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1 Non-Target and Suspect Screening of Per- and Polyfluoroalkyl
2 Substances in Airborne Particulate Matter in China

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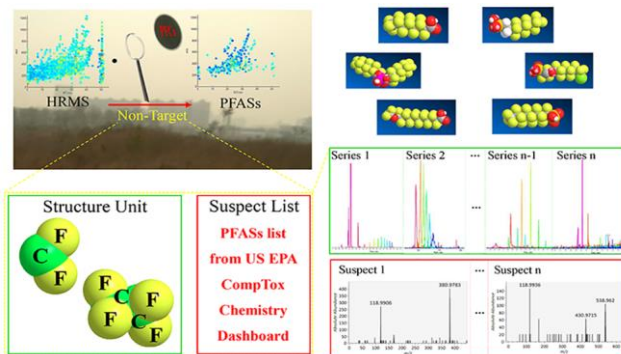
16 ABSTRACT

17 Airborne particulate matter (APM) has an important role in inhalation exposure,
18 especially in China. The environmental occurrence of conventional and unknown per-
19 and polyfluoroalkyl substances (PFASs) in APM remains unclear. Therefore, in this
20 study, a two-stage experiment was designed to identify potential PFASs and to
21 investigate their distribution in APM. Indoor and outdoor APM samples were
22 collected from five selected cities in China. Through PFAS homologue analysis and
23 suspect screening, 50 peaks were identified with different confidence levels (levels
24 1–3). Among the identified PFASs, 34 emerging PFASs including p-perfluorous
25 nonenoxybenzenesulfonate, 6:2 polyfluoroalkyl phosphate diester, n:2 fluorotelomer
26 sulfonates, n:2 fluorinated telomer acids, n:2 chlorinated polyfluoroalkyl ether
27 sulfonic acids, 1:n polyfluoroalkyl ether carboxylic acids (1:n PFECAs),
28 perfluoroalkyl dioic acids (PFdiOAs), hydro-substituted perfluoroalkyl dioic acids
29 (H-PFdiOAs), and unsaturated perfluorinated alcohols (UPFAs) were identified in
30 APM. In particular, 1:n PFECAs, PFdiOAs, H-PFdiOAs, and UPFAs were first
31 detected in APM. Although human exposure to perfluorooctanoic acid via inhaled
32 APM was noted to not be a risk (hazard quotient <0.1) in this study, the expansion of
33 the PFASs screened in APM implies that human exposure to PFASs might be much
34 more serious and should be considered in future risk assessments in China.

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39 INTRODUCTION

40 Per- and polyfluoroalkyl substances (PFASs) have been used in various industrial
41 processes and consumer products owing to their unique physical and chemical
42 properties.¹ Their wide applicability has prompted notable development of the
43 fluorine chemical industry. According to a report by the Swedish Chemicals Agency,
44 there are 2060 PFASs identified on the global market.² Currently, this PFAS list has
45 been included on the NORMAN Suspect List Exchange (SFISHFLUORO,
46 <https://www.norman-network.com/?q=node/236>) and the US EPA CompTox
47 Chemistry Dashboard³ (PFAS List from KEMI,
48 https://comptox.epa.gov/dashboard/chemical_lists/sfishfluoro). Some of these
49 compounds, e.g., perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid
50 (PFOA), have been recognized as pollutants because of their environmental
51 persistence and toxicity.^{4,5} Thus, PFOS has been listed in the Annex B of the
52 Stockholm Convention⁶ and PFOA has been recommended as a persistent organic
53 pollutant (POP) by the POPs Review Committee.⁷ Despite the restrictions and
54 phase-out of PFOS and PFOA in developed countries,⁸ alternatives, such as
55 short-chain perfluoroalkyl carboxylates (PFCAs), short-chain perfluoroalkyl
56 sulfonates (PFSAs), and polyfluoroalkyl phosphate esters (PAPs) have been put into
57 production.^{9,10} Frequent and extensive detection of emerging/unknown PFASs within
58 the environment highlights the risk to humans of continuous exposure to increasing
59 amounts of such compounds.¹¹⁻¹³ Therefore, to evaluate their environmental health
60 implications, previously unreported PFASs in humans and the environment need

61 continuous identification.

62 Non-target analysis combined with high-resolution mass spectrometry (e.g., Orbitrap
63 and quadrupole time of flight, QTOF) makes it possible to detect and recognize a
64 wide range of substances.¹⁴⁻¹⁶ Orbitrap and QTOF with data dependant acquisition
65 (DDA) provide high resolving power and mass accuracy both in full scan (MS1) and
66 MS/MS.^{15,17} TOF-MS data directly show the isotopic distribution and provide
67 accurate m/z for each chemical feature, as well as highlight potential links among
68 chemical features, such as homologues¹⁸. MS/MS data include structural information
69 of the chemical features. Based on mass accuracy and MS/MS fragmentation,
70 strategies such as Kendrick mass defect plots¹⁸ and data-independent precursor
71 isolation and characteristic fragment method¹⁹ have been designed to identify
72 congeners. Investigations to identify emerging PFASs have been directed primarily
73 toward aqueous film-forming foams (AFFF)²⁰⁻²³, occupational exposure¹⁷, wastewater
74 from fluorochemical industries²⁴, rivers around manufacturing facilities²⁵, and
75 drinking water near fluorochemical industries²⁶. Over 240 PFASs have been identified
76 in AFFF and AFFF-impacted groundwater.²⁰ Meanwhile, a series of unknown
77 fluorinated sulfonic acids (e.g., Cl-PFOS and ketone-PFOS), have been identified in
78 the serum of AFFF-exposed firefighters,¹⁷ suggesting both persistence of these PFASs
79 in the environment and their potential toxicity to humans. For the general population,
80 exposure pathways are associated more commonly with the ingestion of food²⁷ and
81 drinking water,²⁸ and with the inhalation of household and ambient airborne
82 particles.^{29,30} Furthermore, several emerging PFASs (e.g., polyfluoroether sulfonates)

83 have been detected in airborne particulate matter (APM).³¹ However, similar
84 exploratory efforts toward PFAS screening have not considered these exposure
85 sources.

86 Recently, China has been suffering from frequent and severe fog/haze events.³² Given
87 that fine particulate matter (PM_{2.5}) exposure is a primary factor leading to adverse
88 health effects,^{33,34} it is evident that the Chinese population is confronted with a
89 substantial health risk. The size distribution characteristics of APM play an important
90 role in its adverse effects on health. Generally, the size distribution characteristics are
91 both source and health-impact related.³⁵ On the one hand, the size distribution of
92 organic chemicals varies depending on substances.³⁶⁻³⁸ On the other hand, the size of
93 APM affects the region in which APM is deposited in the respiratory system.
94 According to the International Commission on Radiological Protection model, smaller
95 APM could penetrate into deeper regions of the respiratory system.³⁹ Previous studies
96 on organophosphate flame retardants have found that ignoring particle-size
97 characteristics in exposure assessment could overestimate the exposure level.⁴⁰
98 Furthermore, PFASs are distributed differently in indoor and outdoor
99 environments.⁴¹⁻⁴³ Therefore, it is necessary to assess the risk posed by PFASs based
100 on the particle-size distribution of PFASs and different exposure scenarios.

101 In this study, we established a complete procedure from PFAS screening to
102 quantitative analysis to comprehensively investigate the distributions of PFASs in
103 APM collected from five cities in China. For the exact mass of peaks, PFAS
104 homologues were recognized based on a mass defect unit of CF₂. For suspect

105 screening, PFASs were screened based on the list from the US EPA CompTox
106 Chemistry Dashboard (https://comptox.epa.gov/dashboard/chemical_lists/sfishfluoro).
107 Through target analysis, legacy PFASs were quantified in both indoor and outdoor
108 APM to explore their particle-size characteristics. Furthermore, the regional
109 deposition of PFOA (the major legacy PFAS in APM) in the human respiratory tract
110 was modeled to assess its health risks via inhalation in different urban regions of
111 China.

112 **MATERIALS AND METHODS**

113 **Chemicals**

114 Details regarding the authentic and internal standards used in this study are provided
115 in the Supporting Information (SI) **Section 1**. Additional PFCA or PFSA homologues
116 were checked for all standards, and the errors of quantitation were controlled at 0.6%
117 (Table S2). All solvents and reagents used were of high-performance liquid
118 chromatography (HPLC) grade.

119 **Sample Collection**

120 During 2014–2015, we collected indoor and outdoor APM samples from five selected
121 cities in China: Beijing (BJ), Ji'nan (JN), Nanjing (NJ), Changshu (CS), and Guiyang
122 (GY), with two sampling sites per city (details regarding the sampling campaign are
123 provided in **Table S4**). Indoor APM samples were collected on quartz fiber filters
124 (prebaked at 550 °C for 8 h) using an Eight-Stage Non-Viable Andersen Cascade
125 Impactor (Tisch Environmental., Cleves, OH, U.S.A.) for nine separated size fractions
126 (i.e., >9.0, 5.8–9.0, 4.7–5.8, 3.3–4.7, 2.1–3.3, 1.1–2.1, 0.7–1.1, 0.4–0.7, and <0.4 μm).

127 The sampling program was conducted for nearly 48 h at a flow rate of 28.3 L min⁻¹ in
128 the living room of residences. Outdoor APM samples were collected on glass fiber
129 filters using a cascade impactor (KC-120H, Laoshan Applied Technology Research
130 Institute, Shandong, China) for two size fractions (i.e., >2.5 and <2.5 μm). The
131 sampling program lasted for nearly 48 h at a flow rate of 100 L min⁻¹.

132 The filtered sample of each size fraction was folded, wrapped in aluminum foil, and
133 placed in a sealed bag. Samples were extracted immediately after returning to the
134 laboratory, and the extracts were stored at 4 °C until analysis.

135 **Sample Preparation**

136 For sample preparation, a procedure established previously with some modifications
137 was followed (details in **SI Section 2**).³⁰ Briefly, each filtered sample was immersed
138 fully in methanol in a polypropylene centrifuge tube and subjected to four rounds of
139 extraction in a 40 °C ultrasonic bath. Supernatants of each sample were combined in a
140 separate polypropylene centrifuge tube and reduced to a volume of 1 mL by
141 evaporation under a gentle stream of nitrogen. Then, the concentrated extracts were
142 cleaned further using a Supelclean™ ENVI-carb cartridge (Supelco, Bellfonte, USA).
143 The final concentrated extract was passed through a polypropylene-membrane syringe
144 filter (Acrodisc® GHP, 13 mm, 0.2 μm, Waters, USA).

145 Unused fiber filters from the sampling trip and prebaked fiber filters were extracted
146 using the same sample preparation procedure, and these extracts were used as trip
147 blanks and procedural blanks. In procedural recovery experiments, 1 ng of each native
148 analyte was spiked to the prebaked fiber filters prior to extraction. To avoid sample

149 contamination, all equipment was precleaned with methanol. Furthermore, one
150 procedural blank was included with the samples for every batch.

151 **Target HPLC-QqQ Analysis**

152 According to the standard availability in our laboratory, 6:2 diPAP, PFCAs, and
153 PFASs were determined using HPLC (Infinity 1260, Agilent Technologies,
154 Waldbronn, Germany) coupled with tandem mass spectrometry with an electrospray
155 ionization source (API-4000, AB SCIEX, USA). The mass spectrometer was operated
156 in the negative ion mode with multiple reaction monitoring. Compared with
157 HPLC-QTOF, HPLC-QqQ has a higher sensitivity and could detect PFASs with
158 lower levels. Details regarding HPLC-QqQ analysis parameters are provided in **SI**
159 **Section 3**.

160 Quantification of all target analytes was performed using an internal standard
161 calibration curve with calibration standards (Details are provided in **Table S3**). The
162 limit of quantification (LOQ) was defined as the lowest point on the calibration curve
163 that could be measured accurately within $\pm 20\%$ of its theoretical value or ten times
164 the standard deviation of the procedural blanks ($n = 6$). All target analytes in the
165 procedural blank were either not detected or were below half of their corresponding
166 LOQs. The LOQs for each analyte were 0.17–0.45 and 0.61–1.6 pg m^{-3} for the
167 outdoor and indoor samples, respectively. The procedural recovery of target PFASs
168 ranged from 74.9% to 103%; the recoveries and blank values are shown in **Table S3**.
169 There was no difference between the level of PFAS in the trip and procedural blanks,
170 suggesting that no contamination occurred during travel and storage. For samples with

171 signal-to-noise ratio of one PFAS below 3, the analyte was defined as not detected
172 and a value of zero was accepted. For samples with concentrations of one PFAS
173 below the LOQ, a value of half the LOQ was accepted. The total concentration of one
174 PFAS in APM was calculated as the sum of the concentrations of the PFAS in each
175 fraction (indoor air samples, number of fraction = 9; outdoor air samples, number of
176 fraction = 2).

177 **HPLC-QTOF-MS Analysis**

178 HPLC-QTOF-MS analysis was performed using an HPLC system (Infinity 1260,
179 Agilent Technologies, Waldbronn, Germany) coupled with a high-resolution QTOF
180 mass spectrometer (Triple TOF 5600, AB SCIEX, Foster City, CA, USA) with an
181 electrospray ionization source operating in the negative ion mode. The MS/MS
182 acquisition was performed using IDA, which was composed of a TOF MS scan and
183 20 dependent product ion scans in high-resolution mode ($R = 30000$). Dynamic
184 background subtraction was applied to the IDA criteria for dynamic exclusion. The
185 fragment ions were generated from collision-induced dissociation with nitrogen.
186 Details regarding HPLC-QTOF-MS analysis parameters are provided in **SI Section 4**.
187 To subtract background contamination, a default sample/blank peak intensity ($= 3$)
188 was set for all chemical features. To guarantee a mass error <5 ppm, the instrument
189 was automatically calibrated every 5 sample injections using a calibration solution
190 delivered via a calibration delivery system (AB Sciex). Additionally, several internal
191 standards were added to each sample and the mass error was 1.5 ppm (0.1–4.8 ppm).
192 The sensitivity of the non-target analysis process was tested using several known

193 PFAS standard solutions, which proved that several PFASs were detected at the level
194 of $0.1 \mu\text{g L}^{-1}$ and all the PFAS standards were detected at the level of $5 \mu\text{g L}^{-1}$ (**Table**
195 **S5**). Furthermore, the sensitivity of QTOF and its mass accuracy were noted to
196 decrease at low concentrations.

197 **PFAS Screening and Identification**

198 *PFAS Peak Picking and Homologue Classification.* During the process of peak
199 picking, the peak list was extracted from the QTOF-MS raw data by the “Enhance
200 peak find” function in PeakView[®] 1.2 (AB SCIEX, USA). The difference in structure
201 for PFAS homologues is the CF_2 unit, and CF_2CF_2 is the substructure unit for
202 fluorotelomer-based PFASs. Thus, the PFAS homologues were identified by mass
203 differences of 49.99681 Da ($-\text{[CF}_2\text{]-}$) and 99.99362 Da ($-\text{[CF}_2\text{CF}_2\text{]-}$) among the exact
204 mass of peaks. Then, the exact mass of extracted peaks was transformed to the CF_2
205 normalized mass defects according to a previously described method.¹⁹ The extracted
206 peaks with mass defects for PFASs (>0.85 or <0.15) were retained. For each series, an
207 ascending trend of m/z vs. retention time (RT) should be observed.¹¹ To exclude
208 dimers, adducts, and isotopes in the identified PFAS homologues, the exact mass of
209 peaks with the same RT ($\Delta\text{RT} < 0.1 \text{ min}$) were checked. Homologues series (over 3
210 congeners) meeting all those rules were further carried out for molecular formulae
211 calculation and structure speculation. Details are shown in **SI Section 5**.

212 *PFAS Identification.* Molecular formulae were calculated using a calculator in
213 PeakView[®] 1.2 based on accurate mass, isotope distributions, and fragments in the
214 MS/MS spectrum (exact mass error $< 5 \text{ ppm}$, isotope ratio difference $< 20\%$, and

215 fragments mass error < 5 mDa). Details are provided in **SI Section 5**. The structures
216 were identified using the MS/MS spectrum from literature and mass spectral database
217 (commercial database from AB Sciex and MassBank⁴⁴ (www.massbank.eu)). The in
218 silico fragmenters MetFrag⁴⁵ and CFM-ID⁴⁶ were used to diagnose the potential
219 structure of PFASs. Suspect screening was also conducted with the list of PFASs on
220 the global market, which can be obtained from the NORMAN Suspect List Exchange
221 (SFISHFLUORO, <https://www.norman-network.com/?q=node/236>) and the US EPA
222 CompTox Chemistry Dashboard (PFAS List from KEMI,
223 https://comptox.epa.gov/dashboard/chemical_lists/sfishfluoro). PFASs were screened
224 by formula in the suspect lists. The confidence level for each molecule and its
225 proposed structure was assigned based on established criteria.⁴⁷

226 *Data analysis.* Pearson correlation and cluster analysis were performed with the R
227 program (version 3.3.3). The identified PFASs with detection frequencies >50% were
228 used and the undetected PFASs were assigned half of the intensity condition for
229 PFAS screening (peak intensity = 100).

230 **Health Risk Assessment**

231 The particle size distributions of PFASs were used to calculate the fractions of PFOA
232 that could be inhaled and deposited in several regions of the respiratory system.
233 According to the International Commission on Radiological Protection model,³⁹ we
234 estimated the deposition fluxes using the concentrations of PFOA in each size fraction.
235 A 24-h time-activity inhalation model based on activity levels of people of different
236 ages was considered for risk assessment.⁴⁸ Based on the descriptions of the five

237 activity levels, we classified the levels into two groups: indoor activity levels and
238 outdoor activity levels. Two scenarios of environmental exposure were assumed: a
239 mean exposure scenario and a high exposure scenario. Calculations for the mean and
240 high scenarios were performed using the mean and maximum concentrations in each
241 city, respectively.

242 The non-cancer risk from inhalation exposure was evaluated based on the hazard
243 quotient (HQ):⁴⁹

$$244 \text{HQ} = \sum_i^n (D_{\text{PFOA},i} \times \text{IR}_i / (\text{BW} \times \text{RfD})),$$

245 where D_{PFOA} (pg m^{-3}) is the concentration of PFOA deposited in three respiratory
246 regions; IR ($\text{m}^3 \text{day}^{-1}$) is the daily inhalation volume for five age groups of people;
247 BW (kg) is the body weight based on the “Exposure Factors Handbook: Chapter 8 -
248 Body Weight Studies” published by the U.S. EPA;⁵⁰ RfD is the reference dose for
249 PFOA ($= 77 \text{ ng kg}^{-1} \text{day}^{-1}$, as suggested by the Minnesota Department of Health
250 (USA);⁵¹ and n is the number of defined activity levels. Detailed parameters are
251 provided in **Table S6**.

252 **RESULTS AND DISCUSSION**

253 **PFAS Screening and Identification**

254 The process of PFAS screening is illustrated in Figure 1. Through PFAS homologue
255 screening 121 peaks were selected, while another 4 peaks were selected by suspect
256 screening. Based on established criteria⁴⁷, levels were assigned to 125 peaks; 20 peaks
257 were identified as level 1 by standards, 19 peaks were identified as level 2 by the
258 MS/MS spectrum, 11 peaks were identified as level 3 with uncertain substituent

259 positions by the MS/MS spectrum, 18 peaks were identified as level 4 with molecular
260 formulae, and 57 peaks were identified as level 5 only with m/z and RT. Details are
261 provided in Figure 2, Figure S2-3, and Table S7-8.

262 *PFCAs*. Thirteen peaks corresponding to m/z between 362.9690 and 912.9296 were
263 identified as PFCAs. The mass error of the exact mass ranged from 0.7 ppm to 4.2
264 ppm. Neutral loss of CO₂ (43.9882, mass error 1.6 mDa) and a perfluorocarbon chain
265 fragment ($[C_nF_{2n+1}]^-$ mass error < 5mDa) were found in the MS/MS spectrum of this
266 series, which is consistent with the reported mechanism on the fragments of PFCAs.⁵²
267 Eleven of these peaks were successfully confirmed as level 1 by standards ($\Delta RT =$
268 0–0.1 min). Perfluoropentadecanoic acid (PFPeDA) and perfluoroheptadecanoic acid
269 were identified as level 2b based on their exact mass and MS/MS spectrum (mass
270 error = 0.9–1.4 ppm and fragment mass errors = 0.38–7.3 mDa for PFPeDA). The
271 identification of PFCAs is summarized in **Figure S2, S4, and S5**. The identification
272 of C15–C18 PFCAs was indeed unexpected because analysis of homologues >C14 in
273 APM has generally not been performed or has failed to detect them.^{42,53} However,
274 Plassmann and Berger found PFCAs (C6–C22) present in snow collected in a ski
275 area.⁵⁴ In our result, C15–C18 PFCAs were detected in APM from all cities, except
276 for GY, and their existence in APM might be due to the presence of local fluorine
277 chemical plants and/or long-range transport from a manufacturing plant.

278 *PFSAs*. The identification of PFSAs is shown in **Figure S2 and S6**. Fragments with
279 m/z 98.9557 (FSO₃⁻, mass error = 1.0 mDa), m/z 79.9571 (SO₃⁻, mass error = 0.26
280 mDa), and m/z 168.9885 ($[C_3F_7]^-$, mass error = 0.9 mDa) have been reported as

281 product ions of PFASs in quantitative analysis.^{13,30,55} According to the accurate mass
282 and fragment information, PFOS (mass error = 2.7 ppm), perfluorohexane sulfonate
283 PFHxS (mass error = 2.6 ppm), and perfluorobutane sulfonate (PFBS, mass error =
284 2.9 ppm) were identified. Then, PFOS, PFHxS, and PFBS were confirmed as level 1
285 by standards ($\Delta RT = 0.03\text{--}0.05$ min).

286 *Polyfluoroalkyl ether carboxylic acids (PFECAs)*. Six fluorinated homologues of this
287 series were selected with the CF_2 unit, as shown in **Figure S2 and S7**. Neutral loss of
288 CO_2 (43.9938, mass error = 4.0 mDa) and fragments $[\text{C}_n\text{F}_{2n+1}\text{O}]^-$ ($n = 1\text{--}4, 10, 11, 14$
289 and fragment mass error = 0.1–5.4 mDa for $\text{C}_{15}\text{F}_{29}\text{O}_3\text{H}$) were observed in the MS/MS
290 spectrum, which were also noted in previous reports on PFECAs^{11,56}. We noticed that
291 the fragment CF_3O^- (fragment mass error = 0.1–2.5 mDa) was the smallest ion of the
292 $[\text{C}_n\text{F}_{2n+1}\text{O}]^-$ fragments in the MS/MS spectrum. Thus, we suspected that CF_3O was a
293 terminal group of this compound based on the mechanism of fragmentation of
294 PFECAs¹¹. Therefore, the final structural formulae were identified as
295 $\text{CF}_3\text{O}(\text{CF}_2)_n\text{COO}^-$ ($n = 10\text{--}15$) (1:n PFECAs) with level 2b. Recently, PFECAs have
296 been discovered in rivers¹¹ and drinking water⁵⁶, and most studies have detected
297 PFECAs with less than eight perfluorinated carbon atoms. To the best of our
298 knowledge, in this study, PFECAs with more than eight perfluorinated carbon atoms
299 in APM were detected for the first time. An extensive search for the proposed
300 molecular formulae in online chemical databases (e.g., ChemSpider, PubChem,
301 MassBank, and CompTox Chemistry Dashboard) returned no matches, and although
302 we did not find product information about our reported PFECAs, we knew that GenX

303 (from DuPont $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COO}^-\text{NH}_4^+$, CAS No. 62037-80-3) and ADONA
304 from 3M/Dyneon ($\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCHF}_2\text{COO}^-\text{NH}_4^+$, CAS No. 958445-44-8)
305 were used as PFOA alternatives in the fluoropolymer manufacturing industry⁵⁷.,
306 Additionally, the RT of 1:n PFECAs was slightly larger than that of PFCAs with the
307 same carbon atom number. Considering their similarities in terms of RT and structure,
308 1:n PFECAs might be used as alternatives to PFCAs, and the intensity ratios of 1:n
309 PFECAs vs. PFCAs with the same carbon atom number ranged from 21% to 77%,
310 indicating a close contribution.

311 *Fluorinated telomer acids (n:2 FTAs) and fluorinated telomer sulfonates (n:2 FTSs).*

312 Three n:2 FTAs and three n:2 FTSs were identified in our PFAS homologue analysis
313 (mass error = 2.2–4.8 ppm). For n:2 FTAs, a neutral loss of 84 Da was noted in the
314 MS/MS spectrum, which is equal to $\text{CO}_2(\text{HF})_2$ (mass error = 0.53 mDa). This neutral
315 loss reaction has been used for the quantitative analysis of n:2 FTAs.⁵⁸ Furthermore,
316 8:2 FTA were identified as level 2a by the MS/MS spectrum (match score 85.2) in the
317 database from AB Sciex (Figure S8). For n:2 FTSs, a neutral loss of HF (mass error =
318 0.3–1.8 mDa) and fragments with m/z 80.9651 (HSO_3^- , mass error = 0.1 mDa) and
319 m/z 79.9581 (SO_3^- , mass error = 0.7 mDa) were observed in the MS/MS spectrum
320 (Figure S9). We further confirmed 6:2 FTS and 8:2 FTS as level 1 by standards (ΔRT
321 = 0.03–0.04 min) and identified three n:2 FTAs and 10:2 FTSs as level 2b based on
322 their exact mass (mass error = 0.4–4.8 ppm) and MS/MS spectrum. It is believed that
323 n:2 FTAs and n:2 FTSs are principal degradation products of fluorotelomer
324 surfactants^{59,60} and applied as alternatives to PFOS in metal plating.⁶¹

325 *Perfluoroalkyl dioic acids (PFdiOAs)*. A neutral loss of 108 Da was noted for this
326 homologue series in the MS/MS spectrum, which is equal to $(\text{CO}_2)_2\text{HF}$ (mass error =
327 1.3 mDa). Additionally, fragments $[\text{C}_n\text{F}_{2n+1}]^-$ and $[\text{C}_n\text{F}_{2n-1}]^-$ (mass error = 0.2–4.3
328 mDa) were detected in the spectrum (Figure S10A). These fragment ions and neutral
329 loss reaction were also observed in the MS/MS spectrum of the PFdiOA standard
330 (Figure S10B). Perfluorodecanedioic acid and perfluorododecanedioic acid were
331 confirmed as level 1 by standards ($\Delta\text{RT} = 0.02\text{--}0.04$ min, mass error 1.2–3.1 ppm).
332 The other five PFdiOAs were identified as level 2b based on the exact mass (mass
333 error = 0.4–2.3 ppm) and MS/MS spectrum.

334 *Hydro-substituted perfluoroalkyl dioic acids (H-PFdiOAs)*. A neutral loss of 128 Da
335 was noted in the MS/MS spectrum of this homologue series, which is equal to
336 $(\text{CO}_2)_2(\text{HF})_2$ (mass error = 0.1 mDa). Compared with PFdiOAs, $[\text{C}_n\text{F}_{2n-3}]^-$ fragments
337 were detected in the MS/MS spectrum (mass error = 0.9–4.1 mDa) due to the loss of
338 one more HF molecule (Figure S11). Three H-PFdiOAs were identified based on the
339 exact mass (mass error = 0.8–2.0 ppm) and MS/MS spectrum. Because of the
340 uncertainty regarding the substituted position of the hydrogen atom, three H-PFdiOAs
341 were identified as level 3.

342 *Unsaturated perfluorinated alcohols (UPFAs)*. A neutral loss of 66 Da was noted in
343 the MS/MS spectrum of this homologue series, which is equal to COF_2 (mass error =
344 0.5 mDa). $[\text{C}_n\text{F}_{2n-1}]^-$ fragments (mass error = 0.8–3.6 mDa) were detected in the
345 MS/MS spectrum, which implied that one double bond was contained in the carbon
346 chain (Figure S12). Although the double bond was not located between ω and $\omega - 1$

347 carbon atoms based on $[C_nF_{2n+1}]^-$ fragments ($n \geq 2$, mass error = 0.6–3.6 mDa) in the
348 MS/MS spectrum, the position of the double bond was still uncertain. Thus, eight
349 UPFAs were identified as level 3 (mass error = 0.4–4.4 ppm).

350 *Suspect Screening.* Based on molecular formulae, another four PFASs, including 6:2
351 diPAP (CAS No. 57677-95-9), 6:2 chlorinated polyfluoroalkyl ether sulfonic acids
352 (6:2 Cl-PFESA, CAS No. 756426-58-1), 8:2 Cl-PFESA, and p-perfluorous
353 nonenoxybenzenesulfonate (OBS, CAS No. 271794-15-1), were selected from the
354 suspect list (mass error = 3.4–4.7 ppm). They were further identified based on the
355 MS/MS spectrum.

356 The MS/MS spectrum of 6:2 diPAP is summarized in **Figure S13**. Fragments with m/z
357 442.9700 ($C_8H_5O_4F_{13}P^-$, -2.3 mDa) and m/z 96.9706 ($H_2PO_4^-$, 1.0 mDa) were
358 detected in the MS/MS spectrum. These were consistent with previously reported
359 fragments of 6:2 diPAP in nominal mass data⁶². Finally, we confirmed 6:2 diPAP as
360 level 1 by standards ($\Delta RT = 0.01$ min, mass error = 3.4 ppm, fragment ion mass error
361 0.6–6.7 mDa).

362 The MS/MS spectrum of 6:2 Cl-PFESA is illustrated in **Figure S14**. Fragments with
363 m/z 98.9554 (FSO_3^- , mass error = -0.37 mDa) and m/z 34.9731 (Cl^- , mass error = 3.7
364 mDa) were observed in the MS/MS spectrum, suggesting that this compound may
365 have a sulfonic group and contain chlorine. Finally, 6:2 Cl-PFESA was confirmed as
366 level 1 by standards ($\Delta RT = 0.04$ min, mass error = 4.4 ppm, fragment ion mass error
367 0.2–3.7 mDa). This compound, which is a principal component of F-53B, has been
368 used in the Chinese chrome-plating industry for about 30 years⁶³ and has been

369 detected in wastewater,⁶⁴ fish,⁶⁵ human serum,⁶⁶ and even human placenta.⁶⁷ The
370 MS/MS spectrum of 8:2 Cl-PFESA is also illustrated in **Figure S14**. Fragments with
371 m/z 82.9655 (FSO_2^- , mass error = 4.7 mDa) and m/z 450.9402 ($\text{C}_8\text{F}_{16}\text{ClO}^-$, mass error
372 = 1.4 mDa) were observed in the MS/MS spectrum. The fragmentation was similar to
373 the 6:2 Cl-PFESA standard. Thus, 8:2 Cl-PFESA was identified as level 2b in the
374 APM samples (mass error = 4.1 ppm).

375 The MS/MS spectrum of OBS is illustrated in **Figure S15**. In the MS/MS spectrum,
376 fragments with m/z 171.9821 ($[\text{C}_6\text{H}_4\text{SO}_4]^-$, mass error = -1.5 mDa) and m/z 464.9676
377 ($[\text{C}_{13}\text{H}_4\text{F}_{11}\text{SO}_4]^-$, mass error = 1.6 mDa) were observed; this was consistent with the
378 reported MS/MS spectrum in literature.⁶⁸ Thus, OBS was identified as level 2a (mass
379 error = -4.7ppm). This compound has been used as a surfactant in oil production and
380 has been detected in the surface water around an oilfield in China.⁶⁸

381 Overall, through PFAS homologue analysis and suspect screening, 50 peaks including
382 16 peaks for legacy PFASs and 34 for emerging PFASs were identified as level 3 or
383 above. Furthermore, this study was the first to find and identify 1:n PFECAs, PFdiOA,
384 H-PFdiOA, and UPFAs in APM; however, PFECAs with less than 8 perfluorinated
385 carbon atoms have been identified previously in natural waters¹¹ and drinking water⁵⁶.
386 Identification of alternative PFASs in APM implies expansion of their use, which has
387 raised concern regarding APM pollution.

388 After standardizing by sampling volume, the total peak area of possible PFASs in
389 indoor APM was noted to be 1.9 times (range: 1.3–2.9) higher than that in outdoor
390 APM. Based on their Pearson's correlation coefficients, the hierarchical clustering of

391 APM samples showed that the patterns of PFASs in indoor APM were similar;
392 however, these patterns were distinct from those in outdoor APM (**Figure S16**). The
393 patterns of PFASs in outdoor APM were found to vary markedly. The sources of
394 PFASs in the indoor environment were generally common, such as carpets, outdoor
395 equipment, and paper products.^{69,70} Although the indoor environment was a primary
396 source of PFASs in the outdoor environment, outdoor specific sources like
397 fluorination plants were also important contributing factors to contamination by
398 PFASs. Actually, a large number of PFASs with low detection frequencies were noted
399 in CS, JN, and NJ, all of which are industrial cities (**Figure 2 and SI Tables S8**).

400 **Target Analysis of PFASs**

401 For the thirteen PFASs (level 1) identified by non-target analysis, as well as
402 perfluoropentanoic acid, a target analysis strategy was applied to investigate their
403 distributions in APM in China.

404 *PFAS Distributions in Outdoor APM.* Thirteen legacy PFASs, including C4, C6, and
405 C8 PFASs; C5–14 PFCAs; and 6:2 diPAP were quantified in the outdoor APM
406 samples; the total concentrations of legacy PFASs (PFASs and PFCAs) ranged from
407 4.87 to 4509 pg m⁻³ with a mean value of 351 pg m⁻³ (**Table S9**). The predominant
408 compound in outdoor APM was PFOA, which contributed 48.1% (19.4%–94.9%),
409 followed by PFHxA and PFOS, which contributed 9.23% (0.58%–27.4%) and 6.09%
410 (0.08%–17.6%) on average, respectively (**Figure 3**).

411 Concentrations of PFASs found in this study were similar to results obtained in two
412 cities in the UK (299 and 325 pg m⁻³) but much higher than those noted for Norway

413 and Ireland.⁷¹ Mahiba et al. reported that ionic PFASs in outdoor APM in Vancouver
414 were below their detection limits (0.02-0.03 pg m⁻³), except for PFOA and PFHpA
415 with mean concentrations of 2.5 and 1.7 pg m⁻³, respectively.²⁹ Dreyer et al. reported
416 a mean PFAS concentration of 2.8 pg m⁻³ in outdoor APM in Germany and the
417 predominant compounds were PFOA and PFOS.⁷² However, PFOA was always found
418 to be the predominant compound in outdoor APM.

419 In addition to legacy PFASs, PAPs, which are used widely in food packaging
420 material⁸ and are a class of PFCA precursors,⁷³ were detected and quantified in
421 outdoor APM in our study. Here, 6:2 diPAP was detected only in outdoor APM with a
422 mean concentration of 1.97 pg m⁻³; however, this accounted for nearly 0%–8.08% of
423 the quantified legacy PFASs. Compared with the results of dust samples from
424 different countries,⁷⁴ this ratio is relatively low, which could indicate comparatively
425 lower use of diPAPs in China. However, because different media were analyzed, it is
426 difficult to draw a robust conclusion in this regard.

427 *PFAS Distributions in Indoor APM.* Ten indoor APM samples with nine fractions for
428 each sample were analyzed. Most PFCAs were detected in all the indoor APM
429 samples, except for PFPeA, which was detected only in three rooms. PFSAs were
430 present but with low detection frequencies, and the sum of the concentrations of the
431 analyzed PFASs ranged from 3.87 to 375 pg m⁻³. PFOA and PFHxA were the
432 predominant components and accounted for 41.2% (1.0%–71.6%) and 28.8%
433 (14.4%–53.3%), respectively (**Figure S17a**). The profile obtained is consistent with a
434 report based on PFASs in North America but different from that based on PFSAs in

435 Tromsø (Norway).^{29,42}

436 *PFAS Particle-Size Distributions.* Based on the abovementioned results, we
437 considered the particle-size distributions of the principal components (PFHxA and
438 PFOA), as well as the Σ legacy PFASs (**Figure S17b**). The convex line shows that
439 PFHxA, PFOA, and Σ legacy PFASs were easily absorbed in finer particles. Their
440 mass fractions in PM_{2.5} were also mostly >50%. However, the fluctuations in the
441 curves imply that the features of each specific indoor environment were important in
442 influencing the distribution of PFASs in indoor APM.

443 For outdoor APM, the ratio of PFOA in a coarse particle fraction (>2.5 μ m) vs. a fine
444 particle fraction (<2.5 μ m) was 1.5 ± 0.48 , which suggests preferential attraction of
445 PFOA to coarser particles. Previous studies investigating particle-size distributions of
446 PFASs have reported different features in outdoor APM. The particle-size distribution
447 of PFOA in Japan showed that PFOA in airborne dust was absorbed more easily in
448 the respirable fraction (1.1–11.4 μ m) than the smaller fraction (<1.1 μ m).⁷⁵ Dreyer et
449 al. observed that PFOA existed predominantly in the smallest fraction (<0.14).⁷²
450 However, differences in terms of both sampling methods and location could account
451 for the observed inconsistencies in the particle-size distributions. Therefore, defining
452 uniform sampling methods could facilitate easier comparison of results obtained by
453 different studies.

454 *Risk Assessment.* Because PFOA was still the predominant component in indoor and
455 outdoor APM, we assessed the health risk related to the inhalation of PFOA in APM.

456 It is known that the deposition efficiency of PM in the respiratory tract might vary

457 with PM size.³⁹ Moreover, the inhalation rate is related to activity level and age group.
458 Therefore, a 24-h time-activity model was used to calculate the HQ values of PFOA
459 via inhalation exposure, as shown in **Figure S18**. The HQ values for PFOA in the
460 different studied cities were generally <0.1, which suggests that PFOA exposure via
461 inhalation in some areas of China is at least one order of magnitude lower than its
462 RfD value. Thus, human exposure to PFOA via inhaled APM might not be a critical
463 issue in China.

464 Previous studies have found that air and dust are potentially important pathways to
465 PFAS exposure.²⁹ Ericson et al. calculated the mean and maximum PFOA exposure
466 from house dust to be 0.48 (0.65) and 1.05 (2.15) ng day⁻³, respectively, in average
467 case scenarios for toddlers (adults).³⁰ Based on a study in China, Zhang et al.
468 estimated the daily intake of PFOA via dust ingestion to be 12.15 and 9.02 ng day⁻¹
469 for toddlers and adults, respectively. Our study estimated the mean (maximum) value
470 of the daily intake of PFOAs via inhaled APM to be 0.47 (1.63) and 0.63 (1.80) ng
471 day⁻¹ for toddlers and adults, respectively. In a worst-case scenario, inhalation
472 exposure for toddlers and adults could be as high as 6.2 and 6.0 ng day⁻¹, respectively.
473 Therefore, compared with dust ingestion, inhalation of APM might be non-negligible.

474 **IMPLICATIONS AND LIMITATIONS**

475 We performed PFAS homologue analysis and suspect screening to identify PFASs in
476 APM in China. Several clarifications were obtained after PFAS screening. First,
477 although the ENVI-carb cartridge has been shown to be effective for analyzing legacy
478 PFASs, it is possible that several unknown PFASs were removed during sample

479 preparation. Most studies on the non-target screening of PFASs are concerned with
480 the PFAS source (e.g., AFFF²⁰⁻²³ and wastewater²⁴) and contaminated samples (water
481 affected by AFFF or wastewater^{20,25}). However, general environmental samples
482 contain more interfering substances and a lower level of PFASs. Therefore, there is a
483 balance between specificity and coverage in the non-target screening of PFASs.
484 Second, all identified PFASs were detected in the negative ionization mode. In
485 positive mode measurements, only 15 peaks (level 5 in SI Table S10) were selected.
486 However, the low intensity and the absence of the MS/MS spectrum prevented the
487 identification of PFAS structures. Most of the positively charged and zwitterionic
488 PFASs have been discovered in AFFF, commercial surfactants, and groundwater
489 affected by AFFF²⁰⁻²³. Although there is no information on the environmental
490 behavior of these PFASs, it is possible for them to transform to degradation products
491 in the environment. We did not find positively charged and zwitterionic PFASs in our
492 study. Another reason for not finding these PFASs could be the clean-up conducted
493 during the extraction of PFASs. Finally, there were still many peaks without
494 structures with levels 4 and 5 in our study. The reason for this is that most peaks had a
495 low intensity and/or were without an MS/MS spectrum. Thus, there was insufficient
496 evidence for the identification of structures.

497 However, we successfully identified well-known PFASs such as PFOS and PFOA, as
498 well as emerging unknown PFASs (1:n PFECAs, PFdiOAs, H-PFdiOAs, and UPFAs).
499 For the emerging unknown PFASs, it is necessary to conduct further tests regarding
500 their toxicity and environmental behavior. Meanwhile, the question of how to

501 improve the identification capability of non-target analysis must be considered. Our
502 target analysis and health risk assessment suggest that the distributions of PFASs in
503 APM in China might be locally/regionally specific because of the atmosphere and the
504 geographical locations of the fluorine chemical industry in the country.

505 **Supporting Information**

506 Standards and reagents, sample preparation, PFASs screening and identification, the
507 MS/MS spectrum of PFASs, the structure and detection of PFASs, Table S1-S10, and
508 Figure S1-S18. (PDF)

509 The identified PFASs with level 4 or above. (XLS)

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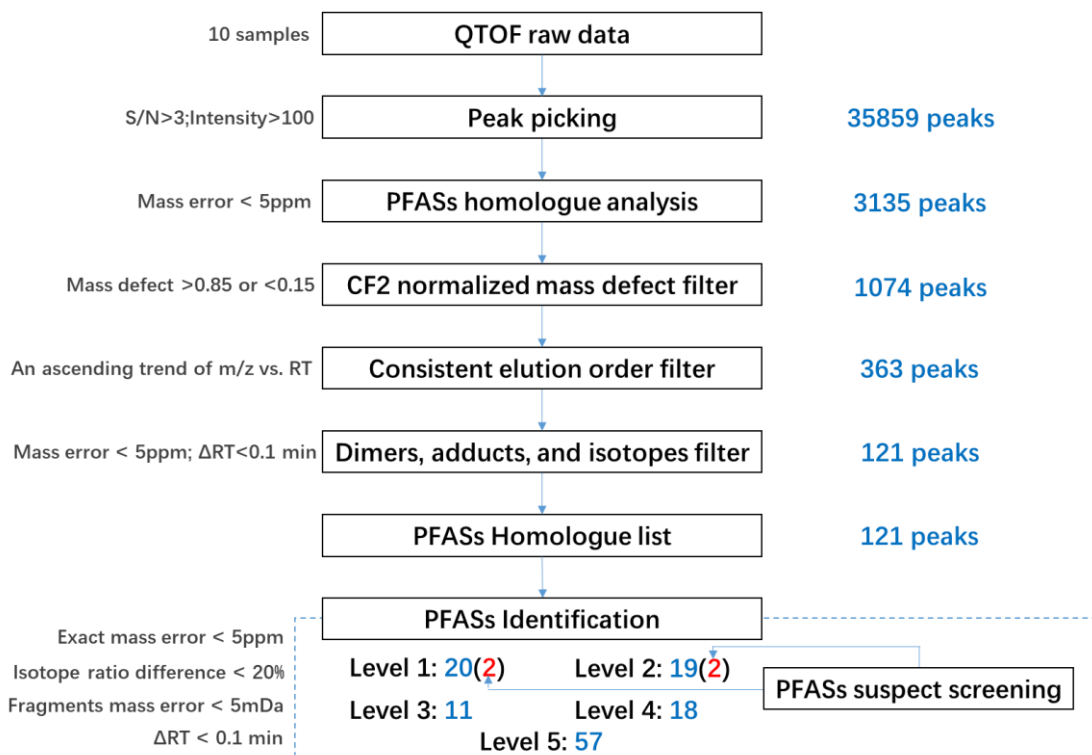
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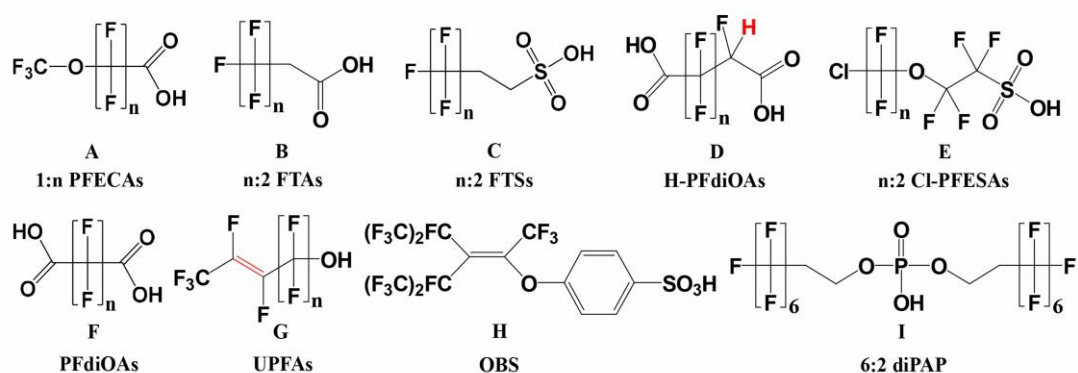
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768 Figure 1. Workflow for PFAS screening with PFAS homologue analysis and suspect

769 screening

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Homologue	Formula	Level	Proposed Structure	Detection in APM		Homologue	Formula	Level	Proposed Structure	Detection in APM		
				Indoor	Outdoor					Indoor	Outdoor	
1:n PFECAs	C10F19O3H	2	A(8)		CS	PFdiOAs	C9F14O4H2	2	F(7)	GY;NJ	BJ;CS	
	C11F21O3H	2	A(9)		CS		C10F16O4H2	1	F(8)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ		
	C12F23O3H	2	A(10)		CS		C11F18O4H2	2	F(9)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ		
	C13F25O3H	2	A(11)		CS		C12F20O4H2	1	F(10)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ		
	C14F27O3H	2	A(12)		CS		C13F22O4H2	2	F(11)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ		
	C15F29O3H	2	A(13)		CS	C14F24O4H2	2	F(12)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ			
n:2 FTAs	C10F17O2H3	2	B(8)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ		UPFAs	C15F26O4H2	2	F(13)	BJ;GY;NJ	BJ;CS;GY;JN;NJ	
	C11F19O2H3	2	B(9)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ			C7F13OH	3	G(4)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ		
	C12F21O2H3	2	B(10)	CS;GY; BJ;CS;GY;JN			C8F15OH	3	G(5)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ		
n:2 FTSs	C8F13SO3H5	1	C(6)	BJ;CS;GY;JN;NJ	CS;GY;JN;NJ		C11F21OH	3	G(8)		CS	
	C10F17SO3H5	1	C(8)		NJ		C12F23OH	3	G(9)		CS	
	C12F21SO3H5	2	C(10)		JN		C13F25OH	3	G(10)	CS	CS;GY;	
H-PFdiOAs	C12H3F19O4	3	D(9)	BJ;CS;GY;JN;NJ	BJ;CS;GY;JN		C14F27OH	3	G(11)		CS	
	C13H3F21O4	3	D(10)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ			C15F29OH	3	G(12)		CS	
	C14H3F23O4	3	D(11)	BJ;CS;GY;JN;NJB;CS;GY;JN;NJ			C16F31OH	3	G(13)		CS	
n:2 Cl-PFESAs	C8HClF16O4S	1	E(6)	BJ;JN;NJ	BJ;CS;JN;NJ		OBS	C15H5F17SO4	2	H		GY;NJ
	C10HClF20O4S	2	E(8)		CS;JN;NJ		6:2 diPAP	C16H9F26O4P	1	I		BJ;CS;JN;NJ



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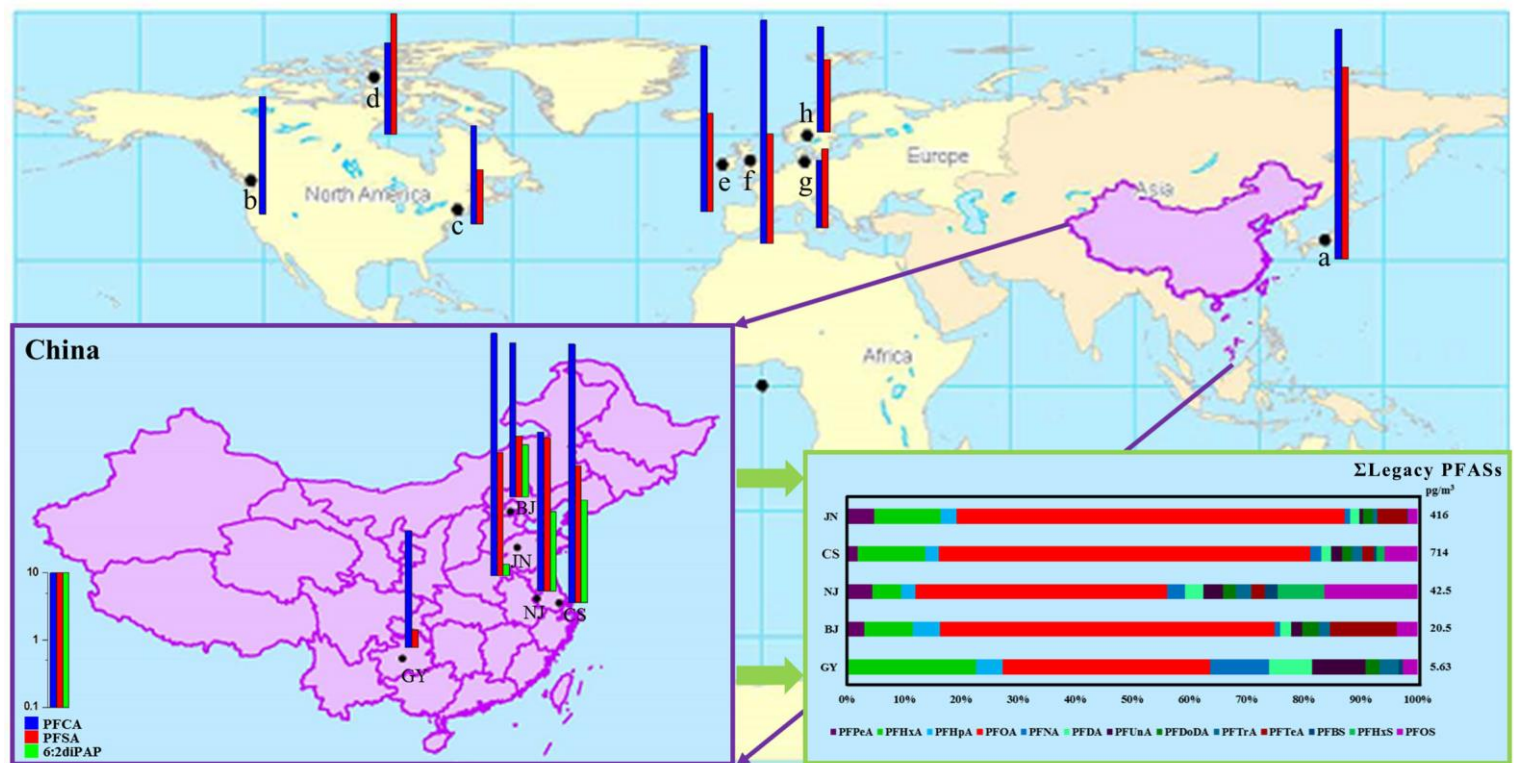
772 Figure 2. Structure and detection of emerging PFASs with level 3 or above in APM.

773 The letters in the “Proposed Structure” column refer to the generic structure

774 represented by the same letters, and the numbers in parentheses in the “Proposed

775 Structure” column indicate fluorinated chain length.

776



777

778 Figure 3. Distribution of PFCAs, PFSA, and 6:2 diPAP in outdoor APM (data for China were obtained from this study, and those for other
 779 countries were obtained from previous studies; a: Japan,⁷⁶ b: Canada,²⁹ c: USA,⁷⁷ d: Arctic,⁷⁸ e: UK,⁴² f: Ireland,⁴² g: Germany,⁷⁹ h: Norway⁴²)
 780 and proportional distribution of legacy PFASs in outdoor APM (value of legacy PFASs is arithmetic mean).