Risk assessment and source identification of perfluoroalkyl acids in surface and ground water: spatial distribution around a mega fluorochemical industrial park , China

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As I have stated before I believe this manuscript whilst containing very nice information is very long. This makes it hard work to read, this may be fine for reports but reduces your ability to reach and influence a wider audience. There are many further ways the discussion could be shortened without undue pain being caused! I have done my very best to make the text flow. The major omission is the absence of data on the groundwater geology.

ABSTRACT: Perfluoroalkyl acids (PFAAs) can be released to water bodies during manufacturing and application of PFAA-containing products. In this study, the contamination pattern, attenuation dynamics, sources, pathways, and risk zoning of PFAAs in surface and ground water was examined within a 10 km radius from a mega fluorochemical industrial park. Among 12 detected PFAAs, perfluorooctanoic acid (PFOA) was the dominant component, followed by shorter-chain perfluoroalkyl carboxylic acids (PFCAs). PFAA-containing waste was discharged from the fluorochemical industrial park, with levels reaching 1.8 mg/L in the nearby rivers flowing to the Bohai sea together with up to 273 μg/L in the local groundwater in the catchment. These levels constitute a high human health risks for PFOA and other shorter-chain PFCAs within this location. In addition, an aquatic ecological risk was predicted in the Dongzhulong River due to these extremely high concentrations of PFOA. Concentrations of ∑PFAAs in surface water and groundwater nearby showed a positive correlation. The dominant pollution pathways of PFAAs included (i) discharge into surface water then to groundwater through seepage, and (ii) air deposition from fluorochemical industrial park, then through infiltration to groundwater. As the distance increased from the source, the concentration of ∑PFAAs in groundwater showed a sharp initial decrease followed by a more gentle decline. The contamination signal of the fluorochemical industrial park on PFAAs in groundwater existed within the radius of 4 km, while that existed within the lateral distance of at least 3km from seriously polluted Dongzhulong River. The major controlling factor in PFAA attenuation processes was likely to be dilution together with dispersion and adsorption to aquifer solids. The relative contribution of FPOA (C8) declined while those of C4-C6 shorter-chain PFCAs increased during surface water seepage and further dispersion in groundwater.

KEYWORDS: PFAAs; fluoropolymer; spatial distribution; source identification; risk assessment

1. Introduction

Perfluoroalkyl acids (PFAAs) have been widely used in manufacturing processes and products, such as surfactants and surface protectors, performance chemicals, lubricants and pesticides, due to their unique properties, including surface activity, heat and acid resistance, and water and oil repellency (Giesy and Kannan, 2001; 2002). However, concerns have been raised due to the environmental persistence, toxicity, long-range transport and bioaccumulation properties of PFAAs (Lescord et al., 2015; Liu et al., 2015; Wang et al., 2015b). Continuous release of these substances from various products and applications has made them ubiquitous in environments, such as air (Taniyasu et al., 2013), water (Wang et al., 2015a), sediment (Yeung et al., 2013), wildlife (Persson et al., 2013) and even the human body (Zhang et al., 2013). In addition, water has become the primary reservoir of PFAAs and the major medium for their transportation due to the relatively high polarity and solubility of ionic PFAAs (Prevedouros et al., 2006; Sharma et al., 2015).

PFAAs can be released to the surrounding environment during manufacturing and the application of PFAA-containing products (Wang et al., 2014b). The presence of Perfluorooctane sulfonate (PFOS) in the environment is usually associated with discharge from industries such as metal plating, textile treatment and FPOS manufacture, while most Perfluorooctanoic acid (PFOA) is derived from PFOA/PFO production and fluoropolymer manufacturing and processing (Xie et al., 2013b; Li et al., 2015). Whilst industry is a major source for PFAAs in surface and ground water, they are also discharged in domestic sewage (Eggen et al., 2010; Xie et al., 2013a).

The mobility of longer-chain PFAAs is reduced by their sorption potential to organic carbon in soil and sediment, whilst the less hydrophobic, shorter-chained, PFAAs are more likely to undergo long-distance transport in surface water or penetrate to groundwater (Armitage et al., 2009; Murakami et al., 2009). The generally slow movement of groundwater makes this environment more of a sink, whilst contamination of surface water can lead to widespread dissemination (Lin et al., 2015). High concentrations of PFAAs in surface and ground water could represent not only a potential health risk via drinking water but also a risk to wildlife in aquatic ecosystems (Giesy et al., 2010; Post et al., 2012).

Although the production of PFAA-related chemicals has been discontinued in Europe and America, it has continued to increase in China due to the domestic and international demands. The fluorochemical industrial park in our study is a mega fluoropolymer production base, with an annual capacity of 50,000 tons of tetrafluoroethylene (TFE), 37,000 tons of polytetrafluoroethylene (PTFE), 10,000 tons of hexafluoropropylene (HFP) and more than 200,000 tons of different types of fluorinated refrigerants (Dongyue Group Limited, 2012). Previous studies demonstrated that fluoropolymer manufacturers can seriously contaminate surface water with PFAAs (Wang et al., 2014a; Heydebreck et al., 2015; Shi et al., 2015), but less is known about local groundwater contamination by such industrial sites?

This study was conducted to advance our understanding of PFAA emissions in surface and ground water in association with ongoing fluoropolymer production with particular emphasis on (i) studying contamination pattern and attenuation dynamics,

(ii) analyzing pollution sources and pathways, (iii) conducting risk zoning to evaluate surface and ground water safety.

2. Materials and methods

2.1. Sampling design and collection

Beneath the fluorochemical industrial park in Huantai County, Shandong Province, China groundwater can be found at a depth of 5 m from the surface (Table S12)??? This is an alluvial sandy aquifer which is unconfined which is typical of this region?? The groundwater is/isn't a drinking water source?? The groundwater samples were collected from a series of boreholes which had been installed five years previously. Sampling was done using a submersible pump, with over 100 L being pumped and discarded before taking the actual sample in 1-L polypropylene bottles. Surface water samples were collected from the Dongzhulong River and Xiaoqing River together with groundwater samples from the Dongzhulong River catchment (Fig. 1). In October 2014, 10 samples of surface water and 37 samples of groundwater were collected. Collected samples were stored in an icebox during transportation, all samples were extracted within 1 week after arrival in the lab, and the remainder stored at -20°C for long-term reference. Parameters, including pH, dissolved oxygen, conductance, water temperature and salinity, were determined *in situ* using an HQd Portable and Benchtop Meter Configurator (HACH Company, USA) (Table S1). Before analysis, all the samples were allowed to stand for 24 h to settle any sediment and then 400 mL of supernatant was taken from each sample for analysis. Latest official monitoring data of groundwater level and well depth was also acquired in the study area (Table S12).

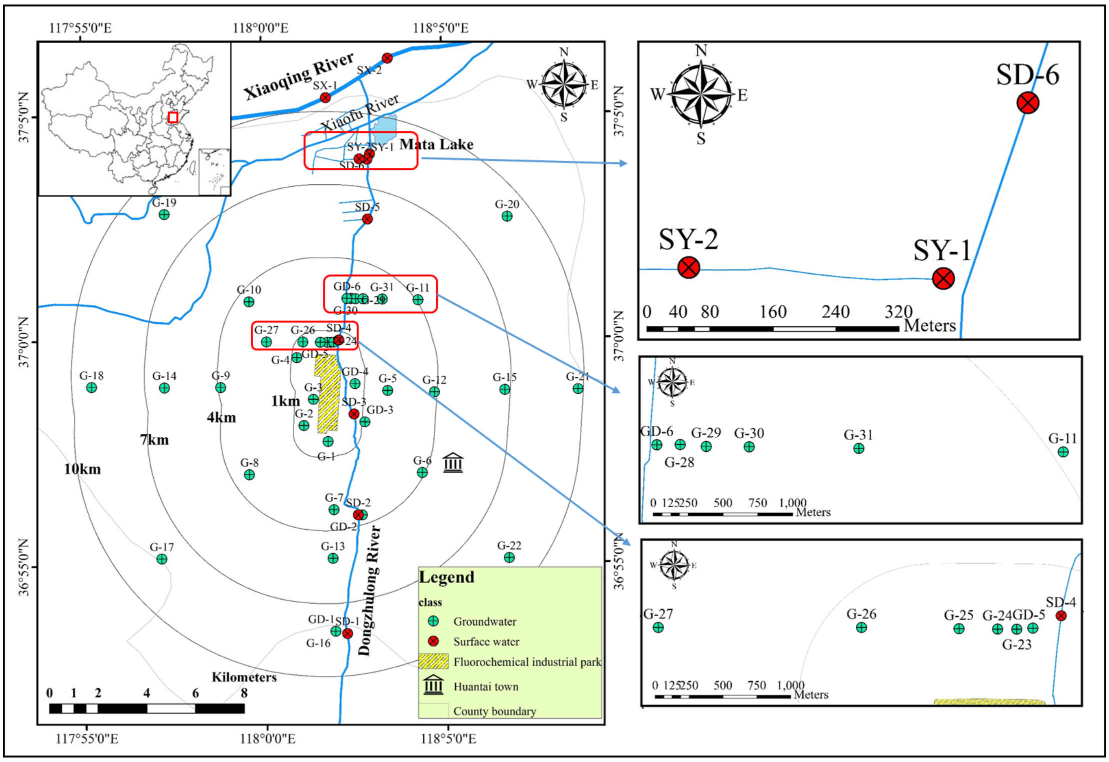

Fig.1 Map of the sampling locations for surface water and groundwater in Huantai County

2.2 Standards and Reagents

All samples were analyzed for 12 PFAAs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), potassium perfluorobutanesulfonate (PFBS), sodium perfluorohexanesulfonate (PFHxS), potassium perfluorooctanesulfonate (PFOS). The detailed descriptions on standards and reagents are available in

Supplementary Material.

2.3 Extraction and cleanup

Water samples were extracted by OASIS WAX-SPE using a previously described method (Taniyasu et al., 2005) with minor modification and optimization. Briefly, the Oasis WAX cartridges (6 cc, 150 mg, 30 mm, Waters, Milford, MA, USA) was preconditioned with 4 mL of 0.1% NH_4OH in methanol, 4 mL methanol and 4 mL Milli-Q water. The 400-mL aliquot of water sample was spiked with 5 ng internal standard ($^{13}C_4$PFBA, $^{13}C_4$PFHxA, $^{13}C_4$PFOA, $^{13}C_4$PFNA, $^{13}C_4$PFDA, $^{13}C_4$PFUdA, $^{13}C_2$PFDoA, $^{18}O_2$PFHxS and $^{13}C_4$PFOS)， mixed thoroughly and then loaded into the cartridge. The cartridge were washed with 4 mL of 25 mM ammonium acetate (pH 4), air-dried overnight, and successively eluted with 4 mL of methanol and 4 mL of 0.1% NH_4OH in methanol. The eluents were collected and concentrated to 1 mL under a gentle stream of high-purity nitrogen (99.999%, Haidian District, Beijing, China), then filtered through a nylon filter (13 mm, 0.2 mm, Chromspec, Ontario, Canada) into a 1.5-mL PP snap top auto-sampler via with polyethylene (PE) septa.

2.4 Instrumental analysis and quantitation

Individual PFAA were separated and quantified using Agilent 1290 Infinity HPLC System equipped with an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA, USA) in the negative electrospray ionization (ESI) mode. Quantification was performed using Analyst 1.4.1 software provided by SCIEX. The detailed descriptions on instrumental analysis were available in

Supplementary Material.

2.5 Quality Assurance and Quality Control (QA/QC)

Field blanks, transport blanks, procedure blanks and solvent blanks were conducted with every sample set to examine if any external contamination occurred during the sampling/extractuin and analytical process. The internal standard calibration curve consisting of a concentration gradient (0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, and 100 ng/mL), spiked with 5 ng internal standard was prepared for quantification of individual PFAA with coefficients (r^2) for all target analytes exceeding 0.99. Quantification was performed using with a correlation coefficient greater than 0.99 for each analyte. The limit of detection (LOD) and limit of quantification (LOQ) were defined as the peak of analyte that needed to yield a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. Matrixes spiked with a standard solution were analyzed to determine the recovery of each target PFAA and matrix spike recoveries(MSRs) ranged from 79.00% to 109.07%. Supplementary Material and Table S2 described detailed QA/QC information .

2.6 Statistical and spatial analyses

Statistical analysis was performed using SPSS Statistics V22.0 (SPSS Inc. Quarry Bay, HK). During the analysis, concentrations less than the LOQ were set to one-half of the LOQ, and those less than the LOD were assigned to values of LOD/ √ 2 (Bao et al., 2011). Spatial distributions of PFAAs were analyzed using the Arcmap module in ArcGIS V10.0 software (ESRI, Redland, CA, USA).

2.5 Data Representation

Because of the large variation on the orders of magnitude, the accuracy of all data were presented with three significant figures. Units for concentrations in water were ng/L, µg/L or mg/L.

3. Results and discussion

3.1 Occurrence and source identification of PFAAs in surface and ground water

Each of the 12 PFAAs were detected in this study (Table S2-S3). The concentration of sum PFAAs (∑PFAAs) ranged from 55.7 ng/L to 1.86 mg/L in surface water samples, and from 1.66 ng/L to 273 µg/L in groundwater samples (Table S3). PFOA was the dominant component with a mean contribution of 81.60% to ∑PFAAs in surface water and 65.29% to ∑PFAAs in groundwater, followed by C4-C7 short-chain perfluoroalkyl carboxylic acids (PFCAs) including PFBA, PFPeA, PFHxA and PFHpA. Long-chain PFCAs (C9-C12) and perfluoroalkane sulfonic acids (PFSAs) including PFBS, PFHxS and PFOS were only observed in low concentrations or below the MDL, which were likely due to limited production and application of these components in this region (Xie et al., 2013b).

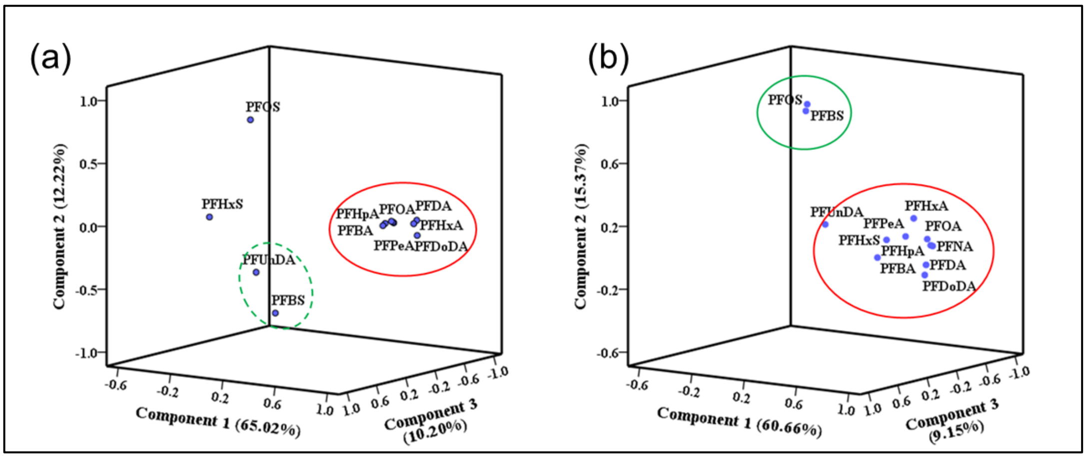

Fig. 2 PCA results using concentrations of 12 PFAAs in surface water (a) and groundwater (b)

PCA analysis on the 12 PFAAs in surface and ground water showed that the concentrations of PFCAs, such as PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA and PFDoDA, were strongly associated, indicating that these compounds might come from similar sources (Fig. 2, S2; Table S4-S7). The fluorochemical industrial park in our study area included not only PFOA production but also fluoropolymer manufacturing and processing and these two industries contribute 83.7% and 8.3% of PFOA in environment, respectively (Li et al., 2015). The increase of most PFAAs, especially PFOA, nearby or immediately downstream of the fluorochemical industrial park indicated it was principal source of PFAAs in not only surface water but also groundwater. However, other sources of PFAAs in surface and ground water were inferred to exist based on PCA results. Domestic emission, WWTP effluent and other industrial emissions were also likely to be potential sources of PFAAs (Bossi et al., 2008; Wang et al., 2014c). The concentration of ∑PFAAs increased to various degrees after receiving emissions from these sources.

To the best of our knowledge, the PFOA concentration in surface water (1.71 mg/L) reported in this study is the highest ever found. Previous studies in this location reported 0.58 mg/L (Heydebreck et al., 2015) and 0.37 mg/L (Shi et al., 2015). The lowest concentration of PFOA in surface water was also at a high level in Northern China (0.55-82 ng/L) (Wang et al., 2012). Except for 7.09 mg/L caused by AFFF infiltration in Tyndall Air Force Base(USA)(Moody and Field, 1999), the concentration of PFOA in groundwater(240 μg/L) in our study was also at the highest level (reviewed in Table S8-S9). In recent years, studies on PFAAs in groundwater around fluoropolymer facilities have been reported sporadically. Most of the studies were conducted in the USA, once the largest country of PFAA manufacturing and application. PFOA was dominant in groundwater with maximum measured concentrations of 78μg/L near a fluoropolymer manufacturing facility in Parkersburg (Davis et al., 2007), 42 μg/L around a 3M facility in Minnesota (Oliaei et al., 2013), 20μg/L surrounding a PFAA-manufacturing facility in Minneapolis St. Paul (Xiao et al., 2015) and 13.3μg/L around DuPont's Washington Works facility (Hoffman et al., 2011). However, contamination pattern, attenuation dynamics, transport pathway, and risk extent of PFAAs in groundwater were not systematically analyzed in these studies.

3.2 Pollution pathway and attenuation dynamics of PFAAs in surface and ground water

The Dongzhulong River flows through Zibo City and converges with the Xiaoqing River, which accepts domestic wastewater and industrial discharge including waste from the fluorochemical industrial park. ~~The concentrations of ∑PFAAs in surface and ground water along the river and detailed site information were showed in Fig.3 and Table S1,S3.~~ At the upstream of fluorochemical industrial park, the concentrations of ∑PFAAs in surface water of the Dongzhulong River and groundwater nearby were negatively correlated with the distance from the fluorochemical industrial park. PFOA was dominant with concentration of 1.2 ng/L-401 ng/L and a contribution of 47.86%-81.75% to ∑PFAAs (Fig. 3). PFAAs level at site SD-1 was notable with a total concentration of 55.7ng/L, which suggested domestic emissions from the Zibo City were present (Wang et al., 2014b). The concentration of ∑PFAAs at site GD-1 (groundwater adjacent to SD-1) was 2.09 ng/L was much lower than that in nearby surface water. The concentration of ∑PFAAs at site SD-2 and GD-2 increased to 73.8 ng/L and 37.8 ng/L respectively， probably due to effluent from a wastewater treatment plant (WWTP) (Muller et al., 2011; Eschauzier et al., 2012). With decreasing distance from fluorochemical industrial park, the concentrations of ∑PFAAs increased up to 368 ng/L in surface water at SD-3 and 410ng/L and 490 ng/L in groundwater at GD-3 and GD-4, respectively. Although located before the waste discharge point from the fluorochemical industrial park, these sites might be influenced through diffusion and dispersion of PFAAs from general industrial activity in the area.

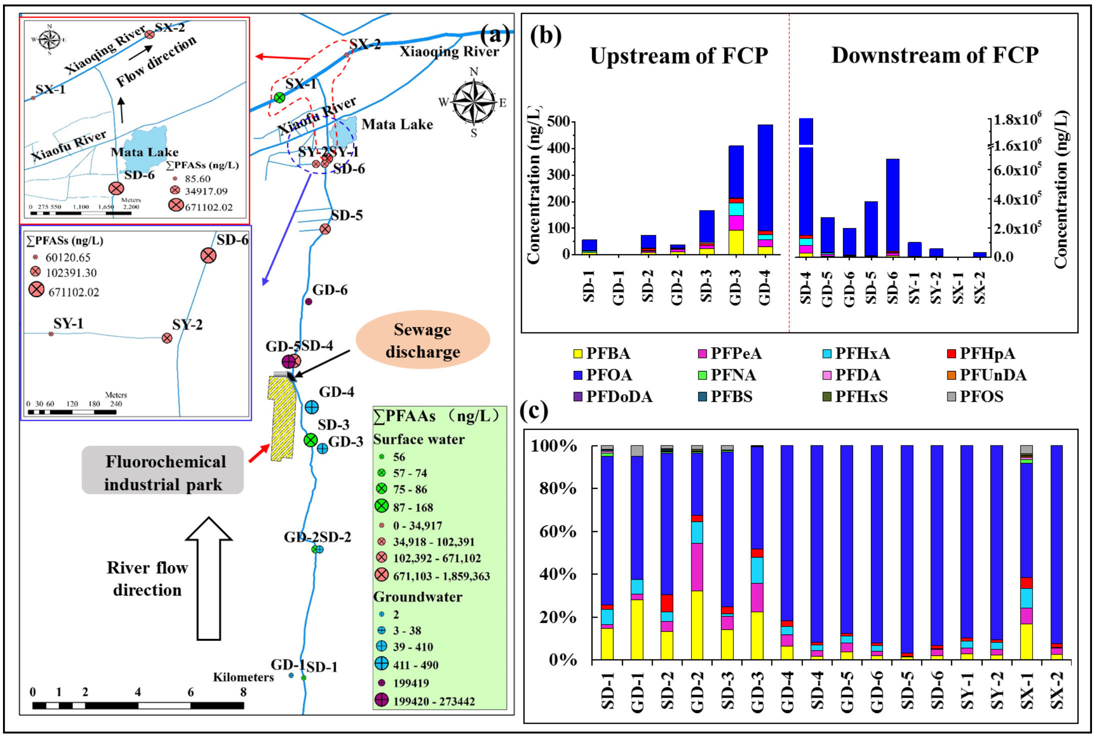

Fig. 3. Spatial distribution of PFAAs in surface and ground water adjacent to the Dongzhulong River

Note: GD: groundwater adjacent to the Dongzhulong River; SD: surface water in the Dongzhulong River; SX: surface water in the Xiaoqing River; SY: surface water diverted from Yellow River

Downstream of fluorochemical industrial park, the concentrations of ∑PFAAs in surface water of the Dongzhulong River and the Xiaoqing River and groundwater increased to extremely high levels and relative contributions of individual PFAA also changed. The sharp increase was linked to the fluorochemical industrial park. Location SD-4 was immediately at the downstream of the effluent from fluorochemical industrial park into the river. The concentration of ∑PFAAs in surface water at SD-4 soared to 1.86 mg/L, and that in groundwater at GD-5 also increased up to 273 μg/L. PFOA at SD-4 exhibited the highest contamination with a concentration of 1.71 mg/L, which was 91.8% of ∑PFAAs, followed by PFPeA (51.4 μg/L, 2.77%), PFHxA (50.3 μg/L, 2.71%), PFBA (28.3 μg/L, 1.52%) and PFHpA (21.3 μg/L, 1.15%). The concentration of PFOA at GD-5 also increased up to 240 μg/L, which contributed 87.64% of ∑PFAAs, followed by PFPeA (10.6 μg/L, 2.77%), PFBA (10.5 μg/L, 3.85%), PFHxA (8.88 μg/L, 3.25%), and PFHpA (3.73 μg/L, 1.37%). Although total contribution of C9-C12 long-chain PFCAs in these two sites were less than 0.04%, they also showed notable concentrations such as PFNA(SD-4:430 ng/L,GD-5:33.5ng/L), PFDA(SD-4:181 ng/L,GD-5:18.7 ng/L) and PFDoDA(SD-4:83.6 ng/L,GD-5:17.1ng/L). With increasing distance from fluorochemical industrial park, the concentrations of ∑PFAAs in surface water (SD-5: 380μg/L, SD-6: 671μg/L) as well as groundwater (GD-6: 199 μg/L) showed a downward trend, while the relative contributions of individual PFAA had no obvious change. Seepage to groundwater can be an important source for subsequent contamination or re-contamination of rivers (Lin et al., 2015; Wang et al., 2015a). The proportion of surface water seepage in the Northern Plain of China is estimated to be about 12% (MWR, 2011;2013;2014). Similar source and positive correlation of PFAA concentrations in surface and ground water indicated that most PFAAs in groundwater may come from seepage of contaminated surface water (Huset et al., 2008), then transport through diffusion, dispersion and advection (Lin et al., 2015; Xiao et al., 2015).

After confluence with the Dongzhulong River, the concentration of ∑PFAAs in the Xiaoqing River (an important source of domestic water and agricultural water) increased from 85.6 ng/L at site SX-1 to 34.9μg/L at site SX-2. Previous studies have shown that the concentrations of PFAAs in the Xiaoqing River can reach 5.07 μg/L at a distance of 30 km from the confluence with the contaminated Dongzhulong River, and 3 μg/L at the estuary 92 km away from the fluorochemical industrial park (Wang et al., 2014a). Most farmlands in the northern part of the study area are irrigated by surface water abstraction. To avoid exchange and dispersion of polluted water, irrigation canals were isolated from the Dongzhulong River, and Yellow River for irrigation and aquaculture. However, the concentration of PFAAs in diverted Yellow River water at site SY-2 which is 20 m away from the Dongzhulong River was up to 102 μg/L, and it was still 60.1 μg/L at the site SY-1 350 m away from the river. The pollution pathway might be water exchange between diverted Yellow River water and contaminated shallow groundwater.

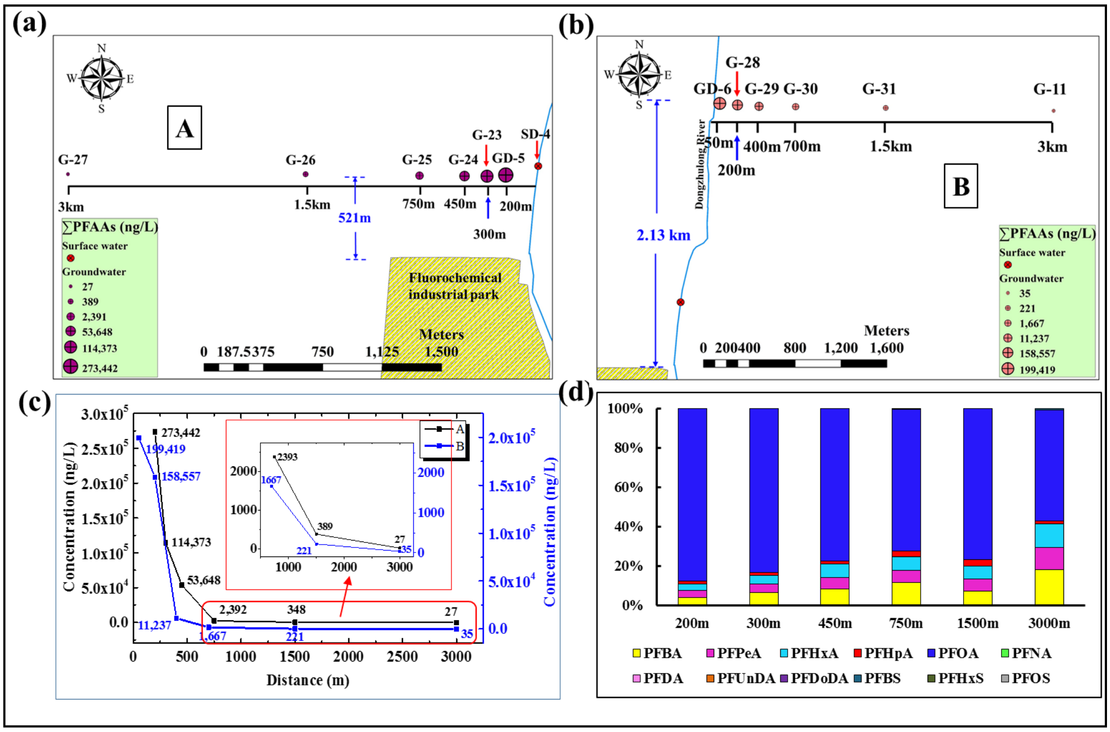

Fig. 4. Attenuation dynamic of PFAAs with the increase in distance from swage river

[(a) and (b)]; Concentration change of ∑PFAAs (c) and relative contribution of individual PFAA to ∑PFAAs (d) with the increase in distance

Along the lateral direction from the Dongzhulong River (1.86 mg/L, max) which received sewage from the fluorochemical industrial park, the concentration of ∑PFAAs in groundwater decreased with an exponential trend, showing a sharp initial decrease followed by a more gentle decline (Fig. 4a, 4b, 4c). Moving west from the from the fluorochemical industrial park (transverse A) (Fig. 4a), the concentration of ∑PFAAs in groundwater sharply decreased by 99.13% (from 273 μg/L to 2.39 μg/L) within a distance of 200-700 m, and then declined by 0.73% to 348.3 ng/L within the distance of 700 m-1.5 km. Once the distance had increased to 1.5 km to 3 km from the factory complex the concentration of ∑PFAAs was 27.0 ng/L. To the East of the fluorochemical industrial park(transverse B)) (Fig. 2b), the concentration of ∑PFAAs in groundwater rapidly decreased by 99.16% (from 199 μg/L to 1.67 μg/L) within the distance of 50-700 m, slowly attenuated by 0.73% to 221 ng/L within the distance of 700 m-1.5 km, and then gently declined by 0.09% to 34.8 ng/L within the distance of 1.5 km-3km. The concentrations of ∑PFAAs at the distance of 3 km in sample groups (a) and (b) were both an order of magnitude higher than most sites further from the sewage river (Fig. 5a and 5b). Based on these findings, the contamination signal of PFAAs in groundwater existed within the lateral distance of at least 3 km from seriously polluted Dongzhulong River. Since most of PFAAs are resistant to chemical decomposition and biochemical attenuation, adsorption to aquifer solids and the dilution caused by dispersion were major controlling factor in PFAA attenuation processes.

The contribution of PFOA(C8) decreased in the process of surface water seepage and further dispersion in groundwater relative to the short-chain (C4-C6) PFCAs . For example, after seepage of PFAAs from the Dongzhulong River to the local groundwater the average contributions of PFBA, PFPeA and PFHxA increased by 8.04%, 5.05%, and 3.92% respectively while percentage of PFHpA and PFOA decreased by 0.96% and 15.64%. During surface water seepage, relative contributions of individual PFAA at upstream of fluorochemical industrial park showed more significant changes than those at downstream of fluorochemical industrial park, which may be due to extremely high concentrations of PFOA in surface water and limited saturated adsorption by sediment and soil. In the process of PFAAs dispersion in the aquifer, the relative contributions of PFBA, PFPeA, PFHxA, PFHpA increased by 14.19%, 7.65%, 8.65% and 0.06%, respectively while the percentage of longer chain PFOA deceased by 34.17% in transverse A; the relative contributions of PFBA, PFPeA, PFHxA, PFHpA increased by 16.4%, 8.04%, 6.15% and 1.73% respectively, while percentage of PFOA deceased by 32.71% in transverse B(Fig. 4d, S1). Thus, the relative contribution of PFBA(C4) showed the largest increase with distance/time from the contamination source, followed by PFPeA(C5) and PFHxA(C6). The relative contribution of PFHpA(C7) varied little, while relative contribution of PFOA(C8) decreased significantly in the process of surface water seepage and further dispersion in aquifer. This phenomenon supports the observation that the removal efficiency increases with the chain length (Murakami et al., 2009). Shorter-chain

PFAAs with a higher aqueous solubility and a lower adsorption affinity showed better transportability and filterability and poor sorption to sediment, soil and aquifer solids during surface water seepage and dispersion in groundwater (Eschauzier et al., 2012).

3.3 Distribution and transportation of PFAAs in groundwater from the fluorochemical industrial park

~~Radiated distribution of fluorochemical industrial park in groundwater was showed in Fig. 5.~~ There is has a relatively developed industry system in Huantai town, which mainly covers four industrial areas as follows: A: fluorochemical industry; B: petrochemical, fine chemicals and paper industry; C: petrochemical, metallurgical machinery and agricultural processing; D: tourism and village group.

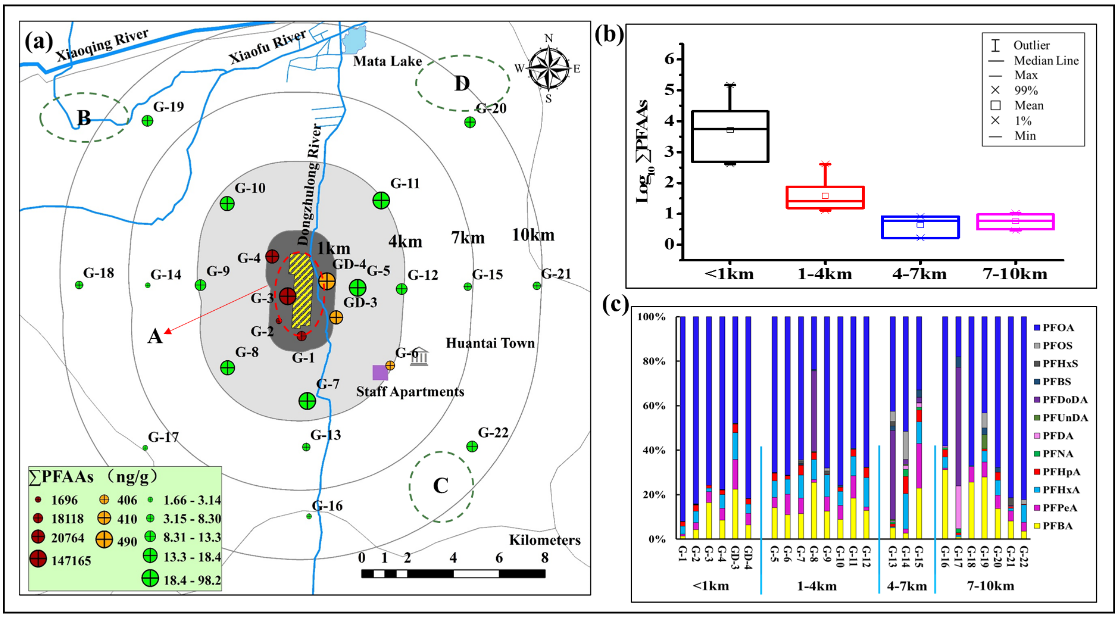

Fig. 5. Distribution of ∑PFAAs in the groundwater with increasing distance from fluorochemical industrial park(a); Change of ∑PFAAs levels (b) and relative contribution of individual PFAA to ∑PFAAs (c) with the increase in distance

With increasing radius from the fluorochemical industrial park, the concentration of ∑PFAAs in groundwater also showed a similar tendency, exhibiting a sharp and then gentle decline (Fig. 5). Within a 1 km radius, the groundwater concentration of ∑PFAAs was extremely high (31.4 μg/L); then dropping to a low level (86.3 ng/L) within the distance of 1-4 km; before a further decline to 5.35 ng/L within the distance of 4-7 km (Fig. 5b). The concentrations of ∑PFAAs at site G-1 (18.1 μg/L), G-2 (1.70 μg/L), G-3 (147 μg/L) and G-4 (20.7 μg/L) south and west from the fluorochemical industrial park were much higher than those on the east side at sites GD-3 (410 ng/L) and GD-4 (490 ng/L). Perhaps the Dongzhulong River, which is east of the site, is intercepting much of the PFAAs on this side (Fig. 5a). In contrast to this trend, the concentration of PFAAs at on the south eastern side at site G-6 (406 ng/L) was particularly high despite not being within the factory grounds. This G-6 site was near staff apartments of the fluorochemical industrial park in the county town, which might be affected by passing traffic or staffs from fluorochemical industrial park and domestic waste (Fig. 5a). Interestingly, the proportion of short-chain PFCAs (the more mobile and persistent of the PFAAs) at site GD-3 was much higher than those on the west side of the river (Fig. 5c). The concentration of ∑PFAAs in groundwater usually decreased sharply within a very short distance from the point source. In Minneapolis St. Paul, (USA), the concentration of PFOA in groundwater also decreases from 20 μg/L near a former fluoropolymer production facility to <100 ng/L within the distance of 1.4 km from the facility (Xiao et al., 2015). These results show that the groundwater pollution radius of this fluorochemical industrial park was at least 4 km. The pollution scope was larger than that of a PFAA manufacturing facility

(<2 km) in Wuhan, China, which might be due to the sheer scale of the manufacturing site here (Wang et al., 2010). Location G-7 was located near many chemical plants, such as corrugated paper plants and cable plants, which may be major users of PFAAs leading to 58.6 ng/L PFAA here (Fig. 5a). Compared with those within the distance of 4-7 km, the concentration and proportion of PFOA was slightly higher within the distance of 7-10 km, which was probably due to small discharge of PFAAs from the industries and villages in B, C and D areas (Fig. 5a, 5c).

As the radial distance from the fluorochemical industrial park increased, the relative contributions of shorter-chain PFCAs also increased while the proportion of PFOA reduced as observed previously (Fig. 5c). Compared with those within the distance of 1km, mean contributions of PFBA, PFPeA, PFHxA, PFHpA increased by 4.41%, 0.36%, 3.51% and 0.43% within the distance of 1-4km while proportion of PFOA decreased by 14.03%. Mean contributions of PFOA within the distance of 4-7km continued to decline by 20.14%, ~~however mean contributions of C4-C7 short-chain PFCAs showed irregular changes, which was due to proportion changes of C9-C12 long-chain PFCAs and PFOS(C8). Normally longer-chain PFAAs are more easily removed during dispersion in groundwater, the relative contributions would decrease faster.~~ However, the total proportion of C9-C12 long-chain PFCAs and PFOS(C8) increased from 0.2% within the distance of <1km to 24.21% within the distance of 4-7km, which implied a different external input of longer-chain PFAAs to groundwater, not the factory complex.

Dispersion from the areas with extremely high concentrations and atmospheric deposition then further infiltration were dominant pollution pathways of PFAAs in groundwater around the fluorochemical industrial park. Similar change tendency of PFAAs levels and contribution of individual PFAAs with those in transverse directions from the Dongzhulong River suggested dispersion from seriously polluted areas was a major pollution pathway of PFAAs around the fluorochemical industrial park. Previous studies have assessed the fate and transport pathways of longer-chain PFAAs emitted from direct sources (i.e., manufacturing and use) (Armitage et al., 2009), and atmospheric transport makes an important contribution to transport potential for longer-chain PFAAs. Relatively high concentrations of C9-C12 long-chain PFCAs in surface and ground water within the radius of <1 km indicated that fluorochemical industrial park was the dominant source, while PFAAs can also be released into air with exhaust gas from fluorochemical industrial park (Wang et al., 2013; Li et al., 2015). Based on the information and analyses presented above, it is suggested the external input of longer-chain PFAAs to groundwater came from air emission of PFAAs from fluorochemical industrial park (Liu et al., 2009; Kwok et al., 2010) and then leached by precipitation to groundwater(Davis et al., 2007). In fact, about 18.4% of the total PFOA/PFO environmental releases is emitted into air, and most of them reached to the ground through atmospheric deposition(Li et al., 2015). Due to many PFAA using facilities, concentrations of ∑PFAAs, dominated by PFOA, were up to 152 ng/L in precipitation in Weifang, China. Therefore, this pollution pathway might also explain some high concentrations in groundwater samples around PFC but not adjacent to the sewage river and waste. PCA results and correlation matrix also indicated the PFAAs at these sites had similar sources as those located nearby the sewage river.

3.4 Risk zoning of PFAAs in surface and ground water

As groundwater is an important source for drinking water (UGWA, 2013), risk zoning was made in the study area to evaluate groundwater safety. The concentrations of PFOS in all sites were much lower than reported health and ecological risk threshold. Risk zoning was mainly based on PFOA concentrations and corresponding drinking water standards. Preliminary Health-Based Guidance (PHBG) of 40 ng/L for PFOA in New Jersey, US is the lowest reported assessment threshold for drinking water and expected to be protective for both non-cancer effects and cancer at the one in one million risk level (Post et al., 2011). Provisional health advisory (PHA) of 400ng/L for PFOA, USEPA is widely used to assess the potential risk from short-term exposure through drinking water, above which actions should be taken to reduce human exposure(USEPA, 2014). These two typical standards were used to divide different levels of potential risk areas: the areas where the concentrations of PFOA were comparable to or higher than 400 ng/L were defined as high risk areas; the areas where the concentrations of PFOA were between 40 ng/L and 400 ng/L were defined as medium risk areas; and the areas where the concentrations of PFOA were lower than 40 ng/L were defined as low risk areas (Fig. 6).

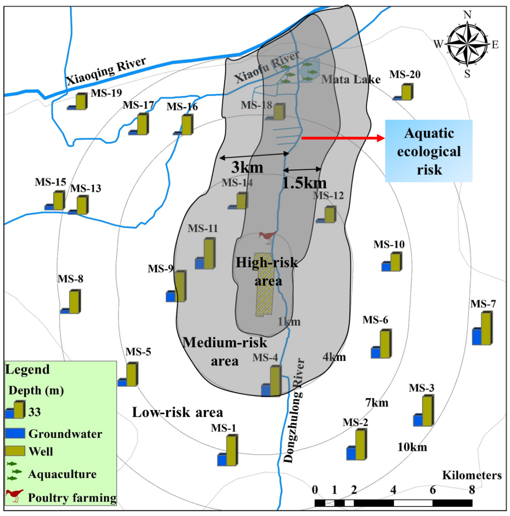

Fig. 6. I don't understand the legend! Where can I find groundwater depth? Are these wells for drinking water? Please be more explicit! Risk zoning of PFAAs in surface and ground water

High risk areas in groundwater including the area within the radius of 1 km from the fluorochemical industrial park were found within a distance of 1.5 km from the polluted river. Extremely high concentrations was detected at more than half of the sites (62.5%), which exceeded almost all reported drinking water quality standards, being 2.57 to 598 times higher than PHA, USEPA limits; and some of them even exceeded Notification of Events(45 μg/L) in UK, which may result in acute health impacts from short-term exposure (Inspectorate, 2009)(Table S10). For short-chain PFAAs including PFPeA, PFHxA, PFHpA and PFBA, the concentrations in groundwater sites along the river and nearest to the PFC were also mostly higher than their Health-Related Indication Values (HRIV) in Germany of 3μg/L, 1 μg/L, 300 ng/L and 7μg/L, respectively (Table S11) (Wilhelm et al., 2010). Due to this health risk, untreated groundwater in these areas must not been used as drinking water.

Dispatching clean tap water and increasing well depth may be viable options for these areas. Two main areas were classified as medium risk areas. The first one was within the radius of 1-4 km from the fluorochemical industrial park, and the concentrations of PFOA at half of the sites in this area were comparable to PHBG in New Jersey, US. The concentration of PFOA at site G-6 near staff apartments of the fluorochemical industrial park was comparable to the Chronic Health Risk Limit (300 ng/L) in Minnesota, US (MDH, 2011). The other one was within the lateral distance of 1.5-3 km from the sewage river, the concentration of PFOA deceased from 299 ng/L to 15.3 ng/L in transverse A and from 125 ng/L to 20.6 ng/L in transverse B, most of which were also comparable to or higher than PHBG in New Jersey, US. Groundwater in these areas was also not suggested to be used as drinking water directly, unless a percolation device, for example granular activated carbon, were applied (Wilhelm et al., 2010). Concentrations of PFOA in other areas were lower than PHBG in New Jersey, US and defined as low risk areas (MECDC, 2014). The concentrations of PFOA in these areas ranged from 0 to 7.15 ng/L, which were comparable to or even lower than those in tap water of most countries (Fujii et al., 2007; Jin et al., 2009).

~~The shallow groundwater level and well depth may contribute to groundwater contamination by the polluted river and precipitation leaching, and result in higher risks through drinking water and contaminated food. According to official annual data from 20 monitoring sites in Huantai county, groundwater depth and well depth showed gradual decrease trend from south to north (Fig 6). The shallow groundwater level implies more frequent water exchange between groundwater and surface water~~

~~contaminated by sewage from fluorochemical industrial park, and the more shallow well depth means that groundwater people got is more vulnerable to PFAA pollution(Xiao et al., 2015) (Table S12).~~ This area is a major grain-producing zone and surface water and groundwater were dominant irrigation water for large tracts of farmland and vegetable plots. Heavily polluted surface and ground water used for irrigation might pose risks due to PFAAs in soils and subsequent accumulation into crops and vegetables and eventual accumulation in humans (Blaine et al., 2014; Wen et al., 2014). Local surface water and groundwater are believed to be also used for poultry farming and aquaculture. Poultry and aquatic products were inclined to accumulate long-chain PFAAs with higher toxicity and accumulation (Gewurtz et al., 2013; Gebbink et al., 2015) and intake of these products may also lead to potential human health risk (Domingo, 2012).

According to the above standards for risk zoning, high risk areas in surface water were downstream of the fluorochemical industrial park in the Dongzhulong River and Xiaoqing River, where concentrations of PFOA ranged from 79.74 to 4,267.23 times more than PHA, USEPA; while medium risk areas were at the upstream of the fluorochemical industrial park in the two rivers, where concentrations of PFOA were comparable to or higher than PHBG in New Jersey, US. Extremely high concentrations of PFOA in the seriously polluted Dongzhulong River were comparable to criteria continuous concentration (CCC) of 2.9 mg/L, and even triple of the predicted non-effect concentration (PNEC) of 570 μg/L in China, indicating the potential aquatic ecological risk (Table S10) (Giesy et al., 2010; Cao et al., 2013).

4. Conclusions and perspectives

Overall, the results of this study indicated that:

- High concentrations of ∑PFAAs were observed in the Dongzhulong River, downstream of fluorochemical industrial park effluent, including 1.71 mg/L in surface water and 240 μg/L in groundwater, respectively. The concentrations of ∑PFAAs in surface water and groundwater nearby showed a positive correlation.
- Emission from fluorochemical industrial park was principal source of PFAAs in surface water and groundwater. Discharge through waste into surface water and air emission from fluorochemical industrial park, were considered the two dominant pollution pathways. Surface water may also be polluted by contaminated groundwater through water exchange.
- PFOA was the predominant PFAA with average contribution of 81.60% in surface water and 65.29% in groundwater, followed by short-chain PFCAs such as PFBA, PFPeA, PFHxA, PFHPA. The relative contribution of FPOA (C8) declined while percentage of C4-C6 shorter-chain PFCAs increased during surface water seepage and further dispersion in groundwater.
- As the distance from a point source increased, the concentration of ∑PFAAs in groundwater sharply decreased and then declined more gently. The clear contamination signal from the fluorochemical industrial park on PFAAs in groundwater existed within a radius of 4 km, while that existed within the lateral

distance of at least 3km from seriously polluted Dongzhulong River. Adsorption to aquifer solids and the dilution were considered the major controlling factors in PFAA attenuation processes.

- High human health risks for PFOA and other shorter-chain PFCAs existed in surface water as well as groundwater within a radius of 1 km from the fluorochemical industrial park and within a distance of 1.5 km along the river. Intake of drinking water, grain and vegetables, chicken and aquatic products, which associated with the contaminated surface and ground water, were potential exposure pathways for health risk. Aquatic ecological risks exist in the seriously polluted the Dongzhulong River due to the extremely high concentrations of PFOA.
- As industry shifts toward the manufacture of fluorinated alternatives including short-chain PFAAs, PFOA and also shorter-chain PFAAs so continued vigilance on the health and ecological risks are needed. In particular, more consideration is required into the potential hazards aquatic products, livestock and poultry, and crops from these chemicals.

Management options

For fluoropolymer manufacturers, non-fluorinated alternatives that are neither persistent nor toxic should be developed while PFAA removal facilities, for example granular activated carbon system, could be considered for wastewater treatment system (Rumsby et al., 2009; Blum et al., 2015). Management of staff uniforms and shuttle buses should be strengthened, and staff suits, trucks and shuttle buses should be regularly cleaned to avoid PFAA pollution during transport.

For government, powerful legislation and policy enforcement should be implemented to extend producer responsibility and strictly control PFAAs emissions. Emerging contaminant monitoring system including PFAAs is necessary to ascertain pollution level in time. Advanced tap water systems and supporting purification device are also vital to ensure the safety of drinking water.

With the collaboration between government and farmers, irrigation and crop safety should be improved using measures such as avoiding sewage irrigation; increasing well depth, dispatching clean irrigation water, and converting land use pattern of the seriously polluted area. Poultry farming and aquaculture should also avoid contaminated water. For communities around the fluorochemical industrial park, they should assist regulatory authorities to supervise illegal discharge of PFAAs and refuse contaminated drinking water and food associated with seriously contaminated water.

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