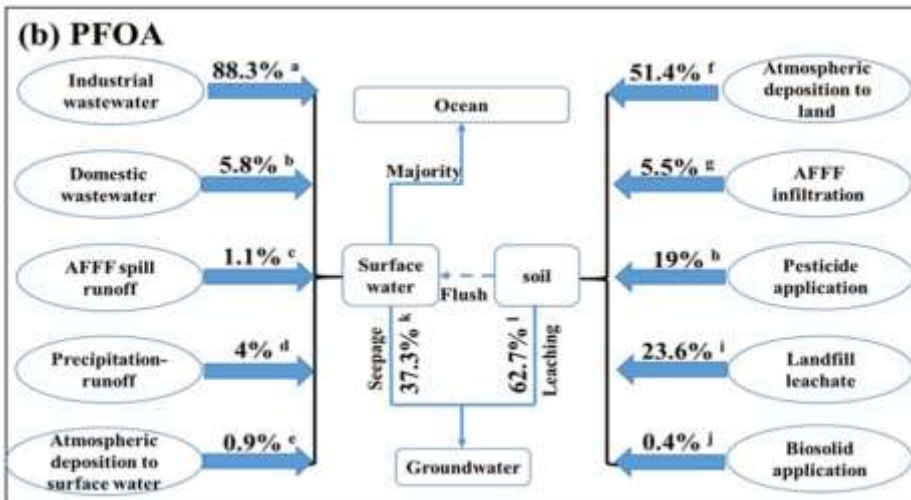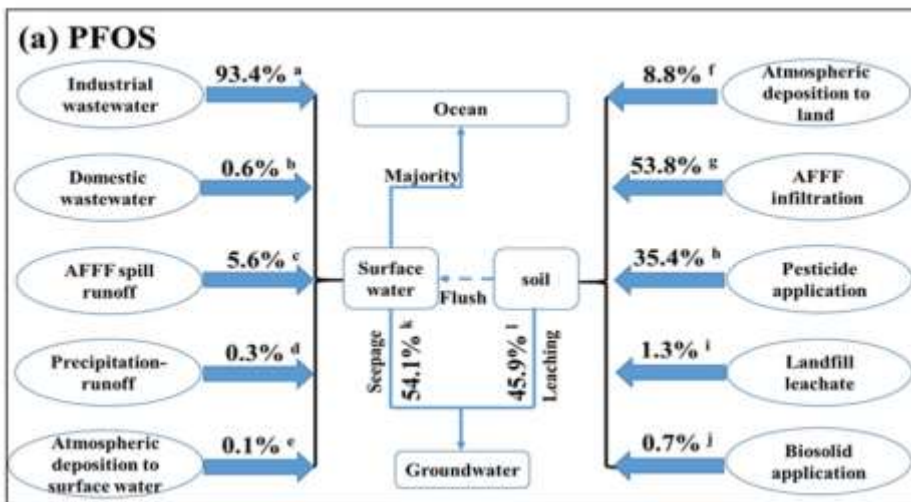390 Overall, domestic emissions are a much less important source of contamination in

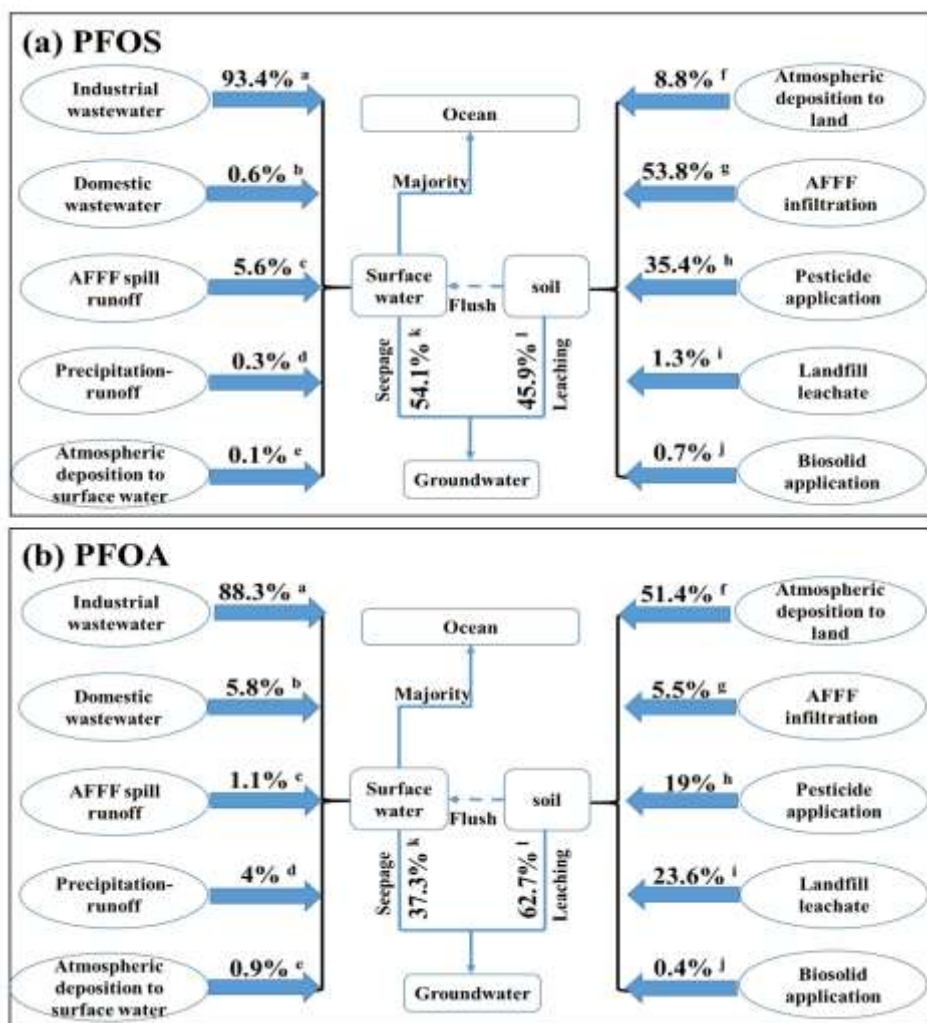391 central and eastern China in terms of quantity (Fig. 2). The higher emissions of PFOS

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*

(a) PFOS

Industrial wastewater	93.4% [a]	
Domestic wastewater	0.6% [b]	
AFFF spill runoff	5.6% [c]	Ocean ← Majority
Precipitation-runoff	0.3% [d]	Surface water — Flush — soil
Atmospheric deposition to surface water	0.1% [e]	Seepage 54.1% [k] / 45.9% [l] Leaching → Groundwater

Atmospheric deposition to land 8.8% [f]
AFFF infiltration 53.8% [g]
Pesticide application 35.4% [h]
Landfill leachate 1.3% [i]
Biosolid application 0.7% [j]

(b) PFOA

Industrial wastewater 88.3% [a]
Domestic wastewater 5.8% [b]
AFFF spill runoff 1.1% [c]
Precipitation-runoff 4% [d]
Atmospheric deposition to surface water 0.9% [e]

Ocean ← Majority
Surface water — Flush — soil
Seepage 37.3% [k] / 62.7% [l] Leaching → Groundwater

Atmospheric deposition to land 51.4% [f]
AFFF infiltration 5.5% [g]
Pesticide application 19% [h]
Landfill leachate 23.6% [i]
Biosolid application 0.4% [j]

403

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

Note: a was calculated by data from Xie et al. (2013b) and Li et al. (2015); b and j were calculated

by Eq. (1, 2, S1, S2, S3, S4) and data from Zhang et al. (2013), Chen et al. (2012) and references

listed in Table S1; c and g were calculated by data from Xie et al. (2013b), Andreas and Leo

(2009) and Brooke et al. (2004); d, e and f were calculated by Eq. (4, 5, 6) and data from Xie et al.

(2013b), Li et al. (2015), Dai (2006), IGSNNR (2014) and Liu et al. (2015b); h was calculated by

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

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

4.3 Uncertainty analysis and study limitation

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

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

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 $\sum$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.

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

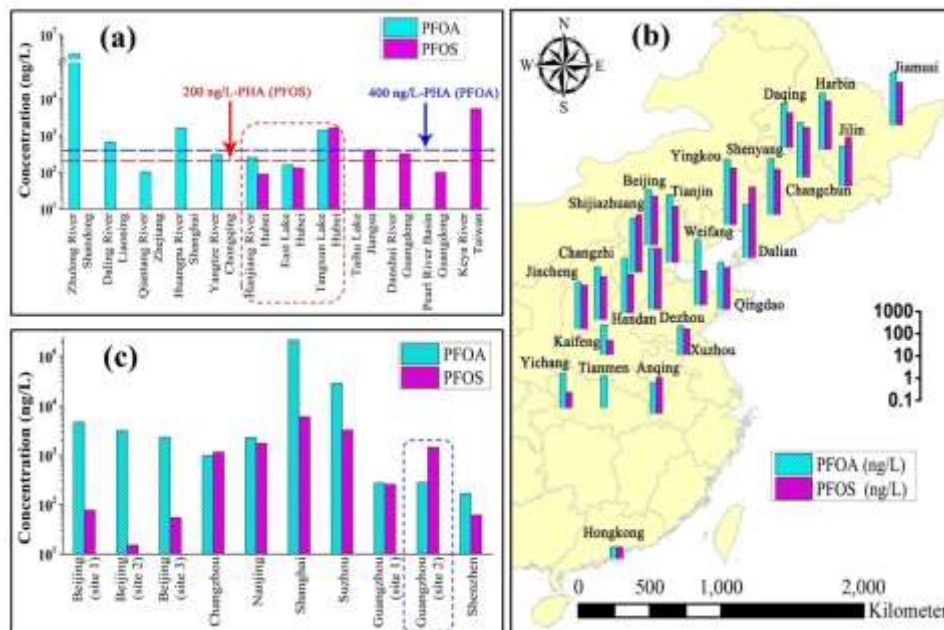482   PFOS/PFOA in soil and surface water.

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

484   ~~monitoring data for the release estimations~~

485
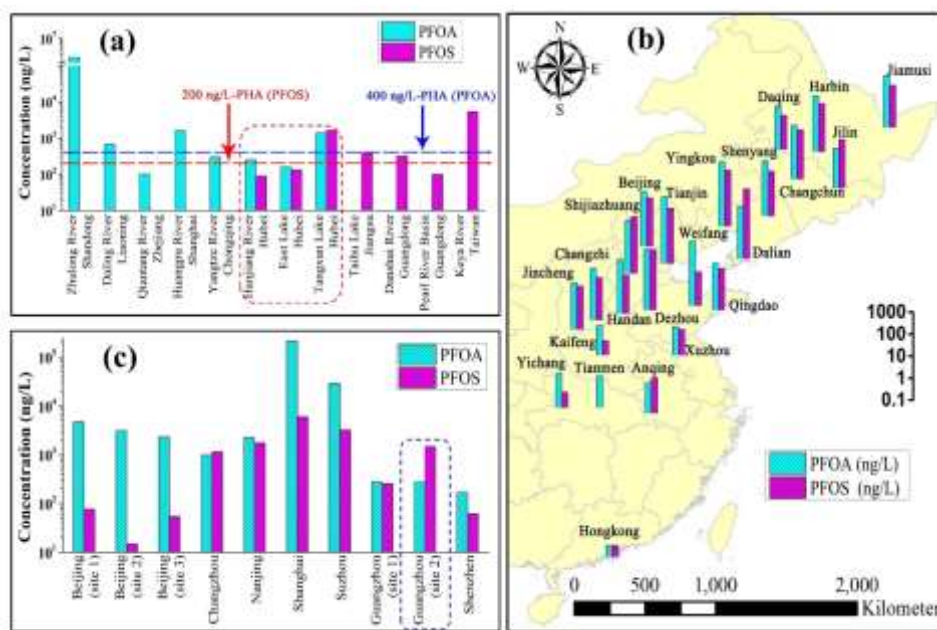
Fig.4 Occurrence of PFOS and PFOA in surface water(a), precipitation(b) and landfill leachate(c).

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

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

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).

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

45. Conclusion and observations

Overall, the results of this study indicated that:

- About 80-90% of PFOS/PFOA contamination in the Chinese environment was estimated to come from manufacturing and use facilities mostly via industrial wastewater discharge.

- For PFOS the next most important contamination sources was the use of AFFF and ~~sulfluramid~~ pesticides, while domestic wastewater and industrial exhaust gas losses were much less important.

- 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.

547   Acknowledgements

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