Assessing the contribution of atmospheric transport and tourism activities to the occurrence of perfluoroalkyl acids (PFAAs) in an Alpine Nature Reserve

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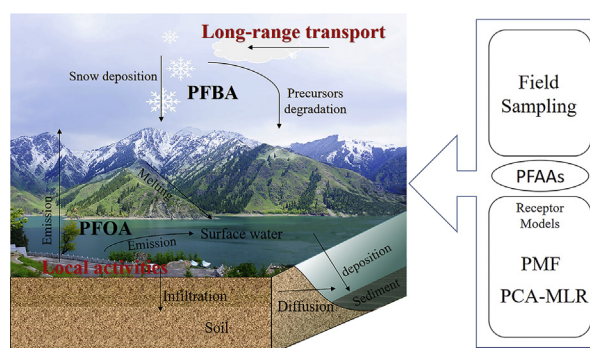[d] Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
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HIGHLIGHTS

- PFBA was the most abundant PFAAs in Tianchi lake.
- Higher levels of PFAAs were observed from sites near scenic spots and ski resort.
- The profile of PFAAs in snow was highly correlated with that in water and soil.
- Two sources were identified with dominances of PFOA and PFBA, respectively.

GRAPHICAL ABSTRACT

ABSTRACT

Perfluoroalkyl acids (PFAAs) are ubiquitous in the global environment, even in remote regions. With increasing production and application of PFAAs in China, their distribution patterns have been widely reported, however with less attention to inland northwestern regions. Long-range transport and direct releases from local activities have been regarded as the main reasons for PFAAs distribution in such a remote area. To identify and quantify the contributions of different sources to PFAAs occurrences, an investigation was conducted in the Tianchi lake, nature reserve. A total of 20 water samples, 8 soil, 4 sediment and 10 fresh snow samples were collected and analyzed in 2015. The mean PFAAs concentrations were 3.38 ng L^{-1} in surface water, 1.06 ng g^{-1} dw in soil, 0.53 ng g^{-1} dw in sediment, and 3.31 ng L^{-1} in fresh snow, respectively. High levels of PFAAs were observed in surface water (15.41 ng L^{-1}) from Western Tianchi pond and surface snow (14.24 ng L^{-1}) from the site near a ski resort around Tianchi Lake indicating potential pollution by local human activities. The correlation between individual concentrations among water, soil and snow indicated the snow deposition as an important source. Although with limited sample size, principal component analysis associated with multiple linear regression (PCA-MLR) and positive matrix factorization (PMF) analyses have identified two major sources, which are

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characterized as tourism activities with dominance of perfluorooctanoic acid (PFOA) and long-range transport with abundant perfluorobutanoic acid (PFBA). Their contributions to total levels were 41% and 52%, respectively. These two sources contributed differently to the PFAAs presences in Tianchi and Western Tianchi Lakes. Source analysis indicates that the western Tianchi lake with a relatively small catchment was affected mainly by local activities.

1. Introduction

Perfluoroalkyl acids (PFAAs) are a group of anthropogenic chemicals known for their desirable properties of high surface tension/leveling, hydrophobicity, lipophobicity, and chemical and thermal resistance (Giesy and Kannan, 2001; Giesy and Kannan, 2002). Since the 1950s, PFAAs have been widely applied in consumer and industrial products such as cosmetics, leather, waxes, semiconductor, oil/liquid repellents, firefighting foams, pesticides and food packaging materials (Kissa, 2001; Lindstrom et al., 2011). With a growing concern about their potential bioaccumulation and toxicity, several PFAAs have been subjected to restriction and regulation in Europe and United States (OECD, 2002; USEPA, 2006). In 2000, 3 M company (the then largest manufacturer) phased out its production of PFAAs products and their precursors (3M, 2000). Following that, international regulatory efforts have been made to restrict the use and production of these chemicals (UNEP, 2009, 2018). Despite the ban in developed world, the production, use and ultimate releases of PFAAs chemicals into the environment is still taking place in fast developing countries like China and India (Moller et al., 2010; Xie et al., 2013a, 2013b).

Due to their wide application and historical production, PFAAs are ubiquitously distributed in abiotic and biotic media (Giesy and Kannan, 2001; Prevedouros et al., 2006; Marcus et al., 2013; Liu et al., 2016, 2017; Su et al., 2017). Even in remote areas, such as Arctic (Martin et al., 2004; Stock et al., 2007; Wong et al., 2018) and Alpine Mountains (Shi et al., 2010; Kirchgeorg et al., 2013), PFAAs have been observed. Previous studies have presented two hypothesized transport pathways, namely indirect and direct routes, to explain how PFAAs reach the remote areas with different contributions in different areas (Stock et al., 2007; MacInnis et al., 2017). The indirect pathway suggests that volatile and semi-volatile precursors, such as fluorotelomer alcohols (FTOHs) and perfluorinated sulfonamides (FOSAs), through atmospheric transport, would be subsequently degraded to several PFAAs through abiotic and biotic processes (Ellis et al., 2004; Martin et al., 2006; Urs et al., 2008; Young and Mabury, 2010; Vento et al., 2012). The dominant contribution of FTOHs observed in precipitation and air samples in remote regions have proved this hypothesis (Scott et al., 2006; Gawor et al., 2014; Xie et al., 2015; Zhao et al., 2017). With the direct transport, PFAAs are transferred to remote area via both the atmosphere and oceanic water currents (Konstantinos et al., 2010). The PFAAs that released directly from consumer products and production processes might be bounded with particles and scavenged to the ground by wet/dry deposition (Dreyer et al., 2010). A variety of PFAAs with high mobility and persistence, such as PFOA, PFOS and perfluorohexane sulfonate (PFHxS), have been wildly detected in the street/indoor dusts (Harada et al., 2005; Murakami and Takada, 2008; Dreyer et al., 2015; Su et al., 2016), arctic and global atmosphere (Prevedouros et al., 2006; Stock et al., 2007), indicating direct transport as an important source. Both direct and indirect sources have been reported to contribute to PFAAs occurrence in the environment and wildlife in remote regions (Casal et al., 2017; Li et al., 2017; Routti et al., 2017). However, their relevance to the regional environment for the various PFAAs remains unclear.

Since China has become the main producer and consumer of PFAAs, many investigations have been conducted, however most of them are in eastern region where populated cities and major manufacturers are

located, with limited reports on remote area (Zhen et al., 2013; P. Wang et al., 2014; T. Wang et al., 2015). Few studies in Tibetan Plateau have observed PFAAs accumulation in snow and ice core, and the results suggested a different composition from varied sources (X. Wang et al., 2014; Wu et al., 2016; Li et al., 2017). Previous studies have reported the significance of long-range transport to the PFAAs deposition in Xinjiang region, showing varied levels of PFAAs in cattle, drinking water and snow (G. Wang et al., 2017; Li et al., 2019; Wang et al., 2019). Recent studies have shown that there is likely a shift toward short-chain chemicals in remote areas globally, which is consistent with the transition in PFAAs production (Holt, 2011; Kirchgeorg et al., 2013; Oliaei et al., 2013). Short-chain PFAAs are similarly persistent as their long-chain homologues (Young and Mabury, 2010; Z. Wang et al., 2015), and are likely to be transported over long distances (Brendel et al., 2018). Due to the phase-out of long-chain PFAAs, the releases and production of short-chain PFAAs are expected to increase in the future. This may lead to continuous accumulation in remote regions (Kirchgeorg et al., 2016). Thus, further investigations are needed to explore the occurrence of PFAAs in these areas.

Tianchi Lake (TC), an alpine cold water lake located in Tianshan Mountains, is known as the World Heritage Site and Biosphere Reserve and also serves as an important drinking water source (Wen et al., 2016). This region had been affected by intensive grazing activities. Fortunately, the region has been protected by the implementation of grazing banning since 2005. However, tourism activities have increased since the 1970s, with an increase of 0.8 million visitors per year (Wen et al., 2016), resulting in the potential emission of chemicals from commercial products. This study aims to investigate why Tianchi Lake which is far from production and industrial input could end up being polluted by PFAAs chemical, and to find out the role of different sources to the environmental occurrence of PFAAs. To address these questions, a comprehensive investigation of the PFAAs in water, sediment, soil and snow was conducted in Tianchi region, and the contributions of potential sources were evaluated by statistical approaches.

2. Material and methods

2.1. Site description and sampling

Tianchi Lake is located at the middle of the eastern Tianshan Mountains, Xinjiang Autonomous Region in northwestern China (Fig. 1). It is a moraine lake receiving snow/ice-melt water from surrounding alpine, e.g. Bogda Peak (5445 m). The total core area of the Xinjiang Tianchi Nature Reserve is approximately 60 km^2 with the longitude 88°00′–88°20′ E and latitude 43°45′–43°59′N in the hinterland of Eurasian continent (UNESCO, 2013). Tianshan Mountains stretch from west to east and block the atmospheric circulation, which leads to a flushing precipitation in this area (Shi et al., 2007).

A sampling campaign of surface water, sediment and soil was conducted in the Tianchi Nature Reserve in October 2015 during a season of little or no melting and or icing. A total number of 20 water samples were taken from Tianchi Lake (TC) and two adjacent ponds, Eastern Tianchi (ETC) and Western Tianchi (WTC). Two sediments were also obtained during water sampling in both TC and WTC. Eight uniformly distributed sites were chosen to investigate PFAAs levels in surface soil. In November 2015, 10 fresh snow samples were collected after
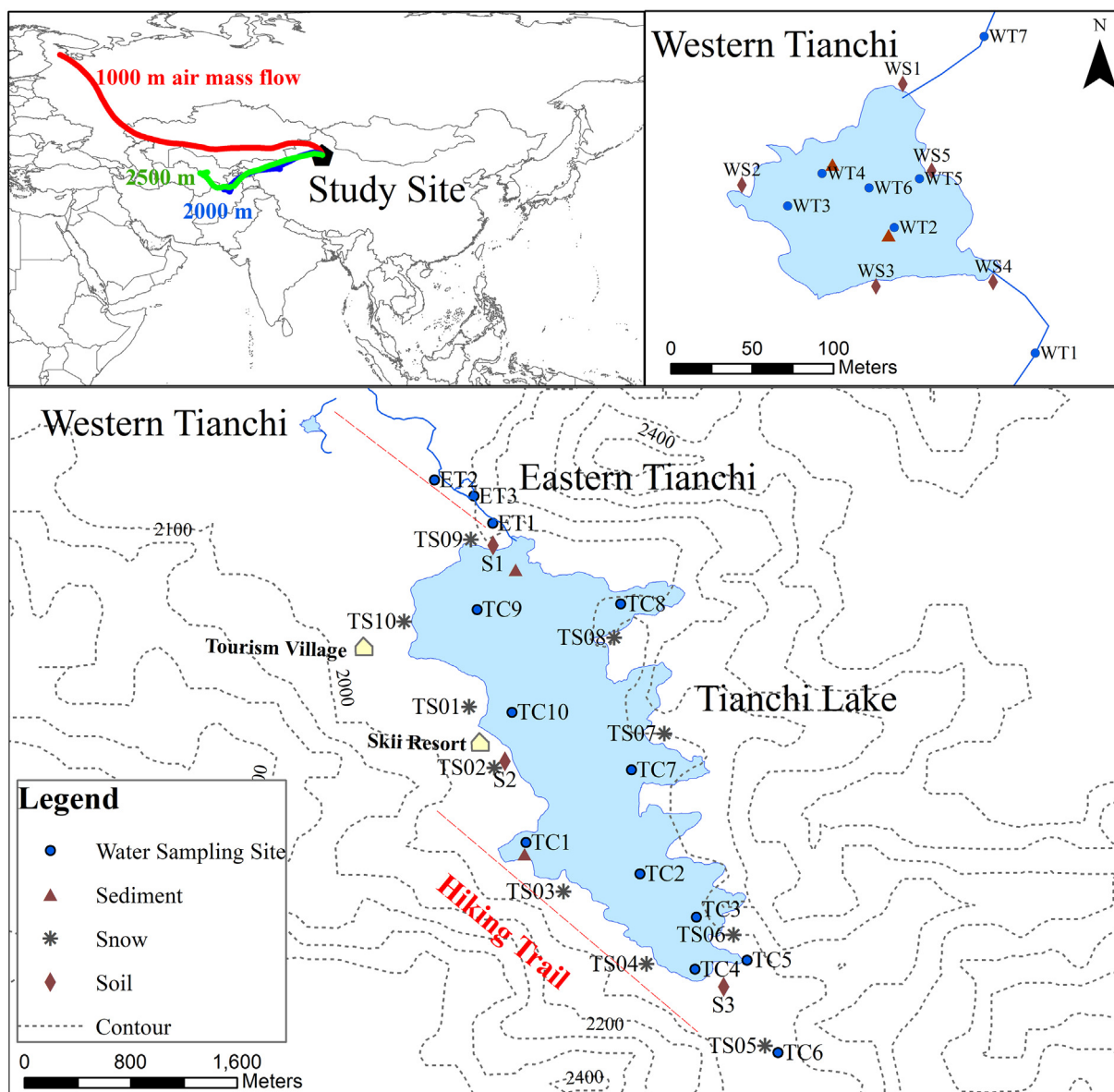
Fig. 1. Study area and sampling sites in Tianchi Lake, northwestern China. Five-day back trajectory result of three-layer air flow.

precipitation. Surface water (top 1–20 cm) and snow samples were collected using 1 L polypropylene (PP) bottles. Soil and sediment samples were stored in two-layer PP bags. All the samples were transported in ice box to the lab. Before analyzing, sediment and soil were freeze-dried and ground through 2 mm mesh. Snow samples were left at room temperature to melt to aqueous phase. All samples were extracted within 2 weeks after arriving in the lab and the leftovers were kept at −20 °C for long-term storage.

2.2. Chemicals and reagents

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFOcDA), potassium perfluorobutanesulfonate (PFBS), sodium perfluorohexanesulfonate (PFHxS), potassium

perfluorooctanesulfonate (PFOS), sodium perfluorodecanesulfonate (PFDS) and 9 mass-labeled PFAAs were used for preparing mixture standard solutions (Table S2). All stock standards and solutions were prepared in methanol and stored at 4 °C. Milli-Q water was used throughout the experiment for rinsing and dilution.

2.3. Sample preparation and chemical analysis

A total of 17 PFAAs including 13 perfluoroalkyl carboxylic acids (PFCAs) and 4 perfluoroalkane sulfonic acids (PFSAs) were analyzed (Table S2). A volume of 1 L unfiltered water or snowmelt was extracted by solid-phase extraction (SPE) processes with OASIS WAX cartridges (Taniyasu et al., 2005). Prior to extraction, water or snowmelt samples were spiked with 5 ng mass-labeled standards. The cartridges were preconditioned with 4 mL of 0.1% NH_4OH in methanol, 4 mL of methanol, and 4 mL of Milli-Q water in sequence. After loading the sample at approximately 1–2 drops per second, cartridges were washed with 4 mL 25 mM ammonium acetate (pH = 4) and then air-dried. Target analytes were then eluted by 4 mL of methanol and 4 mL of 0.1% NH_4OH in methanol. The sample volume was reduced to 1 mL under a

gentle stream of high purity nitrogen. The concentrated samples were filtered through a nylon filter (0.22 μm) and transferred into a 1.5 mL vial for instrumental analysis.

Sediment and soil samples were extracted by alkaline digestion and ultra-sonic extraction method (Loi et al., 2011). Aliquots of 2.5 g dry sediment or soil were spiked with 5 ng mass-labeled internal standards in a 50 mL PP centrifuge tube. The samples were then digested with 2 mL of 100 mM NaOH in methanol (8:2/MeOH:Milli-Q water), and ultra-sonicated for 30 min. Twenty millimeters of methanol were added into the mixture and shaken for 30 min at 250 rpm. After pH adjustment with 0.1 mL of 2 M HCl, the samples were centrifuged at 3000 rpm for 10 min. The extraction procedure was repeated twice. The supernatants were combined into a new 50 mL tube and concentrated to 1 mL under a gentle stream of high purity nitrogen. After cleanup by ENVI-Carb cartridges, the extracts were diluted in 100 mL Mili-Q water and subjected to the same procedure as water samples.

A high-performance liquid chromatography equipped with a triple-quadrupole mass spectrometer system (Agilent Technologies, Palo Alto, CA) was used for PFAAs qualification and quantification. The details of the extraction processes, as well as the instrument conditions were given in the Supplementary Information.

2.4. Quality assurance and quality control (QA/QC)

During the procedure, the usage of materials containing any polytetrafluoroethylene (PTFE) or fluoropolymer was avoided. The bottles or tubes used in analysis were all pre-rinsed by both Milli-Q water and methanol. To check the potential contamination, field blanks, transport blanks, procedure blanks and solvent blanks were conducted. All the PFAAs were below the Limit of Quantification (LOQ) in the blanks. The standard calibration curves with series concentrations of 0.01, 0.05, 0.1, 0.5, 1, 5, 10 and 50 ng/mL were used for quantification, and regression coefficients (r^2) of calibration curves for all target analytes were over 0.99. Limit of detection (LOD) was set as 3 times of signal-to-noise ratio (S/N), and LOQ was defined as 10 times of S/N ratio. Two kinds of recovery tests were performed (Table S4). The matrix spike recoveries ranged from 72% to 125%. Detailed QA/QC results were given in the Supplementary Information.

2.5. Statistical analyses and source partition method

The SPSS 24 software was used for statistical analysis, and significance was set to $p < 0.05$. Concentrations below LOD were assigned as $LOD/\sqrt{2}$, and concentrations below LOQ but above LOD were assigned as half of LOQ for calculations. The Kolmogorov–Smirnov and Shapiro-Wilk tests have been conducted to test the normality of the data distribution, and a Spearman correlation analysis was used to examine the possible correlations among PFAAs levels. Two commonly used receptor models, including principal component analysis associated with multiple linear regression (PCA-MLR) and positive matrix factorization (PMF), were used for source identification and apportionment, since the methods do not require the detailed information of mass flow and are easy to apply (Hopke, 2003; Sofowote et al., 2008; Furl et al., 2011). To further identify the atmospheric transport patterns, air masses were analyzed using back trajectories from HYSPLT model (Draxler and Rolph, 2013). Five-day back trajectories of three layers' air mass flows were calculated every 6 h during the time of snow sampling (Fig. 1). Partition coefficient (K) was calculated for each PFAAs to evaluate the partition behavior. Detailed information for these methods and results were given in Supplementary Information.

3. Results and discussion

3.1. Occurrence and distribution of PFAAs in Tianchi Lake

3.1.1. PFAAs in surface water

Among the 17 determined PFAAs, a total of 11 PFAAs were detected (Table. S5). The predominant compounds in aqueous phase were PFBA (0.10–8.16 ng L^{-1}) and PFOA (<LOD~3.38 ng L^{-1}), and their proportions of the total concentration were 11–89% and 1–57%, respectively (Fig. 2), which is consistent with recent studies on drinking water in Xinjiang province (Li et al., 2019). PFBA was detected in 100% of water samples and PFOA was found in 95% of samples. The detection frequencies for the rest of PFAAs were in the range of 5% to 75%. With the absence of oceanic transport, atmospheric deposition and oxidation of volatile precursors are supposed to be the major sources, which subsequently lead to the high proportion of short chain compounds (Pickard et al., 2018). The total concentrations and the relative proportions of individual PFAAs in surface water were shown in Fig. 2. ∑PFAAs levels in surface water ranged from 0.79 to 15.41 ng L^{-1}, and the highest ∑PFAAs level was found in downstream of Western Tianchi (WTC). The mean concentrations of ∑PFCAs and ∑PFSAs were 3.30 ng L^{-1} and 0.21 ng L^{-1}, respectively. The levels of PFCAs were over 20 magnitudes higher than PFSAs. This is likely due to the worldwide phase-out of the manufacturing of PFOS and its precursors and points toward specific emissions or atmospheric deposition in the study area (UNEP, 2009; Muller et al., 2011). Although there is a production shift to short-chain PFSAs leading to increasing levels in the environment (P. Wang et al., 2016; Z. Wang et al., 2017), the stronger sorption of PFSAs than PFCAs of equal chain length makes them have less potential for long-range transport (Higgins and Luthy, 2006).

The mean concentration (3.52 ng L^{-1}) of PFAAs in surface water of the study area was much lower than that in urbanized and industrialized area of China (P. Wang et al., 2014; Guo et al., 2015; Wan et al., 2017), while it is slightly higher than that in Canadian Arctic ocean (0.04–0.25 ng L^{-1}), pristine stream(0.4–1.30 ng L^{-1}) and Alpine stream (approximately 1 ng L^{-1}), which were only affected by atmospheric input (Muller et al., 2011; Benskin et al., 2012; Filipovic et al., 2015). The highest ∑PFAAs concentration of 15.41 ng L^{-1} at TC7 was comparable with reported levels in drinking water (mean: 28.49 ng L^{-1}) from northwestern China (Li et al., 2019) and surface water (17.4 ng L^{-1}) from the upstream of Pearl river (T. Wang et al., 2016), which were affected by domestic emissions. This indicated a potential pollution of PFAAs in Tianchi Lake area by local human activities. There are several commercial skiing resorts in this area, which are expected to lead to elevated levels in water during snowmelt seasons (Plassmann et al., 2010). The PFAAs profile was also different from that in freshwater of northern China with PFOA and PFOS as the dominant compounds, which implied a different source in the Tianchi Lake (T. Wang et al., 2015). The dominance of PFBA may attribute to both oxidation of precursors during atmospheric transport (X. Wang et al., 2014; Kirchgeorg et al., 2016) and direct releases from commercial products. PFBA and its precursors, e.g. short chain fluorotelomer alcohols (FTOH), have been found in several outdoor consumer products, including outdoor textiles, carpets, leathers, baking and sandwich papers, paper baking forms and ski waxes (Kotthoff et al., 2015).

Differences in the composition of individual PFAAs in surface water were found among the regions (Fig. 2). TC is the core area of the natural scenic region with various tourism activities, including hiking, skiing and boating. The total area of TC is 4.8 km^2 with a catchment area of 380 km^2, while the WTC only covers an area of 0.03 km^2. The ETC is a plunge pool receiving drainage directly from TC, while the water in WTC is mainly supplemented by the underground seepage and infiltration from TC. Because of the geographical isolation, the influence of tourism activities would differ in TC and WTC. PFBA was the most dominant PFAAs found in surface water of Tianchi Lake (TC) and Eastern Tianchi pond (ETC) contributing 45–89% to the total concentrations,
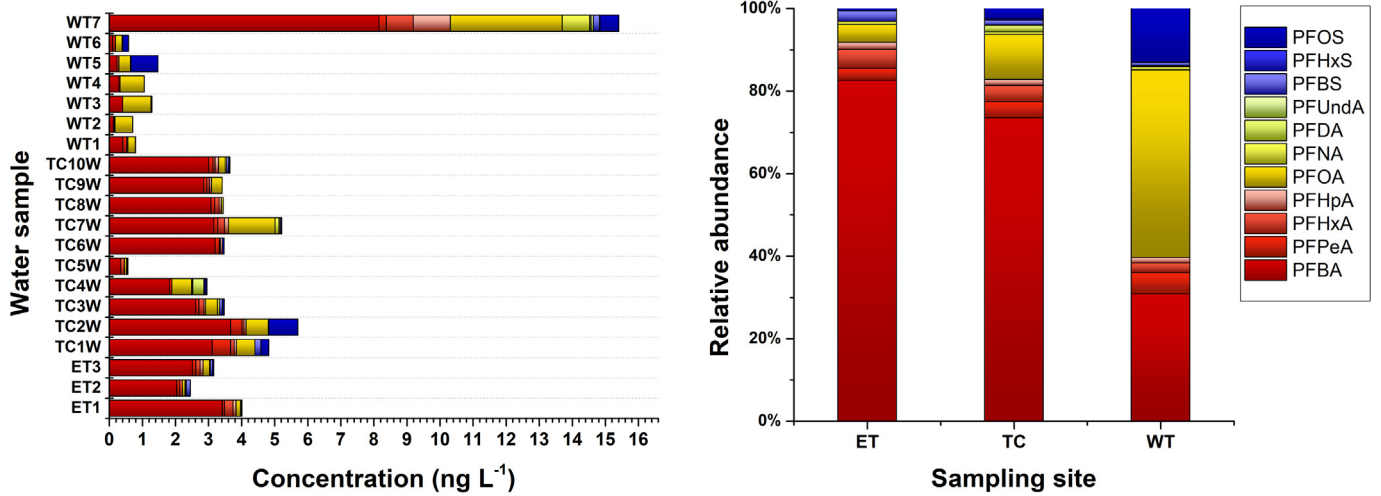
Fig. 2. PFAAs levels and composition in water samples.

while PFOA was the major compound in WTC with contributions of 20–57%. The PFAAs concentrations in TC and ETC were significantly higher (Kruskal−Wallis, $p = 0.014 < 0.05$) than in WTC. Since wet/dry deposition during the atmospheric transport has been regarded as the major pathway of PFAAs to remote area, the significant differences in PFAAs concentrations between the regions would suggest different influences by local activities.

3.1.2. PFAAs in sediments

PFBA, PFOA and PFHpA were found in 100% of the sediment samples, while the levels of PFDS and PFOS in all sediments were below LOD (Table S6). $\sum$PFAAs levels in sediments ranged from 0.51 ng g^{-1} dw to 2.78 ng g^{-1} dw. PFBA (0.28–0.47 ng g^{-1} dw) and PFHxA (<LOD~0.84 ng g^{-1} dw) were the dominant compounds with 17% ~82% and 0.5%~67% contributions to the total concentration, respectively. The concentrations of other detectable PFAAs were as follows: PFOA <LOQ~0.09 ng g^{-1} dw, PFHpA <LOQ~0.08 ng g^{-1} dw, PFUnDA <LOD~0.06 ng g^{-1} dw, PFPeA <LOD~0.04 ng g^{-1} dw, PFNA <LOD~0.03 ng g^{-1} dw (Fig. 3). PFCAs rather than PFSAs contribute to the majority of total concentrations in sediment samples. Different from the results in surface water, long-chain PFAAs with C > 12, including PFTrDA, PFTeDA, PFHxDA and PFDoDA, were all detected with varied frequencies in sediments, although at relatively low levels (<LOD~0.08 ng g^{-1} dw).

The $\sum$PFAAs concentrations (mean: 1.37 ng g^{-1} dw) in sediments were relatively higher than the observations in lakes of Mongolia-Xinjiang (0.33 ng g^{-1} dw) and Qinghai-Tibet regions (0.40 ng g^{-1} dw), but much lower than urbanized eastern regions of China (Qi et al., 2016). The concentrations in surface sediments represented an average condition over recent years (Clara et al., 2009). The higher level than the regional (Xinjiang-Tibet) average indicated that atmospheric deposition might not be the only source and the influence of human activities might exist in the study area. The dominance of short chain PFAAs in sediments was consistent with the observation in surface water, and this is due to their high mobility during the diffusive processes and long-range transport (Clara et al., 2009). The partition coefficients (Ksd-w, concentrations in sediment over that in water) were shown in Fig. S2. The highest Ksd-w was obtained for PFHxA. Different from the result in surface water, PFHxA (C-chain length of 6) was the most abundant compound in sediments. In general, higher Ksd-w was observed for PFCAs with longer C-chain. This is consistent with that long chain compounds are inclined to sorb on particles with higher partitioning coefficients (Higgins and Luthy, 2006; Ahrens et al., 2010). However, this correlation was not significant in this study, which could be attributed to the limited sample size of sediments.

3.1.3. PFAAs in soil

Except for PFDS, 16 determined PFAAs were all found in the 8 soil samples in Tianchi Nature Reserve (Table S6). The most frequently detected compounds in soil samples were PFBA and PFOA with a detection frequency of 100%, while the detection frequencies of PFCAs with long-chain (C > 12) and PFSAs, were relatively lower. The detection frequencies of other PFCAs ranged from 25% to 88% (Table S6). The
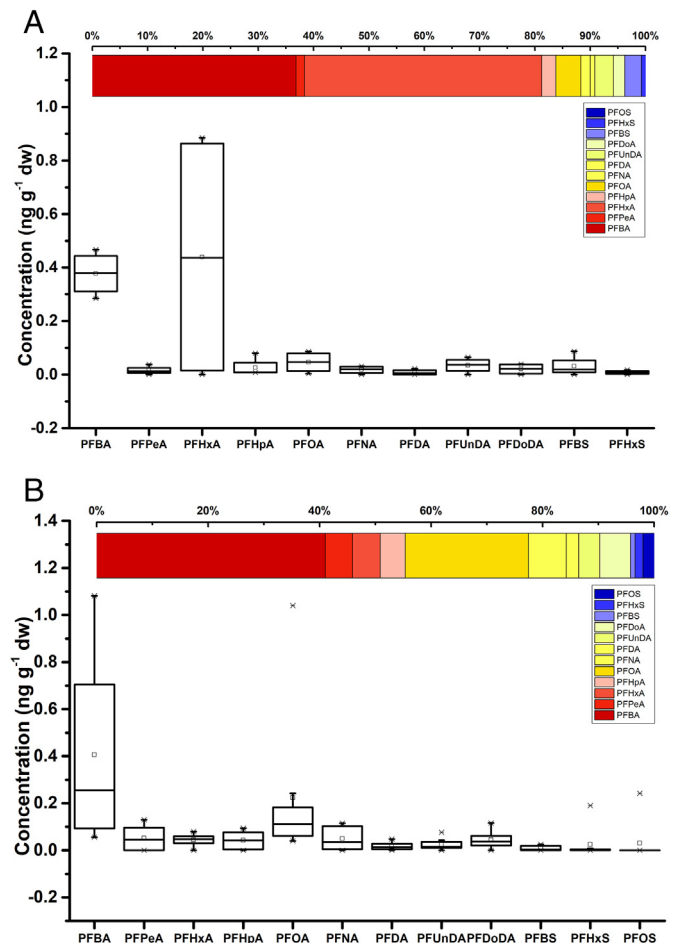

Fig. 3. PFAAs concentrations and compositions in (a) sediment and (b) soil samples.

concentrations and relative abundance of the individual PFAAs were shown in Fig. 3. $\sum$PFAAs levels in soil samples ranged from 0.23 to 1.86 ng g^{-1} dw with a mean concentration of 1.07 ng g^{-1} dw, which is at the same magnitude in sediment. The concentrations of dominant compounds, PFBA and PFOA, contributed 5–58% (mean: 35%) and 6–64% (mean: 19%) to total PFAAs, respectively. PFOS were only detected in one site (S1) with a concentration of 0.24 ng g^{-1} dw, where a hotel is located nearby. The highest $\sum$PFAAs level was found in WS4, while the lowest in S3. Long chain compounds, inducing PFTrDA, PFTeDA and PFHxDA, were also found in soil samples with relatively low concentrations. Compared with other studies conducted in China, the soil concentrations of PFOA in this study area are comparable with that in north Bohai sea and Huaihe watershed, but much lower than in Shanghai region (Wang et al., 2011; Meng et al., 2013; T. Wang et al., 2015). Considering the limited influence by human activities in the study area, the PFAAs in soils mainly come from wet/dry deposition during atmospheric transport. The profile of PFAAs in soil samples was consistent with that in surface water. Similar with that in surface water, the levels of PFPeA and PFHxA were significantly correlated with PFBA (Tables S8 and S9), which suggested the exposure to similar sources. Short chain PFAAs and their precursors can be effectively dissolved in cloud water droplets and scavenged from the atmosphere by wet deposition (Taniyasu et al., 2013; Scheurer et al., 2017), and the PFAAs deposited from the atmosphere are mainly stored in soil which might be further released to the surrounding surface water and sediments (Filipovic et al., 2015). The sorption potential of PFAAs was determined by chemicals characteristics and physico-chemcial conditions (Higgins and Luthy, 2006). The partition coefficient (Ks-w) of individual PFAAs in soil was shown in Fig. S2. Generally, long-chain PFAAs have higher accumulation potential than short-chain compounds in soil. However, non-significant correlation was found between PFAAs and total organic carbon (Table S9 and Fig. S3).

3.2. Snow deposition of PFAAs

3.2.1. PFAAs levels and composition in snow

Out of the 17 determined PFAAs, 11 PFAAs were detected above the LOD in fresh snow (Fig. 4). Similar to the results in surface water samples, 6 PFAAs (PFTrDA, PFTeDA, PFHxDA, PFDoDA, PFOcDA and PFDS) were all below the LOD (Table S7). PFBA and PFOA were detected in 100% of snow samples and the detection frequencies of other PFCAs ranged from 40% to 70%, while PFSAs including PFBS, PFHxS and PFOS were detected in few samples. The concentration of $\sum$PFAAs in snow samples ranged from 0.66 to 14.41 ng L^{-1} (mean: 3.45 ng L^{-1}). The PFAAs concentrations in snow were comparable with that in water samples. The snow sample obtained from site TS02 had the highest $\sum$PFAAs

concentration with 5 fold of the average level. The concentrations of PFPeA (0.55 ng L^{-1}), PFHxA (0.38 ng L^{-1}), PFOA (10.43 ng L^{-1}) and PFOS (1.04 ng L^{-1}) were also observed to be much higher at this sampling site than other regions. PFOS was only detected in site TS02. The site is located near a hotel and ski resort. This high level and composition of PFAAs are consistent with the concentrations in water and snow from urban area and tourist city (Shan et al., 2015; Wang et al., 2018). The levels at the same magnitude of PFHxA, PFBA, PFOA and PFOS were also identified in various consumer products including ski wax, leather, outdoor textiles and baking papers (Kotthoff et al., 2015), which implies potential pollution by local tourism activities. Thus, the concentration observed at TS02 was excluded from the analysis of snow deposition (Fig. 4).

The most abundant compounds in snow were PFBA and PFOA, and their total concentration accounts for 90% of $\sum$PFAAs. The concentrations of PFBA and PFOA in snow samples, except for the one at TS02, were in the range of 0.34–2.66 ng L^{-1} and <LOQ~0.54 ng L^{-1}, respectively. Compared to PFCAs, the proportion of PFSAs was relatively smaller, with an average of 2.6%. Similar with the surface water, long-chain PFAAs were at a relatively low level. Compared with long-chain PFAAs, short-chain PFAAs are more susceptible to long-range transport (P. Wang et al., 2015). PFBA has been found to be uniformly distributed in the global atmosphere due to its high vapor pressure and transformation from certain volatile precursors (Bravo et al., 2010; Bhhatarai and Gramatica, 2011; Wang et al., 2012). The dominance of the shorter chain compounds may be attributed to the shift in manufacturing toward shorter chain products such as the volatile FTOHs, 4:2 FTOH, which was measured in Asia (e.g. India), Arctic and global atmosphere (Li et al., 2011; Gawor et al., 2014; Wong et al., 2018). The significant correlation between the concentrations of PFBA and PFHxA, and PFOA and PFNA (Table S8) also proved the formation of these PFAAs by degradation of FTOH precursors (Urs et al., 2008).

The results were compared with those observed in remote regions and other parts of China, as shown in Table S10. The PFAAs concentrations in snow samples were comparable to the reported concentrations for Antarctica and Arctic area (Young et al., 2007; Casal et al., 2017), Tibetan Mountain (X. Wang et al., 2014), and Swiss/Italian Alps (Kirchgeorg et al., 2013), while much lower than that in northern China where the major fluorine manufacturers and cities are located (Shan et al., 2015), implying the remoteness of this area. By comparing to the PFAAs profile in Tibetan plateau, the composition in the present study was consistent with that in the Namco with PFBA as the dominant compound, while different from that in the Muztagata Mountain with abundances of PFOA and PFOS. The Muztagata Mountain is located at the western Tibetan Mountain, and the Namco is located at the southern Tibet, which are suggested to be affected by different sources (X. Wang
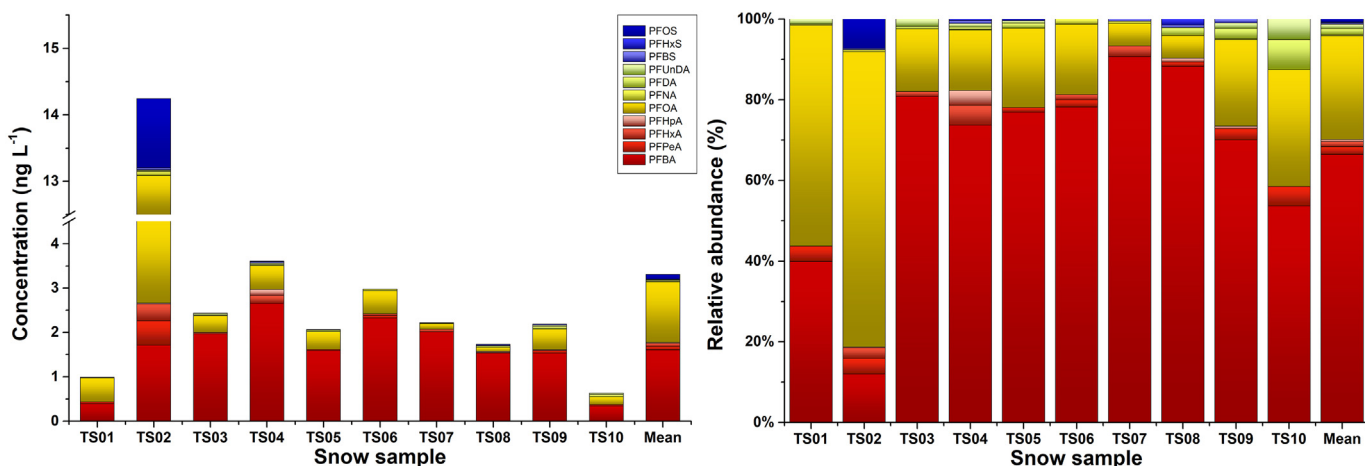

Fig. 4. PFAAs levels and composition in snow samples.

et al., 2014). A recent study has suggested that the PFAAs profiles in snow and ice core from this area (the northwestern China) could reflect the interactions of air circulation patterns, and the dominance of short- and long- chain PFAAs representing different contributions of Indian Monsoon and Westerly wind (Wang et al., 2019). Taking into account the dominating level of PFBA precursors in the Indian atmosphere, the precipitation carried from Indian Monsoon was suggested to be an important external source in this high plateau area (Li et al., 2011; X. Wang et al., 2014). However, it is noted that previous study observed different PFAAs composition with high level of PFOS in deposited snow from Tianshan Mountain, indicating a strong influence by westerly wind (Wang et al., 2019). The trajectory analysis result was shown in Figs. 1 and S4. Three-layer air mass flow analysis indicated that cold lower air at 1000 m originated from Europe and warm upper air originated from central Asia contributing to the snowfall during the sampling period, which suggested potential long-range transport sources from these regions. Since the study area is located at the transition region, the differences might be attributed to the variances of circulation patterns in this area. Furthermore, it is reported that climate change has induced a transformation of the circulation patterns in Xinjiang region with increasing precipitation caused by northeastern wind from easterly Japan Sea, and this may alter the accumulation patterns of PFAAs (Shi et al., 2007; Lu et al., 2019).

3.2.2. Relevance of snow deposition to PFAAs environmental distribution

In the absence of oceanic transport of PFAAs, wet deposition of PFAAs in atmosphere should be the major source in inland Alpine regions. The average concentrations and relative abundances of individual PFAAs in fresh snow, water, soil and sediments were compared to elucidate the relevance of snow deposition as a pathway for PFAAs to the study area.

The partition ratios between average relative abundance of individual PFAAs in surface water (Kw-p) and soil (Ks-p) to that in snow, and partition ratios between sediment (Ksd-w) and water were calculated (Casal et al., 2017). The assessment excluded those compounds with detectability below 50%. The ratio of individual PFAAs ranged from 0.16 to 8.38, as shown in Table 1, which implied differences in the mobility of these compounds and the potential contributions of snow deposition. The Kw-p and Ks-p ratios for PFBA and PFOA were close to 1. The Ksd-w ratio for PFBA was approximately 0.83, while that for PFOA was 0.25. The unchanged ratios of PFBA were consistent with an efficient transport from deposited snow to water, soil and sediments because of their high solubility (Plassmann et al., 2011). The differences between Ks-p and Ksd-w for PFOA might also imply that long chain PFAAs are more inclined to sorb on soil, and its diffusive transport from soil to water and sediment could be limited than short-chain compounds (Zhen et al., 2013; Filipovic et al., 2015). However, it is noted that soil characteristics have great influence on the adsorption of PFAAs, and the occurrence of other pollutants may lead to higher soil adsorption of short-PFAAs (Guelfo and Higgins, 2013). The relative abundance of individual PFAAs in snow was highly correlated with that in water and soil (Spearman's $R = 0.943$ for water and 0.98 for soil, $p = 0.005 < 0.05$), while the sediment did not present significant correlation

Table 1
The partition ratios between average relative abundance of individual PFAAs in surface water (Kw-p) and soil (Ks-p) to that in fresh snow, and the partition ratio between sediment and water (Ksd-w).
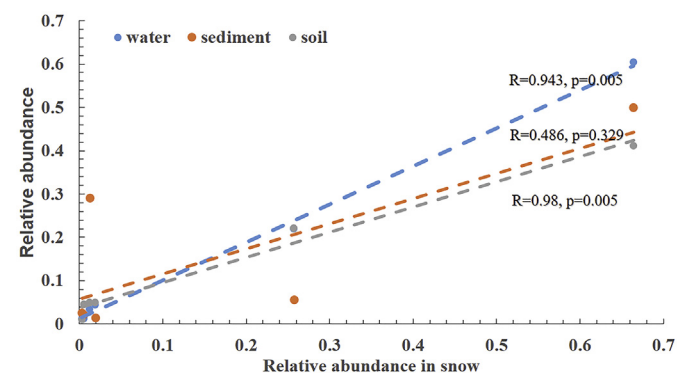
	Site	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS
Kw-p	All	0.91	2.25	2.67	2.10	0.85	4.00
	ETC	1.24	1.49	3.63	3.23	0.16	8.38
	TC	1.11	2.01	3.13	2.72	0.42	3.66
	WTC	0.47	2.69	1.84	2.36	1.77	2.60
Ks-p		0.62	2.55	3.93	8.27	0.86	2.73
Ksd-w		0.83	0.33	8.61	1.91	0.25	2.04

Note: All denotes all the water samples.

(Spearman's $R = 0.486$, $p = 0.329 > 0.05$; shown in Fig. 5). The correlation supports the transport from snow deposition as a major source of PFAAs to Alpine lake (Casal et al., 2017). Furthermore, the result might suggest that the utilization of sediment to represent PFAAs pollution in an area where atmospheric input is the major pollutant source would be unreasonable, without consideration of the varied geochemical behavior of different compounds. The Kw-p and Ks-p ratios for other short-chain PFAAs, including PFPeA, PFHxA, PFHpA and PFBS, were all over 1. The relatively high levels in water and soil suggest a different source for these compounds. Previous studies have observed high level of neutral volatile polyfluoroalkyl substances in the global and Asian atmosphere, and the oxidation of these precursors significantly accounted for the occurrence of short chain PFAAs in remote regions (Gawor et al., 2014; Xie et al., 2015). Meanwhile, a number of unknown perfluorinated precursors have been reported to account for 6–56% of the total concentrations of PFAAs in precipitation, which bears critical concerns over underestimation of PFAAs mass load from precipitation in China (Chen et al., 2019). Thus, further investigations are needed to identify and evaluate the contributions from these precursors, especially those that have not got much attention.

3.3. Source identification and contributions to PFAAs occurrence

The concentrations of 11 detected PFAAs ($\sum_{11}$PFAAs) in surface water were assigned to source apportionment analysis by both PCA-MLR and PMF models to identify the contributions of possible sources. Predicted value given by two models was in a good correlation with observation (Fig. 6). The concentration obtained in TC7 was much higher than other sites, which was statistically characterized as outlier. This site was directly affected by local activities, and the highest level was excluded from the source analysis. A total of 4 factors were identified by PCA analysis, which explained 81% of total variance (Table S11). The rotated factor loadings of three major components in the PCA-MLR analysis were shown in Fig. 6 and Table S11, which showed that the first factor (27.78% of the total variance) had high loads for PFOA, PFNA and PFUnDA. PFOA and other long chain compounds have been widely used and observed in consumer products, such as food packaging, carpets, leathers and outdoor textiles (Begley et al., 2005; Kotthoff et al., 2015). Given the lower contribution of PFOA in snow deposition, the first factor was thus identified as the sources from local tourism activities. The second factor accounting for 25.20% of total variance was identified with high loads of short chain compounds, including PFBA, PFPeA, PFHpA and PFBS. The dominant levels of these PFAAs in snow samples indicated that the second factor could be considered as the sources from long-rang transport (Stock et al., 2007; Li et al., 2011). The contributions of the four factors obtained from the PCA analysis were determined by the MLR analysis. The MLR analysis achieved an excellent regression for the four factor scores at a stipulated minimum 95% confidence with r^2 reaching 0.821. The results of PCA-MLR showed that the

Fig. 5. Relative abundance of PFAAs in snow and its relevance to PFAAs distribution (Note: $p > 0.05$ denotes not significant).
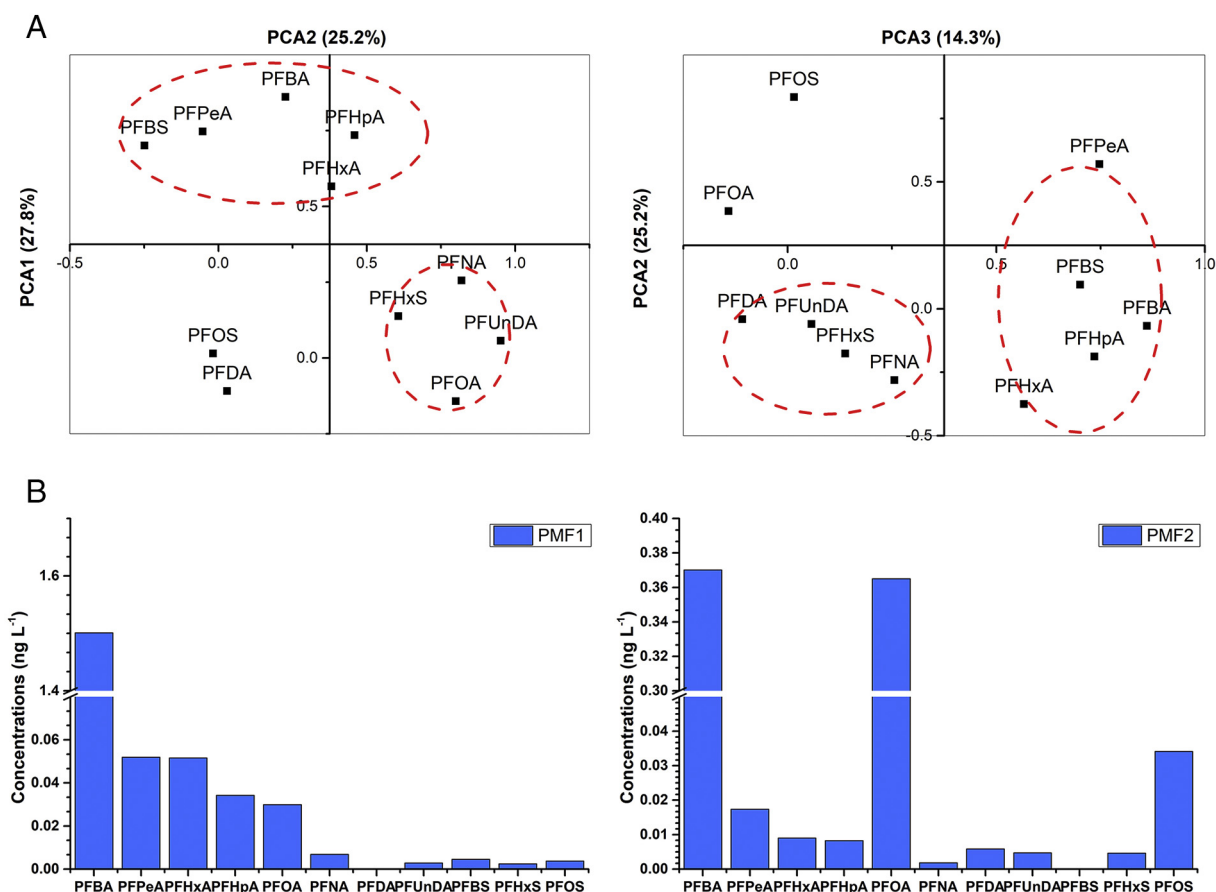
Fig. 6. Factor loadings and predicted source concentrations by PCA-MLR and PMF models.

first factor (PCA1) contributed 28% to the $\sum_{11}$PFAAs, and the second factor (PCA2) contributed 57% to PFAAs in surface water.
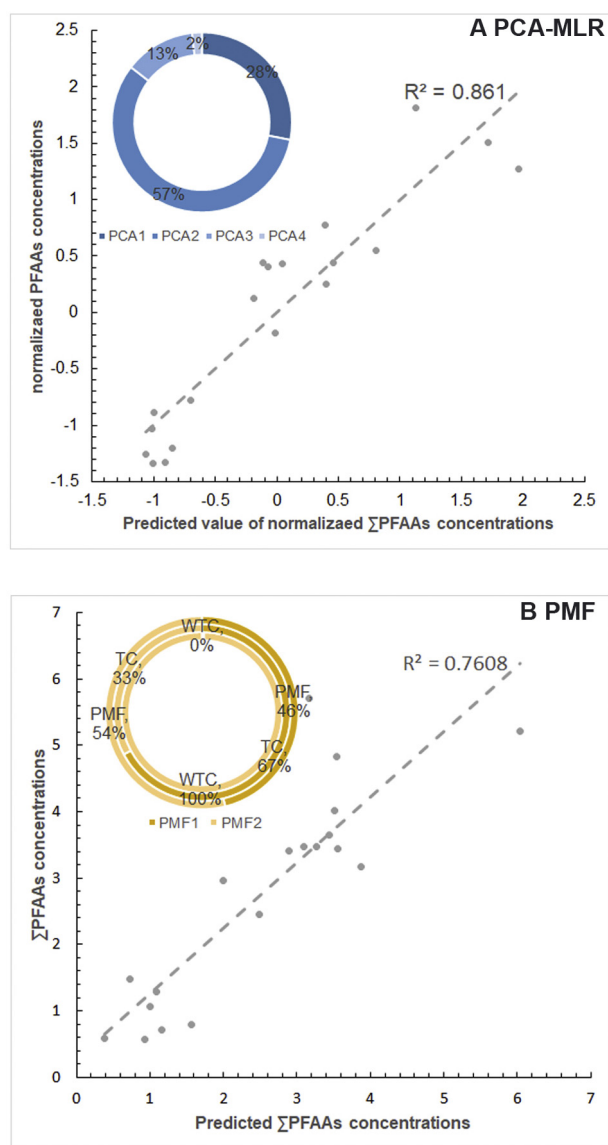
The PMF analysis has identified two sources, which was shown in Fig. 6. The first factor (PMF1) was characterized with high loads of short chain (C < 8) PFAAs, including PFBA, PFPeA, PFHxA and PFBS, which is consistent with the second component obtained by PCA-MLR model, and was deemed to be the source from snow deposition. The PFOA, PFDA and PFOS were the most dominant compounds in the second factor (PMF2) by PMF model, which represented the potential sources from tourism activities. On the average, the contributions to $\sum_{11}$PFAAs in surface water of these two factors were 46% for PMF1 and 54% for PMF2, respectively (Fig. 7). Unlike PCA-MLR, PMF analysis suggested a relatively larger contribution of emission from local tourism activities. Considering the inherited uncertainty and disadvantages of the two methods, precise contributions of the sources should be measured through detail mass flow analysis (Hopke, 2003; Sofowote et al., 2008). Both PMF and PCA-MLR results demonstrated the significant differences between the sources of short- and long-chain PFAAs in the study area. Since high levels of PFOA have been observed in the site WT7, indicating a potentially intensive pollution by local human activities (Stock et al., 2007; Kotthoff et al., 2015), the contributions of two sources were further analyzed between regions. Significant differences in the contributions of the sources were found between the main TC area (as well as ETC) and WTC area. The result showed that local human activities were the dominant source of PFAAs in WTC with a contribution of 99% (Fig. 7). The source of snow deposition accounted for 67% of total concentrations in TC, while that only contributed to 0.4% of PFAAs in WTC. This is consistent with the highest PFAAs level observed in WTC area. The differences between the two regions could be attributed to the effect of size. The area of TC was over 100 times larger than WTC. TC received water from snowmelt of Bogda mountain with a

catchment of 480 km², while the WTC mainly got the water by underground seepage from TC, indicating that less PFAAs input in WTC. The geographical isolation and much smaller size made WTC more susceptible to tourism activities than TC.

To further validate the results, the predicted concentrations of the sources obtained by PMF were compared with the observed concentrations of individual PFAAs. The concentrations of individual PFAAs for PMF1 was highly correlated with that for snow (Spearman's $R = 0.609$, $p = 0.047 < 0.05$, Fig. S5), which further proved that the PMF1 with high loads of PFBA could be characterized as the source of long-range transport. The correlation analysis also showed that good correlation was found between short chain PFAAs. PFOA, PFNA and PFUnDA were highly correlated with each other (Table S8). The consistency of PFAAs compositions between observation and prediction further assert the results by PCA-MLR and PMF models. On the average, emissions from local tourism activities accounted for 41% of total levels, while long-range deposition contributed to 52% in the study area. This result suggested that both local activities and long-range transport were the major sources in the nature reserve. However, the atmospheric transport by westerly wind was also characterized with the dominance of long chain PFAAs (Wang et al., 2019). The identified source PMF2 and PCA1 with abundant PFOA could be attributed to joint influence of the local activities and long-rang transport by westerly wind.

Consistent results were obtained by the two receptor models, which suggested two significant sources with different characteristics. However, PCA analysis has identified four factors while PMF only found two. Due to the differences in theoretical approaches, the results from different receptor models would vary and result in different source characterization (Zhang et al., 2019). The results of the receptor models were mainly based on statistical analysis of given datasets, and the limited sample size would bring uncertainties in this study. The fresh snow

Fig. 7. Contributions of identified factors to $\sum$PFAAs concentrations and correlation between predicted values and observed results.

in the environment. The consistency in PFAAs compositions among water, soil and snow suggested the snow deposition as an important source. The source analysis by PCA-MLR and PMF models has identified two major sources, which are characterized by tourism activities with dominance of PFOA and long-range transport with abundant PFBA. The contribution of long-range transport was estimated to be 52%, while that of tourism activities was 41%, indicating a significance of both sources to PFAAs occurrence. The good correlation between individual concentrations of fresh snow and predicted sources for long-range transport further proved the analysis. Compared with other studies and the assessment on air mass flow, the long-range transport of PFAAs in this study area was potentially affected by both westerly wind and Indian Monsoon. We recommend long-term studies to investigate the PFAAs deposition processes from different sources under the changing circulation patterns in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.133851.

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and water samples were taken only once, which would neglect the seasonal variances leading to reflection of the real condition partially. Several determined PFAAs would occur as degradation products of different precursors, which would also affect the source partition analysis results. To further assess the PFAAs accumulation and transport in the study area, investigations on specific local emission sources, seasonal precipitation patterns and other perfluorinated precursors are needed.

4. Conclusion

This study systematically analyzed the PFAAs occurrences in surface water, sediment, soil and fresh snow deposition in a nature reserve with increasing intensive tourism activities in Xinjiang, northwestern China. The PFAAs concentrations (3.38 ng L^{-1} in surface water, 1.06 ng g^{-1} dw in soil and 0.53 ng g^{-1} dw in sediments) in this area were much lower than urbanized regions. The highest PFAAs level of 15.41 ng L^{-1} was observed in surface water from western Tianchi pond, indicating a potential pollution by local human activities. Regional differences were found in PFAAs levels and compositions between main TC area and WTC pond, and the intensities of human activities were supposed to be the major reason. Short chain PFAAs with the dominance of PFBA were abundant

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