1 **Characteristics, main sources, health risks of PM$_{2.5}$-bound**

2 **perfluoroalkyl acids in Zhengzhou, central China: From**

3 **seasonal variation perspective**

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Abstract

Perfluoroalkyl acids (PFAAs) have become the focus due to their physicochemical stability and potential toxicity. In this study, the investigation aimed to characterize the pollution levels, identify the primary sources, and assess the health risks associated with PFAAs in $PM_{2.5}$. The average concentration range for PFAAs were between 46.68 and 181.63 $pg \cdot m^{-3}$, with the main components being perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorobutanoic acid. PFAA concentrations in $PM_{2.5}$ were greatly influenced by the short- and medium-range air masses, and markedly elevated by industrial activities in surrounding urban areas. The results by positive matrix factorization revealed that PFOA-based products (38.2%) and degradation byproducts of fluorotelomer alcohols (26.7%) were the predominant sources. The average daily inhalation of 17 PFAAs fluctuated greatly (median: 4.35×10^{-3} to 8.78 $pg \cdot (kg \cdot d)^{-1}$), showing different seasonal variations with estimated daily intake of PFOA and PFOS reaching peak value in winter (5869.39 pg) and spring (4219.41 pg), respectively. The research indicated that seasonal regulation of PFOA-related manufacturing and joint pollution control with neighboring cities could reduce PFAAs levels in $PM_{2.5}$. The results provided theoretical support for government to make targeted control plans for PFAAs and basic data for relevant researchers.

Keywords: PFAAs, , PMF model, source apportionment, health risks.

1 Introduction

Perfluoroalkyl Acids (PFAAs), a subset of perfluoroalkyl substances (PFASs), can form smooth surfaces that are waterproof, oil-resistant, and stain-resistant, hence their widespread application in various industrial productions, such as paints, surfactants, coatings, emulsifiers, and fire retardants (Lindstrom et al., 2011). During the production and utilization of PFAA-containing products, PFAAs are released into a variety of environment. Consequently, PFAAs could be detected in the human body (Cardenas et al., 2017), the atmosphere, water, or snow (Dreyer et al., 2009; Hu et al., 2016; Wang et al., 2017) and wildlife (Sedlak et al., 2017). PFAAs, having environmental stability, potential for long-range transport and toxicity, cause significant risks to environment and human health (Wang et al., 2022a; Wu et al., 2022). PFAAs levels in the atmosphere have attracted adequate attention due to people breathe second by second.

The PFAAs concentration range in the atmosphere of Japan and Malaysia were 3.7–330 $pg \cdot m^{-3}$, with perfluorobutanoic acid (PFBA) exhibiting the highest concentrations (Wang et al., 2022b). The atmospheric concentration range of $\sum_{13}$PFAAs in Chinese cities was between 6.19 and 292.57 $pg \cdot m^{-3}$, with an average value of 39.84 ± 28.08 $pg \cdot m^{-3}$, exceeding the values in other countries. The predominant constituent was identified perfluorooctanoic acid (PFOA) (Han et al., 2019). PFOA and perfluorooctane sulfonate (PFOS) were the primary components of PFAAs in the atmosphere of Shenzhen, accounting for approximately 35% and 22% of PFAAs (Liu et al., 2015a). The PFAAs peak concentrations occurred during spring (97.5–709 $pg \cdot L^{-1}$), while autumn recorded the lowest levels (9.27–105 $pg \cdot L^{-1}$), exhibiting a seasonal variation in Chengdu (Fang et al., 2019). Due to their low volatility, PFAAs tend to be more prevalent in the particulate phase (Liu et al., 2018). The previous study found that most PFAAs in the atmosphere are concentrated in the particle phase rather than the gas phase, especially perfluoroalkyl carboxylic acids (PFCAs) tending to distribute in $PM_{2.5}$ (Heydebreck et al., 2016; Lin et al., 2020). $PM_{2.5}$ have the capacity to penetrate deep into the lungs, so health risks of

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66   PM$_{2.5}$-bound PFAAs have more health risks than PFAAs alone, and the synergistic

67   effects of PFAAs in PM$_{2.5}$ have become a key public health priority (Qiao et al.,

68   2024). In a whole, there is a lack of seasonal comparative studies on PM$_{2.5}$-bound

69   PFAAs in densely populated inland urban areas.

70   PFAAs can be directly emitted into the atmosphere during production,

71   transportation, application, and disposal processes (Dong et al., 2021), and enter other

72   environment through atmospheric dry and wet deposition (Barton et al., 2006).

73   Studies have demonstrated that long range atmospheric transport (LRAT) is a

74   significant process influencing the distribution of PFAAs (Gawor et al., 2014; Jahnke

75   et al., 2007), serving as a key source for remote inland regions (Ellis et al., 2004;

76   Murr, 2020) and even polar (Wang et al., 2014). Receptor model was successfully

77   used in source apportionment of PFAAs. Han et al. employed positive matrix

78   factorization (PMF) to identify four sources of PFAAs within the atmosphere.

79   Meanwhile, Chen and Wang combined principal component analysis with

80   back-trajectory model to assess air mass influence PFAA concentrations in

81   precipitation from the Tibetan Plateau (Han et al., 2019) and airborne particulate

82   matter in Chengdu, China (Chen et al., 2021). Direct emissions associated with

83   fluoropolymer manufacturing and indirect contributions from incomplete degradation

84   of precursors are the main sources of PFAAs in the atmosphere (Barber et al., 2007).

85   For instance, fluorotelomer alcohols (FTOHs) are oxidized by hydroxyl radicals

86   leading to the formation of PFAAs (Thackray and Selin, 2017). PFAAs are known to

87   be carcinogenic and exposure assessments were conducted in previous studies. The

88   average daily inhalation (ADI) of PFOA and PFOS were quantified, ranging from

89   0.05–11.97 pg·(kg·d)$^{-1}$ and 0.03–8.90 pg·(kg·d)$^{-1}$, respectively (Lin et al., 2022;

90   Liu et al., 2015a; Liu et al., 2023; Liu et al., 2018). According to human

91   epidemiological studies, the European Food Safety Authority (EFSA) has

92   delineated a tolerable weekly intake for PFOS at 13 ng·kg^{-1} and for PFOA at 6

93   ng·kg^{-1} (Yeung et al., 2019). In brief, few studies have begun to focus on the

94   source and health risks of PFAAs, however no systematic studies have been

95   conducted of PFAAs in PM$_{2.5}$.

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96   Given a comprehensive research of PFAAs in $PM_{2.5}$ is important for

97   enhancing our understanding of the environmental activity, so the pollution

98   characteristics, sources and health risks of $PM_{2.5}$-bound PFAAs were studied. The

99    $PM_{2.5}$ samples were collected in Zhengzhou, central China, characterized by dense

100   population (12.828 million resident population in 2022) (Statistics, 2023) and

101   heavy $PM_{2.5}$ pollution (47.7 $\mu g \cdot m^{-3}$ in 2022, exceeding the national average by

102   64.5%) (Department of Ecology and Environment of Henan Province, 2022; Ministry

103   of Ecology and Environment of the People′s Republic of China, 2022), and 17

104   PFAAs were analyzed in this study. The objectives of this study were (1) to

105   characterize seasonal variations in PFAA pollution in $PM_{2.5}$, (2) to employ multiple

106   models (including back trajectory model, potential source contribution function

107   (PSCF) and PMF model) to identify primary sources as well as potential regional

108   sources contributing to PFAAs, and (3) to evaluate health risks associated with

109   PFAAs in $PM_{2.5}$ in four seasons. This study conducted a systemative investigation

110   of $PM_{2.5}$-bound PFAAs in a typical rapidly developing city with relative high

111   $PM_{2.5}$ pollution, providing an integrated analysis of the pollution characteristics,

112   source identification, and health risks of PFAAs, thereby expanding the existing

113   data of knowledge and providing a theoretical basis for the government to make

114   control plans on PFAAs in different seasons.

115   ## 2 Material and methods

116   ### 2.1 Sample collection

117   PM_{2.5} samples were collected from the rooftop of the Collaborative

118   Innovation Building at Zhengzhou University (34°48′N, 113°31′E) on the roof (14

119   m height), approximately 500 meters east of the West Fourth Ring Road and 2

120   kilometers south of the Lianhuo Expressway. A total of 60 valid samples were

121   collected from Dec 2022 to Nov 2023 (details in Table S3). The diameter of the

122   quartz membrane was 90 mm, with sampling conducted from 10:00 to 09:00 on the

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123 following day by using a sampler (JCH-6120-1, Ju Chuang Environmental inc.,

124 China) at a flow rate of 100 L/min. Before sampling, quartz filters were wrapped

125 in aluminum foil and baked in a muffle furnace at 450°C for 5 hours to eliminate

126 organic components. The quartz filters were placed in a super clean room

127 (temperature of $20 \pm 5°C$; relative humidity of $50 \pm 5\%$) for 48 hours. The quartz

128 filters were changed daily in the ultra-clean room. Clean the instrument with

129 alcohol cotton before and after each sample, and record the sampler's standard

130 condition volume. The quartz filters were weighed twice before and after sampling,

131 and the error between the two times was not more than 10 mg. After weighing the

132 sample, the filters were wrapped in aluminum foil and stored at -18°C until the

133 sample was used. The samples would be deemed invalid when adverse weather

134 conditions (such as rain or snow) or power outages occurred during sampling

135 process.

136 ## 2.2 Chemicals and reagents

137 The chemical reagents used in this study were 17 kinds of PFAAs mixed

138 standard solutions and 9 kinds of mass-labeled internal standard mixed standard

139 solutions. 17 PFAAs mixed standard solutions: PFBA, Perfluoropentanoic acid

140 (PFPeA), Perfluorohexanoic acid (PFHxA), Perfluoroheptanoic acid (PFHpA), PFOA,

141 Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA),

142 Perfluoroundecanoic acid (PFUnDA), Perfluorododecanoic acid (PFDoDA),

143 Perfluorotridecanoic acid (PFTrDA), Perfluorotetradecanoic acid (PFTeDA),

144 Perfluorohexadecanoic acid (PFHxDA), Perfluorooctadecanoic acid (PFODA),

145 Perfluorobutane sulfonate (PFBS), Perfluorohexane sulfonate (PFHxS), PFOS, and

146 Perfluorodecane sulfonate (PFDS). 9 kinds of mass-labeled internal standard mixed

147 solutions: $^{13}C_4PFBA$, $^{13}C_4PFHxA$, $^{13}C_4PFOA$, $^{13}C_4PFNA$, $^{13}C_4PFDA$, $^{13}C_4PFUnDA$,

148 $^{13}C_2PFDoDA$, $^{18}O_2PFHxS$, and $^{13}C_4PFOS$.

2.3 Sample preparation and instrument analysis

After the addition of methanol, the extracts were performed 3 times by sonication. Following the centrifugation (4500 r/min, 15 min), the extracts were diluted with ultrapure water. The extracts were purified using weak anion exchange cartridges and then concentrated to 200 μL with nitrogen. Prior to instrumental analysis, the sample was filtered through a 0.22 μm nylon membrane and transferred into a 2 mL brown injection vial. Detailed steps for sample pretreatment are documented in supplementary 1.2.

The analysis of PFAAs was performed using Ultra High Performance Liquid Chromatography-Tandem Mass Spectrometry (Ekspcrt nano Lc425, Singapore) UPLC-MS/MS. The analytical instrument employed consisted of a triple quadrupole liquid chromatography-mass spectrometer. For chromatographic separation, a C_{18} reverse-phase column (150 mm × 2.1 mm, 1.8 μm) was selected. Comprehensive details regarding the instrumental analysis can be found in supplementary 1.2.

2.4 Quality assurance and quality control

During the sample collection, processing, and analysis phases, fluorinated plastic materials were avoided, such as polytetrafluoroethylene (PTFE). Use ceramic scissors to cut quartz filters and wipe the scissor with methanol before cutting another sample to avoid excess particles affecting the next sample. The polypropylene tubes were used. All samplers and containers were precleaned with methanol. The concentrations of the prepared 7-point calibration solution were as follows 0.1, 1, 5, 10, 50, 100, and 200 μg/L. The concentration of internal standard solution was 10 ng/mL. The procedure blanks were prepared using the same methods as the samples. Two field blank membranes were collected during each seasonal sampling period. The final concentrations of PFAAs were determined by subtracting the concentrations of the procedure blanks from those of the samples.

176 Reagent blanks were employed to monitor instrumentation performance. No

177 PFAAs were detected in field blanks and program blanks. The method detection

178 limit (MDL) was calculated based on three times the standard deviation of the

179 blanks. If PFAAs were not detected in the blanks, MDL refers to a concentration

180 corresponding to peak intensity with a signal-to-noise ratio (S/N) of 3. Values

181 below MDL were replaced with half of MDL (Han et al., 2019; Li et al., 2024).

182 The MDL value and Mark recovery ranged from 0.2–0.3 (ng/L) and 71.27%–118.08%

183 respectively. Detailed information on the individual compounds of PFAAs is

184 documented in Table S1.

185 The PMF model was used to cluster PFAAs with similar sources to identify

186 potential sources. The ADI model was employed to quantitatively evaluate the

187 health risks posed by PFAAs to human populations. The detailed information of

188 PMF and ADI models could be found in supplementary 1.2 and 1.3, which

189 provides an in-depth explanation of these analytical frameworks.

3 Results and discussion

3.1 Characteristics of PFAAs in $PM_{2.5}$

192 The seasonal average concentrations ranged from 46.68 to 181.63 pg·m^{-3} in

193 Fig. 1, which was comparable to levels observed in Chengdu (150 pg·m^{-3}) (Fang et

194 al., 2019), but significantly higher than those recorded in Shenzhen (8.80 pg·m^{-3})

195 (Liu et al., 2015a) and the average concentration in China (39.84 pg·m^{-3}) (Han et

196 al., 2019). These factors, which characterized this region as having a dense

197 population, concentrated industrial activities, and serious $PM_{2.5}$ pollution, may

198 contribute to higher PFAA levels than other cities. As shown in Fig. 2, the PFAA

199 concentrations in $PM_{2.5}$ peaked during winter and were 1.7 times higher than

200 autumn level and 3.9 times higher than summer level. The result indicated that

201 PFAAs had obvious seasonal variation. The long-chain PFAA concentrations

202 (1169.60 pg·m^{-3}) significantly exceeded that of short-chain PFAAs (915.24 pg·m^{-}

203   ³), consistent with the findings in researches (Han et al., 2019; Tian et al., 2018).

204   Detection rates for PFOA, PFPeA, and PFBA in four seasons reached 100%, while

205   detection rates for PFHxA, PFHpA, PFBS, and PFOS exceeded 80%. During the

206   study period, PFOA and PFOS along with its primary substitutes accounted for

207   23%–34% and 18.1%–29.9% of total PFAAs, consistent with the research (Liu et al.,

208   2017).
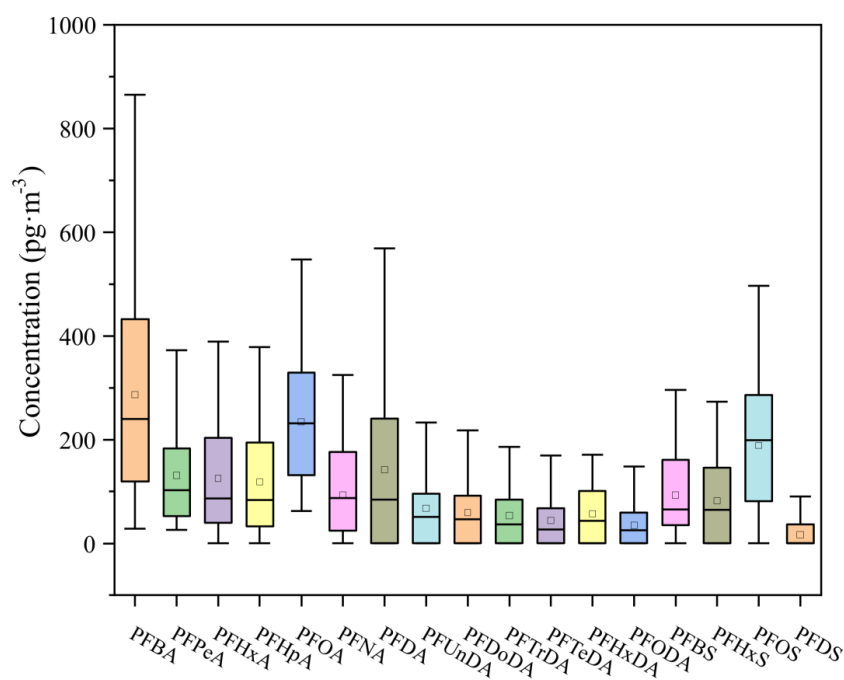
209   Fig. 1. Box diagram of PFAAs concentrations in $PM_{2.5}$

210   The content of PFOA and its substitutes reached 23% of total PFAAs in

211   autumn, 34% in winter and, and 31% in spring and summer. Their applications

212   span across the chemical industry and domestic activities, particularly in the

213   manufacture of plastic and rubber commodities (Liu et al., 2015a; Prevedouros et

214   al., 2006). The rising domestic demand and industrial output of PFOA products

215   were outstanding trends within China (Du et al., 2023). The mean concentration of

216   PFOA (294.52 ± 215.40 pg·m^{-3}) in Zhengzhou markedly surpassed those recorded

217   in Chengdu (42.3 ± 54.4 pg·m^{-3}), Ireland (8.9 pg·m^{-3}), and Japan (Tsukuba, 2.6

9

218   pg·m^{-3}; Morioka, 2.0 pg·m^{-3}), but it fell below the levels detected in Changshu,

219   China (556.0 pg·m^{-3}), a local area of fluorochemical industrial park (Barber et al.,

220   2007; Fang et al., 2019; Harada et al., 2005; Yu et al., 2018). The content of PFOS

221   and its substitutes were more than 25% in winter and summer, more than 20% in

222   autumn, and more than 10% in spring. PFOS is extensively utilized in metal

223   electroplating, firefighting foams, the semiconductor industry, paper treatment,

224   textiles, and leather processing (Liu et al., 2017). PFPeA and PFBS are the

225   principal substitutes to long-chain PFAAs in China, being emitted during the

226   production of PFOS products (Liu et al., 2017). The researches have identified

227   PFHxDA as a degradation byproduct of substances based on FTOHs (Ellis et al.,

228   2004; Loewen et al., 2005). The PFHxDA concentration escalated from 2.2% in

229   winter to 10.4% in spring, potentially attributable to enhanced atmospheric

230   oxidation.
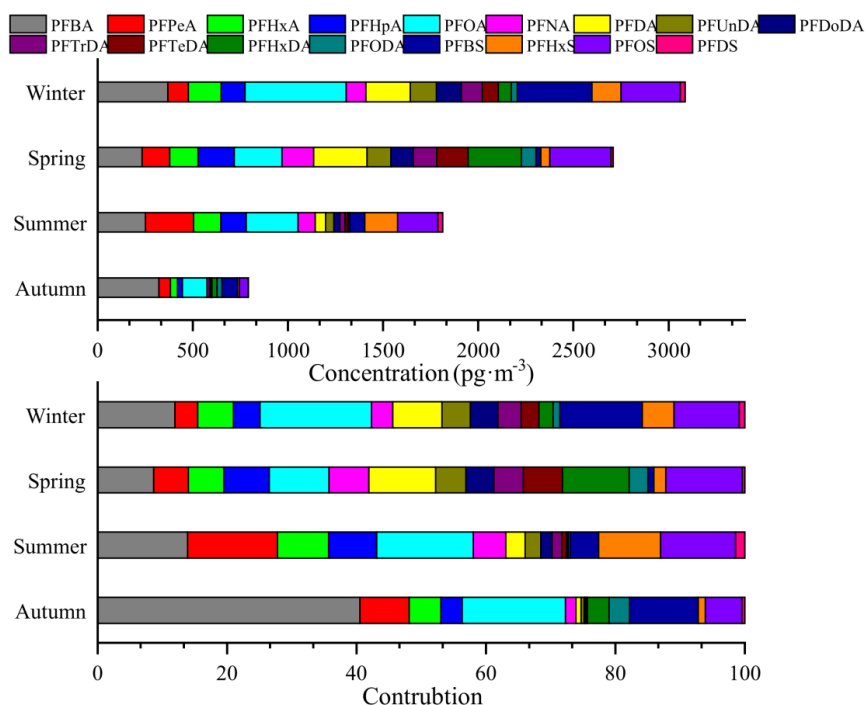
231   Fig. 2. PFAAs concentrations characteristics across four seasons

232   The seasonal distribution of PFAAs in the study region exhibited a pattern

233 where winter concentrations surpassed those of other seasons, with the lowest in

234 autumn. This seasonal variation correlated with the heightened PM$_{2.5}$ pollution

235 during the winter in this region. It was noteworthy that PFAA concentrations

236 during autumn (46.68 pg·m^{-3}), when were at the minimum, still exceeded the

237 national average concentration of 39.84 pg·m^{-3} (Han et al., 2019). The chemical

238 industry and domestic activities were the primary contributors to PFAAs pollution

239 in this region. A comprehensive analysis of the pollution characteristics and

240 sources of PFAAs in PM$_{2.5}$ was important for generating strategies aiming at

241 release PFAAs pollution.

242 3.2 Analysis of potential regional sources of PFAAs in PM$_{2.5}$

243 The content of PFAAs in the atmosphere is easily influenced by the transport of

244 atmospheric air masses (Liu et al., 2015a). As shown in Fig. 3, this study conducted a

245 meteorological trajectory cluster analysis during the sampling period. The spring

246 season was most influenced by short-range atmospheric air masses (accounting for

247 40.4%) in this study region. The air mass originated from Hubei Province, passed

248 through Middle-Lower Yangtze River plains (0.26–1.90 pg·m^{-3}) and then entered the

249 study region (Faust, 2023). This air mass would reduce the content of PFAA

250 concentrations in the study area because of the slow diffusion of pollutants caused by

251 relative stability of this air mass and the lower PFAA concentrations than this region.

252 The study region was also affected by the transport of long-range air masses from the

253 northwest direction (accounting for 38.5%), which passed through the Inner Mongolia

254 and Loess Plateau and the Taihang Mountains. In the autumn, the study region was

255 more influenced by long-range air masses from the northwest (accounting for 57.7%),

256 which passed through Inner Mongolia and the Loess Plateau to reach the study area.

257 In winter, all trajectory clusters, accounting for 10.0%, 23.3%, and 66.7% respectively,

258 originated from the northwest, indicating a pronounced influence of the cold air from

259 that direction. The increased use of urban coal combustion in winter along this

260 direction tended to create polluted air masses, which were then transported and

261 increased the pollution levels in the study region by northwesterly winds. The

262 long-range air masses, passing through the Inner Mongolia Plateau and the Loess

263 Plateau of northwest, generated the most important influence on the seasonal transport

264 patterns during summer, autumn, and winter in the study region. Northwest China is

265 situated in a plateau region. The high-altitude region has a cold-trapping effect on

266 PFAAs in the atmosphere (Gouin et al., 2004), which can effectively reduce the

267 content of PFAAs in atmospheric air masses. The Loess Plateau could weaken the

268 influence of air masses from the northwest on PM$_{2.5}$-bound PFAAs levels in the study

269 region. This result was consistent with the analysis of potential sources of PFAAs

270 using the PSCF below.
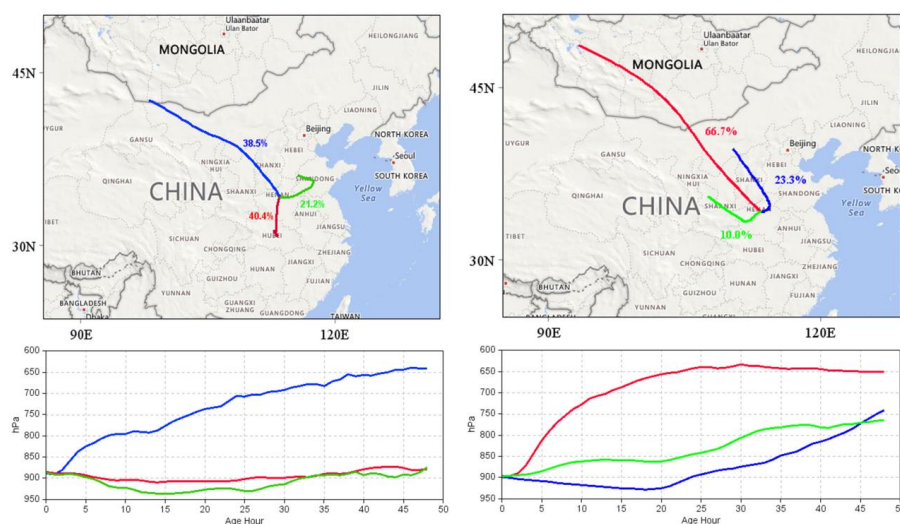
271 Fig. 3. Cluster analysis map of backward trajectories in Zhengzhou City (left and right are spring
272 and winter respectively, created by MeteoInfoMap 3.5.11 (Wang, 2014; Wang, 2019)). ©
273 Microsoft. The software is open.

274 As shown in Fig. 4, the strong potential source regions (WPSCF ≥ 0.5) during

275 spring were primarily concentrated in the southwest region of the province,

276 significantly influenced by the southwest air masses. The strong potential source

277 regions were mainly found in the surrounding regions of the province during summer,

278 transferred to the northwest and southwest outside the province during autumn, and

279 were principally distributed in the northwest and northeast within the province during

280 winter. The study results indicated that the influence of the northeast air masses on the

281 distribution of potential sources was more obvious in the study region. This result

282 could be attributed to the fact that the study region was located in the typical

283 industrial province characterized by industries such as textile treatment, metal

284 electroplating, and fire-fighting foam manufacturing. The wide use of PFAAs in

285 industrial production, such as emulsifiers and fluoropolymers, had led to increased

286 emissions of these substances into the atmosphere. Additionally, human activities,

287 such as the use of non-stick coatings on cookware and waterproof and stain-resistant

288 materials, particularly in densely populated areas near study region, heightened

289 PFAAs pollution levels (Dewapriya et al., 2023; Dhore and Murthy, 2021; Grunfeld et

290 al., 2024; Li et al., 2024; Wang et al., 2024). This result was consistent with

291 conclusions drawn by Chen et al. (Han et al., 2019). Seasonal variation could cause

292 the distribution of strong potential source regions to change. In contrast to spring and

293 summer, the distribution of strong potential source regions were more influenced by

294 the northwest air masses in autumn and winter. In addition to autumn, strong potential

295 source regions mainly distributed in the surrounding regions of the province in spring,

296 summer and winter.

297 Research indicated that the PFAAs levels in $PM_{2.5}$ were more influence by

298 medium- and short-range air masses and terrain. To control PFAAs levels in $PM_{2.5}$, it

299 is necessary to not only manage local emissions but also identify the pollution

300 transport pathways and sources across different seasons. Strengthen the joint

301 prevention and control of neighboring cities on a seasonal basis. The results of this

302 research provided a theoretical basis for the formulation of policies related to the

303 control of PFAAs levels in $PM_{2.5}$.
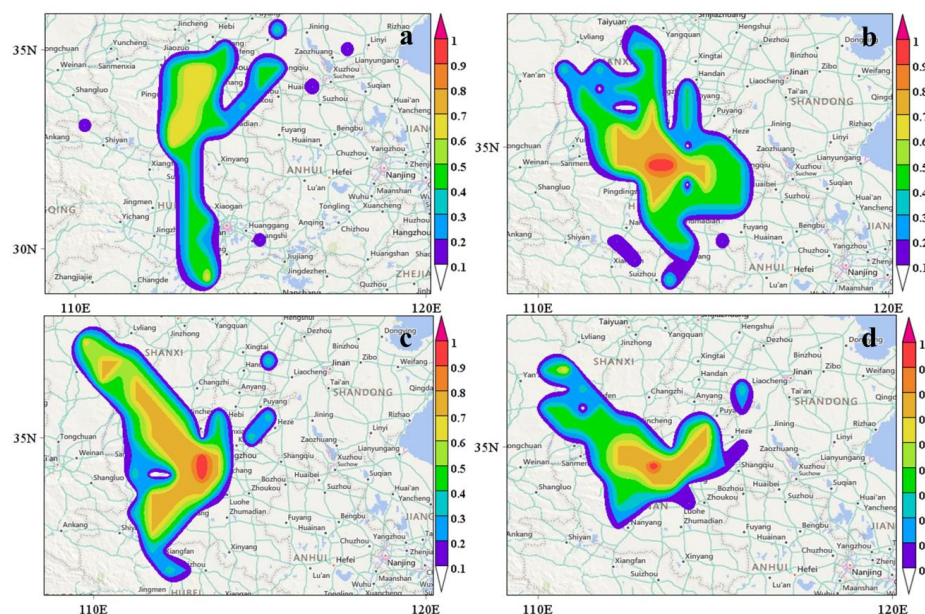
Fig. 4. Map of potential source analysis of PM$_{2.5}$-bound PFAAs in Zhengzhou City in four seasons (a, b, c and d are spring, summer, fall and winter respectively, created by MeteoInfoMap 3.5.11 (Wang, 2014; Wang, 2019)). © Microsoft. The software is open.

3.3 PMF receptor analysis

To further investigate the potential PFAAs sources in PM$_{2.5}$, this study employed PMF for source apportionment of PFAAs. As illustrated in Fig. 5(b), Factor 1 was predominantly characterized by high loadings of PFUnDA (72.5%), PFDoDA (71.4%), PFTrDA (80.4%), and PFTeDA (96.0%). Long-chain PFAAs (C11–C14) were known degradation products of FTOHs (Liu et al., 2017; Thackray and Selin, 2017; Wang et al., 2014). The global accumulated estimates for PFUdA, PFDoDA, PFTrDA, and PFTeDA ranged from 9 to 230 tons from 2003 to 2015, and the research shown an expected release of between 0 to 84 tons from 2016 to 2030 based on the lifecycle use and emission patterns associated with fluorocomplexes and other fluorine-containing products (Wang et al., 2014). Therefore, this factor, contributing 26.7% to total PFAAs, was thought to be the degradation products of FTOHs.
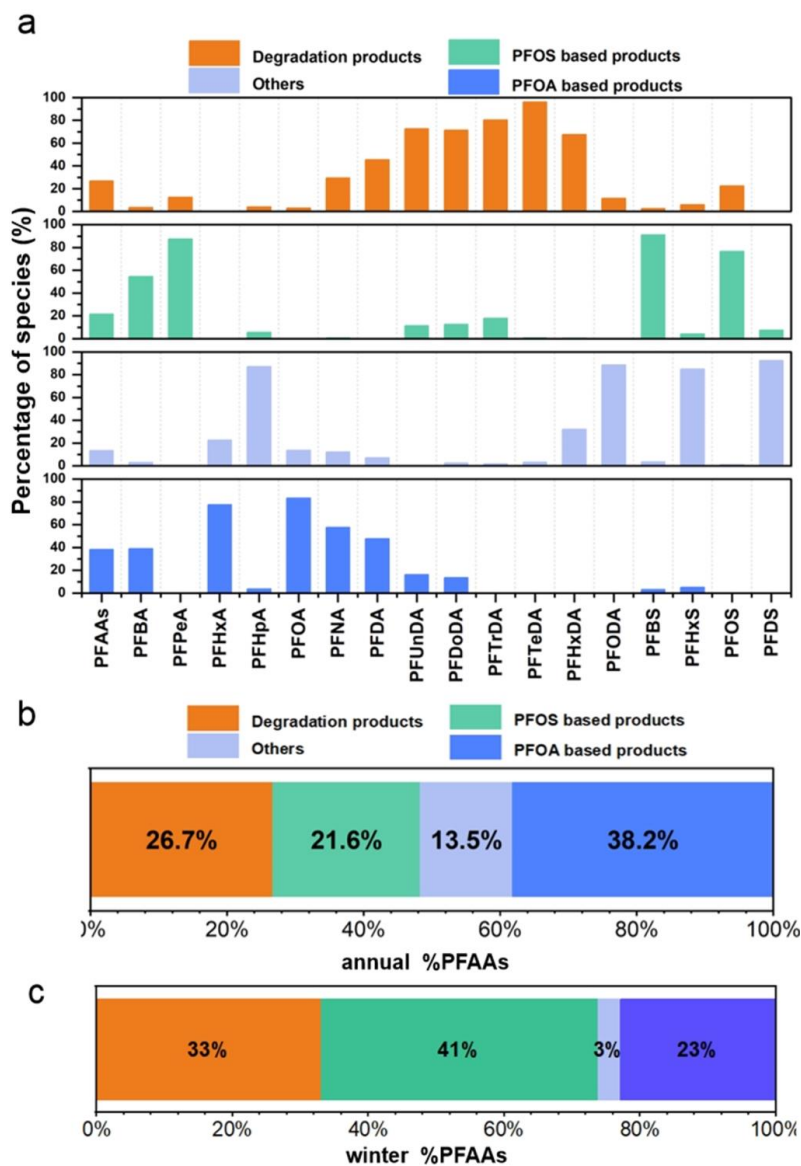
Fig. 5. The source distribution spectrum of PFAAs in PMF (a) and the source proportion diagram (b)

According to the PMF analysis results, it indicated that PFPeA, PFBS, and PFOS may originate from a common source with contribution rates of 87.4%, 91.0%, and 76.6% in Factor 2 respectively. The research indicated hat three primary kinds of chemicals related to PFOS-namely perfluorooctane sulfonates, substances containing

325   these compounds and polymers were widely useded in industrial production (Xie et

326   al., 2013). The use of PFOS-related products have resulted in the emission of PFOS

327   into the atmosphere during both industrial processes and human activities. PFPeA and

328   PFBS, because of being the significant substitutes of long-chain PFAAs, may be

329   released as impurities or by-products during the manufacturing of PFOS-based

330   products (Liu et al., 2017). Therefore, this factor, contributing 21.6% to total PFAAs,

331   was regarded as a direct source of perfluorooctane sulfonic acid products.

332   Factor 3 was characterized by high loadings of PFHpA (loading value: 87.1%)

333   and PFHxS (loading value: 85.0%). The formation and transformation for PFHpA and

334   its derivatives remained unclear. The factor containing only PFHxS did not point to a

335   specific source. Therefore, it was thought to be other sources influenced potentially by

336   atmospheric air masses or alternative origins. Thus, the contribution from the source

337   was thought to be 13.5% for PFAAs.

338   Factor 4 was identified as the primary source of PFOA products manufacturing,

339   characterized by significant loadings of PFHxA (77.5%), PFOA (83.4%), PFNA

340   (77.5%), and PFDA (47.6%). PFOA had been widely used as an emulsifying agent in

341   the production of plastics, rubber products, textile flame retardants, paper surface

342   treatments, fire-fighting foams, and PTFE emulsifiers (Liu et al., 2015b). The research

343   indicated that due to a rapid increase in domestic demand for PFOA products in China,

344   the emissions of PFCAs from factories producing these substances have increased

345   (Wang et al., 2014). PFOA, PFNA and their substitutes could be released through

346   waste gases. The contribution of this source to PFAAs accounted for 38.2%.

347   The sources of PFAAs are multifaceted and seasonal. Source apportionment was

348   conducted in winter when PFAAs pollution was most severe. As shown in Fig. 5(c),

349   PFOS products contributed the most to PFAAs sources in winter $PM_{2.5}$ (41%),

350   followed by FTOHs degradation products (33%). Factor analysis indicated the

351   contributions of PFAAs in $PM_{2.5}$ came from the degradation of specific fluorinated

352   products and direct emissions from industrial productions. The analysis of long-chain

353   PFAAs emphasized the potential environmental impact associated with the production

354   and use of FTOHs with degradation products contributing 26.7% to PFAAs in $PM_{2.5}$.

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355 Furthermore, contributions from PFOS- and PFOA-related compounds to PFAAs in

356 PM$_{2.5}$ were found to be 21.6% and 38.2%. Additionally, it was thought that 13.5% of

357 PFAAs originated from unknown sources, and indicated a significant gap in our

358 understanding regarding their environmental behavior. This finding emphasizes the

359 urgent need for further research aiming at enhancing our comprehension of PFAAs in

360 PM$_{2.5}$.

361 ## 3.4 Environmental indication of health impact risk

362 Fig. 6 illustrated the ADI of PFAAs in PM$_{2.5}$. The median ADI ranged from

363 4.35×10^{-3} to 8.78 pg·(kg·d)$^{-1}$, with relative high values for PFBA, PFOA, and

364 PFOS in four seasons. Notably, PFOA exhibited a median ADI as high as 8.78

365 pg·(kg·d)$^{-1}$, with potential carcinogenicity risk on human immune and reproductive

366 systems (Lin et al., 2022). The high ADI values of these compounds raise concerns

367 regarding their potential health impacts, especially given that PM$_{2.5}$ can be inhaled

368 into human lungs, thereby complicating the health implications of exposure to

369 PM$_{2.5}$ containing PFAAs. Although the ADI levels of these compounds remained

370 below the tolerable intake limits set by the EFSA (Yeung et al., 2019), it is

371 important to consider that PFAAs are resistant to degradation within the human

372 body. For example PFOS has a half-life of approximately 5.4 years (Wei et al.,

373 2023). Therefore, long-term exposure to lower concentrations of PFAAs than limit

374 values still may accumulate over time and potentially lead to adverse health

375 outcomes. This study discovered pronounced seasonal variation in the estimated

376 daily intake (EDI) (Fig. 7). The PFOA and PFOS EDI exhibited the remarkable

377 peak during winter (the median values: 5869.39 pg) and spring (the median values:

378 4219.41 pg) respectively, and recorded the lowest average daily exposure dose

379 during autumn (the median values 1787.21 and 3285.28 pg). A comparative

380 analysis of the seasonal EDI patterns indicated that the winter season was

381 characterized by a relatively elevated daily exposure dose, particularly for PFOA.

382 The observed seasonal fluctuations in EDI were due to changes in concentration

383   due to a combination of influence factors such as ambient temperature, relative

384   humidity, human activities, and atmospheric air mass transport. For example, these

385   factors comprehensively influenced the atmospheric partitioning and deposition of

386   PFOA and PFOS, thereby impacting the population's exposure to these PFAAs.
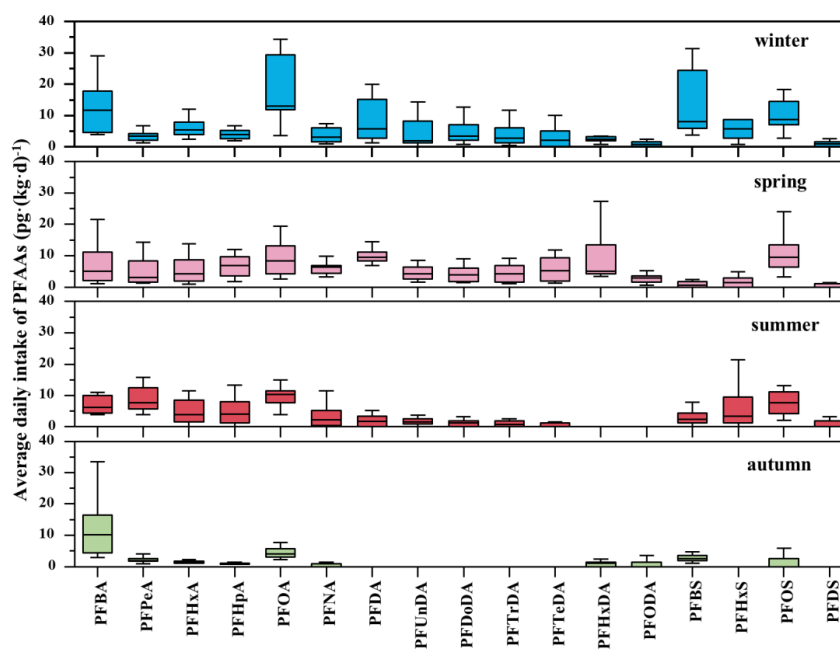
387   Fig. 6. Median Average Daily Intake (ADI) of PFAAs in PM$_{2.5}$ in four seasons

388

18
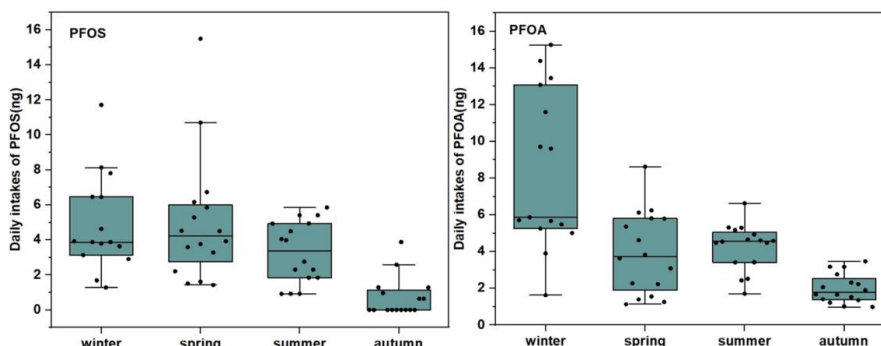
389   Fig. 7. The median daily estimated intake (EDI) of PFOA and PFOS varies by season in $PM_{2.5}$

390   To mitigate PFAAs contamination and protect environmental health, it is
391   recommended to strengthen regulatory controls on industrial emissions, upgrade
392   wastewater treatment technologies, and enhance public awareness of PFAAs risks.
393   Regular monitoring of PFAAs in environmental media is crucial, and industries
394   should be incentivized to adopt safer alternatives. Additionally, further research is
395   needed to better understand the long-term environmental and health impacts of
396   PFAAs exposure.

397   4 Conclusion

398   This study conducted a one-year sampling of $PM_{2.5}$ and utilized UPLC-MS/MS
399   to detect PFAAs in the samples. A comprehensive analysis of the pollution
400   characteristics, source apportionment, and health risk assessment of PFAAs in $PM_{2.5}$
401   was conducted. The results indicated that the detection rates of PFOA, PFPeA and
402   PFBA were 100%, PFHxA, PFHpA, PFBS and PFOS were more than 80%. PFAA
403   concentrations were highest in winter (mean value: 181.63 $pg \cdot m^{-3}$) and lowest in
404   autumn (mean value: 46.68 $pg \cdot m^{-3}$), however the lowest values still significantly
405   higher than the national average from previous study. PFOA and PFOS along with its
406   substitutes were primary PFAAs in $PM_{2.5}$. Backward trajectory analysis of the study
407   region revealed that the PFAA concentrations were susceptible to medium and

408 short-range atmospheric air mass transport. Controlling the concentration of PFAAs in

409 $PM_{2.5}$ requires primarily reducing local emissions and strengthening joint prevention

410 in different seasons. PMF analysis indicated that the main PFAAs sources were

411 products of PFOA and its substitutes (38.2%), degradation products of

412 fluorotelomer-based products (26.7%) and PFOS and its substitutes (21.6%). There

413 was also an unknown source accounting for 13.6%, indicating that there are still

414 significant limitations in our understanding of the PFAAs environmental behavior,

415 and further research is necessary. The PFAAs ADI was below the tolerable intake

416 limit set by the EFSA. The high EDI PFAAs values, which could be inhaled into

417 human lungs through $PM_{2.5}$, should be a concern due to their potential to complicate

418 health effects, making PFAAs research particularly important in regions with heavy

419 $PM_{2.5}$ pollution. Monitoring the impact of atmospheric air mass transport in the study

420 region by season, strengthening targeted joint prevention and control with

421 neighboring cities are crucial steps in reducing the concentration of PFAAs in $PM_{2.5}$.

422 The study results of concentration characteristics, origin and health effects of PFAAs

423 could provide theoretical support and basic data for government and follow-up

424 researchers to reduce PFAAs levels.

Data availability

All raw data can be provided by the corresponding authors upon request.

Author contributions

JZ: Writing-Review and Editing; XM: Writing-Original draft preparation, Writing-Review and Editing; ML: Writing-Review and Editing; ZW: Writing-Review and Editing; NJ: Writing-Review and Editing, Supervision, Project administration; FW: Resources.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgments

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