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Indoor air concentrations of $PM_{2.5}$ quartz fiber filter-collected ionic PFAS and emissions to outdoor air: findings from the IPA campaign†

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Per- and polyfluoroalkyl substances (PFAS) are prevalent in consumer products used indoors. However, few measurements of ionic PFAS exist for indoor air. We analyzed samples collected on $PM_{2.5}$ quartz fiber filters (QFFs) in 11 North Carolina homes 1–3 times in living rooms (two QFFs in series), and immediately outside each home (single QFF), for 26 ionic PFAS as part of the 9 months Indoor PFAS Assessment (IPA) Campaign. All targeted PFAS, except for PFDS and 8:2 monoPAP, were detected indoors. PFBA, PFHpA, PFHxA, PFOA, PFOS, and 6:2 diPAP were detected in >50% of indoor samples. PFHxA, PFOA, and PFOS had the highest detection frequency (DF = 80%; medians = 0.5–0.7 pg m^{-3}), while median PFBA concentrations (3.6 pg m^{-3}; DF = 67%) were highest indoors. Residential indoor air concentrations (sum of measured PFAS) were, on average, 3.4 times higher than residential outdoor air concentrations, and an order of magnitude higher than regional background concentrations. Indoor-to-outdoor emission rate estimates suggest that emissions from single unit homes could be a meaningful contributor to PFBA, PFOA, and PFOS emissions in populated areas far from major point sources. Backup QFFs were observed to adsorb some targeted PFAS from the gas-phase, making reported values upper-bounds for particle-phase and lower-bounds for total air (gas plus particle) concentrations. We found that higher concentrations of carbonaceous aerosol were associated with a shift in partitioning of short chain PFCAs and long chain PFSAs toward the particle phase.

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Environmental significance

Few residential indoor air measurements of ionic per- and polyfluoroalkyl substances (PFAS) exist, even though the indoor environment is a major location for storage and use of PFAS-containing products and materials and a location where people spend a considerable amount of time. Thus, the residential indoor environment is likely a major location for PFAS exposure for many people (*i.e.*, for residents that are not particularly close to point sources or occupationally exposed). This work reports measurements of ionic PFAS from residential indoor and outdoor air, as well as aerosol composition, to provide insights into PFAS fate, transport, and exposure. Estimates are also provided for indoor-to-outdoor ionic PFAS air emission rates.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are manufactured compounds that are ubiquitous in the environment due to their use in many industrial processes and consumer products for their surfactant and oil-/water-repellant properties.[1] They are persistent under typical environmental conditions,[2] prevalent indoors and outdoors, and have been detected in air,[3–5] water,[6–8] and dust.[9–12] Some have been associated with adverse health effects like hepatotoxicity, kidney and testicular cancer, and reduced immune response in children.[13–15] Perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorohexanesulfonic acid (PFHxS), and perfluorononanoic acid (PFNA) have been detected in nearly all blood sera collected from the general United States (US) population, suggesting that exposure to these compounds is nearly universal.[16,17]

Although PFAS are pervasive in the environment and US population, there remains limited information on air concentrations and profiles of ionic PFAS indoors, where people spend roughly 90% of their time.[18] There is a need for air

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measurements of PFOA and PFOS, which have been found in US environmental samples[19] despite being phased out of production in the US in the early 2000s.[20] Air measurements are also needed for replacement compounds,[3,4,21] some of which have been shown to be as environmentally persistent and bioaccumulative.[19] Taking polyfluoroalkyl phosphate esters (PAPs) as an example, measurements of the concentrations of these low volatility compounds in indoor aerosols are warranted due to their detection in food samples and packaging,[22] on used air conditioning filters,[23] in personal care products,[24] household dust,[25] and on people's skin,[26] typically at elevated concentrations in comparison to other ionic PFAS. Food (and food packaging materials),[27,28] water,[7,29,30] and dust[9,11] are the most common environmental media sampled for PFAS in the indoor environment.[31] However, some studies have suggested that inhalation of indoor air and ingestion of settled dust could contribute up to 50% of total PFAS exposure.[32,33] Furthermore, airborne PFAS concentrations can result in the partitioning of PFAS from air to clothing, contributing to dermal exposure, another neglected exposure pathway.[26,34–38] Very few studies have reported indoor air concentrations (gas and/or particle phase) for perfluoroalkyl acids (PFAAs), globally[30,39,40] or in North America,[4,41] and fewer in residences (*i.e.*, Europe,[30,39,40] China,[42] and Canada[41]). Fewer still collected particle-phase PFAAs in residences (*i.e.*, on filters[39] or in total air samples[42]). To our knowledge, residential air measurements of ionic PFAS have not been made in US homes. Thus, there is a need to assess concentrations of ionic PFAS indoors, particularly in US homes.

Additionally, identifying and characterizing sources of PFAS to the outdoor atmosphere is necessary to understand their fate, transport, and ecological and human impacts. Fluoropolymer manufacturing plants,[3,43,44] wastewater treatment plants,[45] landfills,[46] and military bases[47] have been identified as major sources of PFAS to the environment. Emissions of PFAS to ambient air have also been implicated in well water contamination downwind of major PFAS point sources.[43,48–50] PFAS present in buildings can presumably be emitted to outdoor air through open doors and windows, as well as through cracks and leaks in the building envelope.[51] Upon emission to outdoor air, PFAAs, which are highly resistant to degradation, can travel long distances through the air, and contaminate water and soil *via* wet and dry deposition.[52] However, to our knowledge, emission rates of ionic PFAS in air from homes have not been reported.

Uncertainty surrounding the physicochemical properties of many PFAS[53–55] limits our ability to predict the distribution of these compounds between different environmental matrices, including between gases, particles, and indoor surfaces. Despite their low estimated pK_a's, PFAAs have been measured in both the gas and particle phases in air. PFAA gas–particle partitioning behavior can be expected to be influenced by their pK_a and aerosol pH, which determine their degree of dissociation[56–58] and vapor pressure.[57,59] Partitioning of ionic PFAS between air and airborne particles might reasonably be influenced by particulate organic matter (OM), elemental carbon (EC), ion exchange capacity (*i.e.*, electrostatic interaction),[60] pH, or aerosol liquid water content (LWC).[61–63] Inorganic ions such as sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) can enhance the sorption of PFAAs from water to various matrices such as sediment and activated carbon,[64] and thus, it is reasonable to consider that ammonia and ammonium (NH_3/NH_4^+), which are abundant indoors,[65] and other salt-forming cations, may also influence partitioning of PFAAs to aerosols.

The dynamics of indoor chemistry is complex and sometimes counterintuitive, in part because of the much larger role that surfaces play indoors than outdoors. Volatile organic compounds (VOCs), which exist predominantly in the gas-phase outdoors, partition to surfaces indoors due to the high surface to volume ratio present.[66] Several studies have shown that indoor air concentrations of semi-volatile organic compounds (SVOCs) are mediated by surfaces, which act as "buffers" by releasing SVOCs to the air after increased ventilation reduces concentrations in the air.[66,67] While there is a growing understanding of the roles of surfaces and $PM_{2.5}$ composition on indoor partitioning of VOCs and SVOCs, little is known about their influence on ionic PFAS. Because of the likely importance of characteristics of both the indoor environment and indoor aerosol to the indoor ionic PFAS mass balance, we measured relevant environmental parameters, conducted surveys, and characterized the dominant components of $PM_{2.5}$ (particulate matter of aerodynamic diameter 2.5 μm and smaller) composition in addition to measuring ionic PFAS in air in the study reported herein.

To address the lack of ionic PFAS air measurements in US homes, stimulate further hypotheses regarding the fate and transport of ionic PFAS indoors, and provide new information about the magnitude of residential PFAS emissions to outdoor air, we collected $PM_{2.5}$ on two quartz fiber filters (QFFs) in series in the main living area and on one QFF immediately outside participants' homes on multiple occasions for 11 homes in North Carolina during the Indoor PFAS Assessment (IPA) Campaign. QFF collected samples were analyzed for 26 ionic PFAS, organic carbon (OC), and EC. Additional filters were analyzed for particulate sulfate and nitrate. Temperature (T), relative humidity (RH), and carbon dioxide (CO_2) concentrations were measured, and air change rates (ACH) and LWC were estimated. Herein, we report the concentrations and profiles for $PM_{2.5}$ filter collected ionic PFAS in homes, provide estimates of residential PFAS emission rates to outdoor air, investigate associations between PFAS and particle composition, and comment on sampling artifacts associated with ionic PFAS collected onto QFFs.

Materials and methods

Indoor PFAS assessment (IPA) campaign

The work reported herein is part of the IPA Campaign, during which indoor air (gas-phase and particle-phase), surface wipes, tap water, settled dust, heating and air conditioning (HAC) filters, cloth, clothing, and dryer lint were collected from a convenience sample of 11 non-smoking, single-unit homes located in Chapel Hill and Durham, North Carolina, between July 4, 2021 and May 20, 2022 (UNC Chapel Hill IRB# 20-2771).

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Eleven homes were recruited and 10 completed the study; one home (Home 82) left the study after one month. Home characteristics (*e.g.*, building age, renovations, flooring type, occupancy) were recorded at the beginning and end of the campaign. Herein, we focus on active air sampling (*i.e.*, $PM_{2.5}$ filter-collected ionic PFAS) that took place three times in each home over 6 days sampling periods (except one time in Home 82). During active air sampling, participants were provided with an activity checklist to record the frequency and duration of certain activities (*e.g.*, cooking, cleaning, heating/cooling) and *T*, RH, and CO_2 concentrations were logged. At the end of the sampling week, an activity survey was conducted to gather more detailed information about activities that took place during sampling (*e.g.*, types of cookware used, frequency of takeout meals) that may have affected PFAS air concentrations. *T* and RH were logged inside the homes throughout the campaign (*i.e.*, 6–9 months). The eleven homes in the IPA Campaign were detached, single-unit, non-smoking homes.

Estimated home volumes ranged from 162 m^3 to 669 m^3. Homes were built between 1920 and 2002, except for Home 82 (built 2017). Homes had 1 to 4 occupants and 0 to 3 pets. All homes had central heating and air conditioning (HAC) and average ACHs between 0.2 h^{-1} and 0.6 h^{-1}. With two exceptions, homes had open windows between 15 min and the whole day during the fall and winter months; two homes did not open their windows during sampling. Indoor *T* and RH were 10 °C to 32 °C and 18% to 86%, respectively, while outdoor *T* and RH were −9 °C to 38 °C and 14% to 100%, respectively (1 h average). During sampling weeks, stove use ranged from 1 to 16 times, oven use 0 to 7, microwave use 1 to 19, toaster use 0 to 13, and water kettle use 0 to 18 times. See ESI Section S1, Tables S1 and S2† for details about homes and activities; additional details are provided elsewhere.[38]

Chemicals and reagents

Twenty-six ionic PFAS (Section S2 and Table S3†) were targeted for analysis: 13 perfluorocarboxylic acids (PFCAs), 8 perfluorosulfonic acids (PFSAs), GenX (hexafluoropropylene oxide-dimer acid), and four polyfluoroalkyl phosphate esters (6:2 monoPAP, 8:2 monoPAP, 6:2 diPAP, 8:2 diPAP). Native standards and mass-labelled internal standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All other solvents and reagents were HPLC-grade from Thermo Fisher Scientific (Waltham, MA, USA).

$PM_{2.5}$ filter collection for ionic PFAS and OC/EC

$PM_{2.5}$ filter samples were collected onto pre-baked (550 °C, 12 h) 37 mm QFFs (Pall Laboratory, Port Washington, NY, USA) in the main living area and immediately outside each participant's home three times over the course of 9 months, except that Home 82 was sampled once. Samples were collected using an MSP Sampler (Model 400 Micro-Environmental Monitor, MSP Corporation, Shoreview, MN, USA) at an average flow rate of 10.5 L min^{-1} over 6 days. Larger particles were removed in the inlet with a 2.5 μm diameter cut-point impactor. QFFs collect $PM_{2.5}$ with over 99% efficiency,[68,69] but also have a large surface area for gases to absorb to, which can result in an overestimate of particle-phase concentrations of OC[68] and ionic PFAS.[57,70–72] As has been done previously,[68,73,74] we used backup QFFs to estimate the mass of gas-phase OC adsorbed to the front QFF.

Two MSP samplers were placed indoors (0.5–1.8 m off the ground, ∼0.5 m from the wall), one for OC/EC and the other for ionic PFAS analysis; both samplers included two QFFs in series, the second housed in a 47 mm in-line aluminum filter holder (Pall Corporation, Ann Arbor, Michigan) connected 30 mm downstream of the first QFF. An additional MSP for ionic PFAS analysis was deployed outside each home (0.3–2 m from wall; 1–1.5 m off ground) and contained a single filter (no backup). All three MSP samplers collected concurrently at any given home, while sampling across homes was staggered. ESI Section S3† provides sample and blank collection details. In total, 60 indoor QFF samples, 30 outdoor QFF samples, and 10 collected field blanks were analyzed for ionic PFAS. An additional 60 indoor QFF samples and 10 field blanks were analyzed for OC/EC using thermal-optical transmittance[75] with a Model 4L Lab OC-EC Aerosol Analyzer (Sunset Laboratory Inc, Tigard, Oregon) following NIOSH-870 temperature protocol as described in Section S3.† Particulate OC was estimated by subtracting backup filter OC (adsorption artifact estimate) from the corresponding front filter OC, as recommended previously.[68] Particulate OC was multiplied by 1.4, an estimate of the average molecular weight of organic compounds per organic carbon weight, to obtain particulate organic matter (OM).[76] Note that multiplying by 1.4 may underestimate OM. An OM/OC ratio of 1.4 is typical of fresh outdoor aerosol and the ratio is higher for aged outdoor aerosols.[76,77] However, indoor generated OC is not highly oxygenated and thus 1.4 represents our best estimate.[78] Ionic PFAS values on backup QFFs are reported but were not subtracted from front QFF PFAS values. However, insights concerning sampling artifacts which are provided by the backup QFFs are discussed in ESI.†

Ionic PFAS sample preparation and analysis

Filter extraction for ionic PFAS followed the method provided in detail previously by Zhou *et al.*[79] with a few differences. Briefly, all samples and blanks were spiked with 0.5 ng of mass labelled PFAS (Section S2 and Table S3†) prior to extraction by sonication for 15 min in 3 mL of methanol in a polypropylene (PP) centrifuge tube (Corning, Corning, NY, USA) three times for a total volume of 9 mL. The supernatants were combined and evaporated to ∼3 mL under a gentle flow of nitrogen (Airgas, Radnor, PA, USA) at room temperature, filtered (nylon syringe filter, 13 μm diameter, 0.22 μm pore size, VWR, Radnor, PA), and further evaporated to ∼200 μL. Extracts were transferred to pre-weighed 300 μL PP autosampler vials (Thermo Fisher Scientific, Waltham, MA, USA) and further evaporated to ∼25 μL, quantified using the density of methanol. Samples were brought to a final volume of ∼100 μL by adding ∼75 μL of Milli-Q water to match the initial mobile phase composition of 75 : 25 (v/v) Milli-Q water and HPLC-grade methanol for the 9 minutes analytical method as described in Zhou *et al.*[79] in detail. Samples were analyzed using AB SCIEX Triple Quad™ 6500

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ultra-high performance liquid chromatography-electrospray ionization tandem mass spectrometry (UHPLC/ESI-MS/MS) operated in the negative mode with multiple reaction monitoring. Method parameters and operating details are provided in Zhou *et al.*[79] for the PFAAs and GenX, and in Section S2 (Table S4)† for the PAPs. Note that this SCIEX Triple Quad is regularly used for PFAS analysis, and thus Teflon components in the system were previously replaced with PEEK tubing, a delay column (Zorbax RR Eclipse Plus, C18, 4.6 × 50 mm, 3.5 μm) was installed between the pump and injector, and other parts were replaced per the vendor's recommendation (Agilent application note 5991–7863 EN).

Section S2 (Tables S5–S8)† characterizes PFAS data quality. Recoveries ranged from 78%–126% with three exceptions (PFODA; 25%, 6:2 monoPAP; 173%, 8:2 diPAP; 177%). Analytical precision was within 26% for all compounds except 6:2 diPAP (85%) and 8:2 diPAP (204%). Results for the diPAPs should be interpreted with caution. Method detection limits (MDLs; Table S8†) were taken to be the larger of the field detection limit or analytical detection limit, whichever was greatest and ranged from 0.04–0.77 pg m^{-3}, except for PFHpS, 8:2 diPAP, 6:2 monoPAP, and 8:2 monoPAP, which had MDLs of 1.1–2.49 pg m^{-3}. Average field blank concentrations were below 0.2 pg m^{-3} for all PFAS except for PFHpS (0.56 pg m^{-3}).

Filter collection for inorganic ions and estimation of aerosol liquid water content (LWC)

Real-time PM samplers, used for supplemental measurements, included a 37 mm polytetrafluoroethylene (PTFE) filter (1.52 L min^{-1}; 2.5 μm cut point; Pall Laboratory, Port Washington, NY, USA) or 47 mm PTFE filter (1.2 L min^{-1}; DURAG GROUP, Hamburg, Germany) that collected indoor aerosol (9.8–13.7 m^3 sample volume, 0.05–0.22 m off ground) at the same time as the QFFs (one to three times in each home, each with a collection period of 6 days). Filter size and sample flow rate were dependent on the sampler used, either a DataRAM pDR-1500 Aerosol Monitor (ThermoFisher Scientific, Waltham, MA) or GRIMM Optical Particle Counter (DURAG GROUP, Hamburg Germany). These supplemental samplers were placed near other air samplers as space and participant preferences allowed. In total, all 30 collected PTFE filter samples and 10 PTFE filter field blanks were analyzed for anions (acetate, formate, pyruvate, chloride, bromide, nitrate, malonate, maleate, sulfate, and oxalate) and cations (potassium, ammonium, sodium, calcium, and magnesium) using ion chromatography (IC). Additional details regarding data quality are in Section S2 (Tables S9–S13)† and additional sample and blank collection details are in Section S3.† LWC was calculated using IC measurements and Model III from E-AIM.[80] Aerosol pH was estimated using LWC and particle strong acidity, as suggested by Nazaroff and Weschler.[81] This equation does not account for activity coefficient corrections to calculate the relationship between H^+ concentrations and pH.[81] We also did not include organic compounds in E-AIM Model III as LWC is most influenced by sulfate, nitrate, and ammonium concentrations.[82,83] LWC and pH estimation are described in Section S3.†

Emission rates to outdoor air

Net emission rates (kg per year per home) to outdoor air were estimated for targeted ionic PFAS and sum of measured PFAS (ΣPFAS) based on air concentrations (pg m^{-3}) measured on $PM_{2.5}$ front QFFs, recognizing that the QFFs provide an upper-bound on particle-phase concentrations of targeted ionic PFAS due to sampling artifacts.[68] Rates are reported for the average IPA Campaign home and extrapolated to all single unit homes in Raleigh, North Carolina, as well as to all single unit homes in the US. According to the 2019 US Census data,[84] there were 333 600 detached single unit homes in the Raleigh metropolitan area, and the 2021 US Census data[85] reported 81 744 000 single unit detached homes nationally.

A home removes PFAS from the atmosphere by drawing outdoor air into the building; homes are also a source as indoor air is exhausted back to the atmosphere after being attenuated by any removal phenomena taking place in the building envelope. The mass flux of outdoor PFAS lost from the outdoor air during infiltration into (and loss to the building envelope of) an IPA Campaign home is given by the outdoor PFAS concentration (C_{out}, pg m^{-3}), times the home volume (V_{Home}, m^3), and the air change rate (λ, h^{-1}). The mass flux of PFAS to the outdoor air by exfiltration from an IPA Campaign home is given by the indoor PFAS concentration (C_{in}, pg m^{-3}) times V_{Home}, λ, and P, where P is the fraction of indoor PFAS in $PM_{2.5}$ that penetrates the building envelope with exfiltration. Thus, the net indoor-to-outdoor emission rate is given by:

$$\text{Net indoor-to-outdoor emission rate} = (PC_{in} - C_{out})\lambda V_{Home} \quad (1)$$

We used concurrently collected residential indoor and outdoor front QFF measurements, λ, V_{Home}, estimated P of 0.9, as well as eqn (1) to provide base case estimates of net indoor-to-outdoor emission rates from homes. Penetration factors are particle size-dependent and studies have found that P ranges between 0.6–1.0 in real buildings[86] for particles between 0.05 μm and 2 μm. We used $P = 0.9$ because this value has been used in several large exposure studies such as the Relationship of Indoor, Outdoor, and Personal Air (RIOPA) study.[74,87] See Section S4† for additional information regarding emissions calculations.

Recognizing that residential outdoor measurements in this study were collected directly outside homes, we also report upper-bound emission rate estimates from homes with C_{out} set to zero. Average regional background concentrations of 34 ionic PFAS, collected in 2019 and reported by Zhou *et al.*[79] for the Research Triangle Park site (RTP), which is the closest site to IPA Campaign homes were quite low. In that study, only PFOS was measured at concentrations greater than detection limits at the RTP site, and its annual average concentration was <0.5 pg m^{-3}. We did not use regional background estimates of ΣPFAS (total PFAS) because the targeted PFAS in that study are not the same as in IPA Campaign homes; they sampled for several emerging PFAS not targeted in IPA Campaign analyses (*i.e.*, HydroEVE, NVHOS, Nafion Byproduct 1, Nafion Byproduct 2), and did not include the PAPs which were analyzed for in IPA Campaign homes.

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Statistical analysis

Concentrations that were below the MDL were labeled as such and reported as measured. However, for statistical analysis, only PFAS with greater than 50% of samples above the MDL (DF > 50%) were used. Kendall's τ correlation coefficients were calculated to identify associations between auxiliary measurements and natural log-transformed concentrations of PFAS subclasses (ΣPFAS, ΣPFCAs, ΣPFSAs, ΣPAPs, ΣLong PFCAs, and ΣShort PFCAs). PFCAs are perfluorocarboxylic acids, PFSAs are perfluorosulfonic acids. "Long-chain" perfluoroalkyl acids (PFAAs) are defined here as having seven or more carbons for PFCAs and six or more carbons for PFSAs.[88]

We expect that the partitioning of ionic PFAS between the gas and particle phases may well be affected by particle composition. Although we did not measure gas-phase ionic PFAS, the particle–gas partition coefficient (K_p) for these PFAS should be proportional to the difference between the concentrations on the front (C_{Front}) and backup filter (C_{Backup}) normalized by the mass of $PM_{2.5}$ ($m_{PM_{2.5}}$) and divided by the backup filter concentration (C_{Backup}). This is because we expect, for any given compound, adsorption of gas phase PFAS on C_{Backup} will be proportional to the gas phase concentration. Subtracting the backup QFF concentration from the front QFF provides an upper bound on the particle-phase concentration of the PFAS, since adsorption of gases on the backup filter will be lower than on the front filter if gases in the vicinity of both filters have not yet reached equilibrium partitioning. We are calling this parameter κ_p, as shown in eqn (2).

$$K_p \propto \kappa_p = (C_{Front} - C_{Backup})/(C_{Backup} \times m_{PM_{2.5}}) \quad (2)$$

Therefore, κ_p is used as a proxy for the equilibrium partition coefficient, *i.e.*, to examine how shifts in partitioning between the gas and particle-phase are associated with differences in aerosol characteristics. This provides greater insight into the dynamics of ionic PFAS indoors. Auxiliary measurements were selected for stepwise (both direction) MLR if the Kendall's τ correlation coefficients were statistically significant ($p < 0.05$). The step function, which compares models using Akaike information criterion (AIC), in the stats package (version 3.6.2) in R was used for stepwise model selection. Statistical analysis methods are described in Section S4.† All statistical analyses were conducted in RStudio 2022.07.2 Build 576 (RStudio, Posit).

Results and discussion

$PM_{2.5}$ QFF-collected ionic PFAS in homes

Indoors, all targeted PFAS, except for PFDS, PFDoS, and 8:2 monoPAP, were detected on the front $PM_{2.5}$ QFF (Fig. 1, Section S5 and Tables S14–S22†). The following four compounds had median concentrations more than three times the MDL indoors and/or outdoors (front QFF): PFBA, PFHxA, PFOA, and PFOS. Additionally, PFHpA and 6:2 diPAP were present above the MDL in more than 50% of indoor and/or outdoor samples (front QFF). Reported values are field blank subtracted and corrected for recoveries.

Large variations in PFAS profiles and concentrations were observed both across homes and within the same home. In general, PFCAs contributed most to total indoor $PM_{2.5}$ QFF collected ionic PFAS concentrations, with the PAPs also contributing a sizeable share. Indoors, PFOA (median = 0.5 pg m^{-3}), PFHxA (median = 0.7 pg m^{-3}), and PFOS (median = 0.5 pg m^{-3}) had the highest front QFF detection frequency (DF = 80%). PFBA (DF = 67%) had the highest maximum and median concentrations (119 pg m^{-3}; 3.6 pg m^{-3}, Home 43, Week 1; Fig. 1). Although GenX had a lower DF (33%), its maximum measured concentration was 14.5 pg m^{-3}, also in Home 43 during sampling Week 1. Additionally, indoors, 6:2 diPAP (median = 0.7 pg m^{-3}; DF = 57%) was detected at concentrations significantly above the MDL (Wilcoxon Signed Rank Test, $p < 0.05$; MDL = 0.65 pg m^{-3}).

Residential indoor concentrations of ΣPFAS were, on average, 3.4 times (median 1.9 times) higher than residential outdoor concentrations, and around 10 times higher than regional background concentrations, which were collected in North Carolina in 2019 using similar sampling and analytical methods (Fig. 1).[79] In fact, indoor concentrations of ΣPFAS, ΣPFCAs, ΣPFSAs, ΣPAPs, PFOA, PFOS, 6:2 diPAP, and PFBA were significantly higher than outdoor concentrations (Fig. 2) at the same home (paired Wilcoxon Signed Rank Test; $p < 0.05$). PFBA (DF = 67%), PFHxA (97%), PFHpA (50%), and PFOS (67%) were the only targeted analytes detected in at least 50% of outdoor samples (outdoors; PFOA DF = 37% and diPAP = 27%), whereas six analytes were detected >50% in indoor front filters. In contrast to other homes, the outdoor concentration of ΣPFAS was 1.2 times higher than indoors at Home 78. Unlike other homes in this study, Home 78 is located directly along a 4-lane highway, experienced a wildfire haze, and had their lawn treated for mosquitos during the first sampling period. No notable activities outdoors were recorded on the activity logs or activity checklists during the second or third weeks of sampling.

Total PFAS concentrations immediately outside IPA Campaign homes (1.4–23 pg m^{-3}) were substantially higher than the outdoor regional background concentrations (0.18–14.1 pg m^{-3}) measured in NC in 2019 using the same samplers and analytical method (Fig. 1, black†).[79] During the IPA Campaign, outdoor samples were collected right outside homes so in addition to indoor–outdoor emissions,[89] it is possible that coatings and finishing on wooden porches and on outdoor furniture[90] contributed to higher residential outdoor concentrations. The previous outdoor study targeted 34 PFAS, including several emerging PFAS but did not analyze for PAPs. Outdoor regional sampling sites were located far from busy roads and away from fluorochemical manufacturing plants, wastewater treatment plants, and army bases.[79] In the regional outdoor study, PFOS concentrations were greater than the field detection limit (FDL = 0.18 pg m^{-3}) in 13 of 19 samples, while PFOA (FDL = 2.86 pg m^{-3}) and PFHpA (FDL = 0.12 pg m^{-3}) were only detected once. The higher FDL for PFOA in their study likely also contributed to their lower detection rates.

Unlike other measured species, residential outdoor concentrations of PFHxA ($p < 0.05$) were significantly higher than indoor concentrations. PFHxA has been detected with

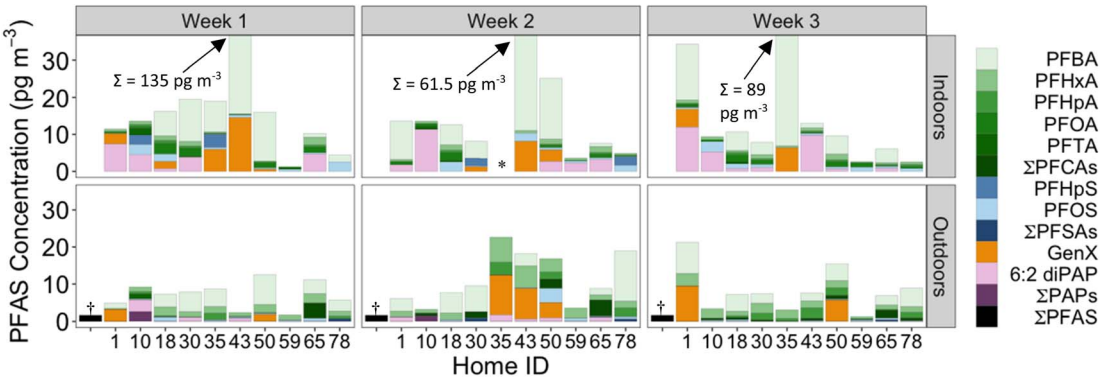

Fig. 1 Indoor (top) and outdoor (bottom) filter-collected PFAS (front filter only) concentrations for each home across the three 6 days sampling periods. Indoors, ΣPFAS concentration exceeded the 35 pg m^{-3} scale for Home 43 in Week 1 (135 pg m^{-3}) and Week 2 (61.5 pg m^{-3}); in Week 3, Home 35 reached 89.2 pg m^{-3}. Values are field blank subtracted, but not corrected for adsorption of gases on the front QFF (*i.e.*, not backup filter subtracted). *Home 35 Week 2 not measured. †ΣPFAS in ambient outdoor "regional background" QFF samples measured by Zhou *et al.*[79] (sum of means, where values below their MDL were set to MDL*(2)$^{-1/2}$). **Individual compounds are reported when detection frequency >50%. Remaining PFAS were summed by subgroup (ΣPFCAs, ΣPFSAs, and ΣPAPs). GenX is the only perfluoroalkyl ether carboxylic acid (PFECA) targeted in this study, and thus is listed despite having DF < 50%.

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increasing frequency and at higher concentrations worldwide, possibly because it is a primary byproduct of short-chain fluorotelomer-based chemistry and the shift away from long-chain PFCAs like PFOA has resulted in increased use of short-chain compounds.[91–94] Terminal PFCAs, such as PFHxA and PFHpA, can be formed by biodegradation of 6:2 FTOH and 8:2 FTOH.[95] Additionally, PFHxA is frequently detected in textiles[38,96] and may plausibly be found in residential outdoor furnishings (such as upholstery material and insulation/foams),[97] as well as clothing indoors.

There are few measurements of ionic PFAS in indoor air, particularly in homes. Barber *et al.*[39] sampled indoors for 16 ionic PFAS (30–50 h; 1.6 m^3 h^{-1}) on glass fiber filters (GFFs) in three homes and one lab between April–June 2005 in Tromsø, Norway. Excluding the fluorotelomer unsaturated carboxylic acids (6:2 and 8:2 FTUCA), which we did not measure, arithmetic mean (AM) concentrations for PFHxA and PFOA were the highest at 17.1 and 4.4 pg m^{-3}, respectively, and larger than the mean concentrations 0.82 pg m^{-3} (PFHxA) and 1 pg m^{-3} (PFOA) reported herein. The air in children's bedrooms (N = 57) in Finland was sampled in 2014/15 for ionic PFAS passively using a sorbent impregnated polyurethane (SIP) foam disk. Median concentrations of PFOS (1.9 pg m^{-3}), PFHxA (9.03 pg m^{-3}), and PFOA (15.2 pg m^{-3}) were higher than median concentrations in IPA Campaign homes (0.5 pg m^{-3}, 0.7 pg m^{-3}, and 0.5 pg m^{-3}, respectively). Ten air samples were collected in the living room of five homes in five Chinese cities onto QFFs using an Eight-Stage Non-Viable Andersen Cascade Impactor (48 h, 28.3

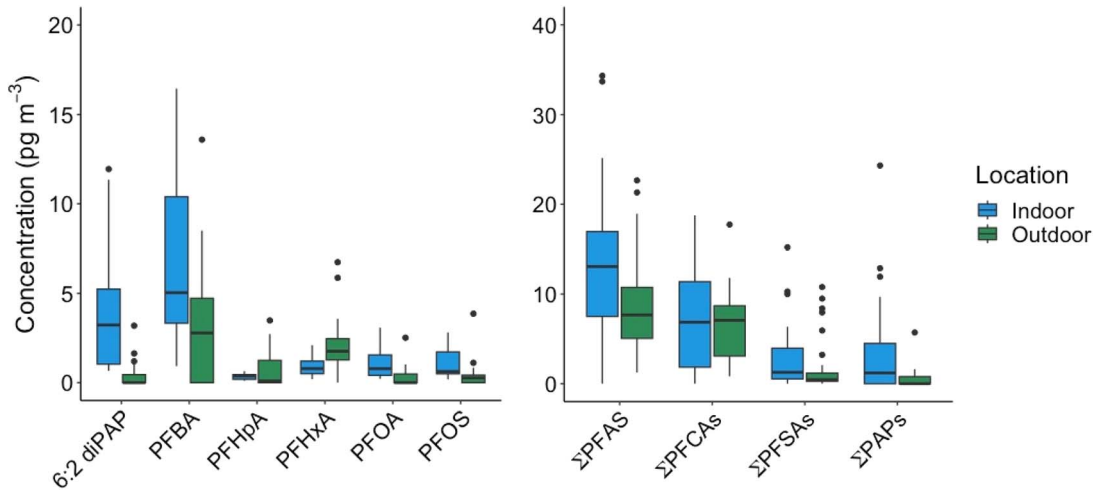

Fig. 2 Distributions of PFAS with DF > 50% on indoor front and/or outdoor filter-collected $PM_{2.5}$ for all homes (left image) and ΣPFAS, ΣPFCAs, ΣPFSAs, ΣPAPs for indoor front and outdoor filter-collected $PM_{2.5}$ (right image). Concentrations are field blank subtracted. Note: the (left image) y-axis was limited to 20 pg m^{-3} for better data visualization. PFBA had three additional outliers (50.1, 82, 119 pg m^{-3}). The (right image) y-axis was limited to 40 pg m^{-3}. There were three additional outliers for ΣPFAS indoor front filter (61.1, 88.8, 135 pg m^{-3}) and three for ΣPFCAs indoor front filter (50.8, 82.5, 119.4 pg m^{-3}).

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L min^{-1}) for nine size fractions.[98] PFOA and PFHxA were the dominant targeted PFAS detected, accounting from 41% and 29% of total targeted legacy PFAS (13 PFCAs and 5 PFSAs). Large variations across homes, regions, and changes over time are expected, based on the large variations in PFAS concentrations in dust.[12,95,96] In part because of the small sample size and difference in timing of the studies, it is not possible to know whether differences between the results in Winkens *et al.*,[40] Barber *et al.*,[39] Yu *et al.*,[98] and this study reflect large between-sample variability, geographic differences, or temporal trends (*i.e.*, decreasing use of PFOA in consumer products[99] and indoor materials, thus lower concentrations in homes and blood serum[100]). This highlights the challenges in measuring ionic PFAS in indoor air as well as comparison across studies.

Emission rates of ionic PFAS to outdoor air

The net (indoor–residential outdoor QFF) ΣPFAS emission rate (mean ± σ) was $1.1 \times 10^{-8} \pm 4.5 \times 10^{-8}$ kg per year per home. When extrapolated to all single unit homes across the US, the net ΣPFAS emission rate was 0.94 ± 3.7 kg per year, with PFBA contributing to over 50% (0.59 kg per year) of ΣPFAS by mass (Section S6 and Table S23†). The second most abundant PFAS emitted from homes was 6:2 diPAP at ∼17%. Both PFOS and PFOA contributed to ∼5% of ΣPFAS by mass, at 4.2×10^{-2} kg per year and 5.9×10^{-2} kg per year, respectively. GenX emissions were estimated to be 3.2×10^{-2} kg per year from US homes. By setting ambient concentrations (C_{out}) to zero based on the low ambient concentration reported at the RTP site,[79] an upper bound on the home emission rate for ΣPFAS from a single home nearly doubled to $2.1 \times 10^{-8} \pm 4.5 \times 10^{-8}$ kg per year per home. Although the mean ΣPFAS net emission rate from homes was positive, net emission rates for PFHpA (-1.7×10^{-2} kg per year), PFHxA (−0.07 kg per year), and PFPeS (-1.4×10^{-3} kg per year) were negative. This suggests that homes may serve as net sinks for these compounds, which we found at higher concentrations on residential outdoor QFFs than indoors. This is not surprising, since losses in the building envelope during outdoor-to-indoor transport and losses *via* surface deposition indoors are well recognized to be substantial for $PM_{2.5}$,[86,101,102] resulting in indoor concentrations of outdoor-generated $PM_{2.5}$ that are roughly one half of their outdoor levels. Losses of oxygenated organic gases with outdoor to indoor transport and indoor deposition have also been documented.[103]

It is difficult to make comparisons with major point sources such as fluorochemical manufacturing plants due to differences in measured PFAS, however, in 2022, the North Carolina Department of Environmental Quality (NCDEQ) reported the atmospheric emission rates of over 60 fluorinated compounds from the Fayetteville Works Chemours Company: emission rates were 4.5×10^{-3} kg per year for PFOA and 1.1 kg per year for HFPO dimer acid (GenX).[104] The 2022 Fayetteville Works atmospheric GenX emission rates are over two orders of magnitude greater than GenX emission rates from all single unit homes in the US. In contrast, PFOA emission rates from all single unit homes in the US are greater than PFOA emission rates from Fayetteville Works. Testing in 2016 of PFAS from the outlets of three fume stacks from Taconic Plastics, headquartered in New York State, reported relatively low emissions of PFBA (3.5×10^{-3} kg^{-1}) and PFOA (5.3×10^{-3} kg^{-1}),[105] both of which are lower than the estimated emissions from all US single-unit, detached homes. It is likely that PFOA emission rates from US manufacturing plants have decreased due to the phase-out of PFOA production in the US in the early 2000s. The continued presence of PFOA in homes and emission to outdoor air is likely due, at least in part, to the presence of legacy products and materials as well as the import/use of new products from overseas (*e.g.*, Asia). This suggests that home emissions may make a meaningful contribution to ambient ionic PFAS concentrations in some locations, for example urban and suburban areas away from point sources such as fluorochemical manufacturing plants, landfills, and military bases. This is especially true for PFBA because of its reasonably high emission rate from homes, perhaps for 6:2 diPAP, and also for PFOA and PFOS, which are still present in indoor air at measurable concentrations, despite their phase-out in the US.

There remains a dearth of air emissions data and standardized sampling procedures to compare emissions between various sources. Regardless, the species concentration profile for home emissions and the geographic distribution of home emissions differ from point sources such as fluoropolymer manufacturing plants[43] and military bases,[106] which have been identified as major sources of PFAS to the environment. Additionally, PFAS present in buildings can be emitted to outdoor air through open doors and windows as well as through cracks and leaks in the building envelope.[51] Upon release to outdoor air, PFAAs, which are highly resistant to degradation, can travel long distances through the air, and contaminate water and soil *via* wet and dry deposition.[52] Emissions from buildings remain incompletely characterized, but home emissions may make a meaningful contribution to ambient concentrations of some PFAS and alter the geographic distribution of atmospheric PFAS in populated areas.

Across home and within home variability

Due to their prevalence in consumer products, we expect that building materials, furniture, building characteristics, and some home activities may influence PFAS profiles and concentrations in the home. We found that within home variability (WHV) was greater for all PFAS classes compared to across home variability (AHV) (Section S7 and Table S24†), suggesting that time–variable activities within the home, rather than more permanent sources (*e.g.*, building materials, carpet, furniture), may influence sources and emissions of some ionic PFAS. However, there were also some species (*e.g.*, PFBA) found consistently within the same home, suggesting a more continuous indoor source; it is noted that PFBA was not detected in all homes. Likewise, PFOS was detected during all sampling weeks in two homes. Higher WHV compared to AHV was also found for all detected neutral species (6:2, 8:2, and 10:2 FTOHs as well as ethylperfluorooctane sulfonamide (EtFOSA) and ethyl perfluorooctane sulfonamidoethanol (EtFOSE) except for

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methylperfluorooctane sulfonamidoethanol (MeFOSE)).[38] Large variations in ΣPFAS and ΣPFAS subclass concentrations within and between homes have been reported in the literature.[30,40,107]

Outdoors, WHV and AHV were relatively similar for ΣPFAS and all PFAS subclasses. This suggests that there are some relatively constant sources of PFAS outdoors, perhaps from deck coatings or outdoor furniture, and time varying activities outdoors and near the home that also elevate PFAS concentrations. It is also possible that outdoor activities near residences are similar, *i.e.*, barbecuing, or that better ventilation outdoors may reduce the influence of time varying activities. Indoor-to-outdoor transport of PFAS (*e.g.*, through ACH and stove exhaust vents) may also contribute to residential outdoor PFAS concentrations. Outdoors, ΣPFAS and all subclasses had lower variability both within and across homes compared to their variability in indoor concentrations. No significant seasonal effect was found for ΣPFAS nor ΣPFAS subclasses (Section S7 and Fig. S1†).

Sampling artifacts associated with QFFs

IPA Campaign QFF-collected ionic PFAS concentrations are upper-bound estimates of particle phase concentrations. While QFFs (and GFFs) are commonly used to collect organic particulate matter, these filters can adsorb some gases. This has been demonstrated extensively for OC[68,74,108] and is demonstrated for ionic PFAS (and OC) in the IPA Campaign by the presence of ionic PFAS on the backup filters (*i.e.*, after removal of particles to the front filter), as presented and discussed in depth in ESI (Section S8 and Fig. S2–S4).† Six PFAS were detected in over 50% of indoor front filter samples. Of these, the mean backup to front QFF ratio (Fig. S4†) was 0.1 for PFBA, PFHpA, and 6:2 diPAP. The ratio was 0.25 for PFOS, and 0.4 for PFHxA and PFOA. This demonstrates that these ionic PFAS are present, in part, in the gas phase in indoor air and they adsorb to QFFs. Ionic PFAS are volatile to semi-volatile;[37,109] they have been measured in both gas and particle phases previously, and their particle–gas partitioning has been measured in the atmosphere.[57,70] The presence of several ionic PFAS on both the indoor front and backup QFF (Table S25, Fig. S3 and S4†) is consistent with previous reports that ionic PFAS gases adsorb to QFFs/GFFs under laboratory and ambient sampling conditions.[3,4,57,70–72,79,110]

As explained in more detail in Section S8 and based on previous measurements that compare denuder and filter samples,[57,70] adsorption of ionic PFAS on the IPA Campaign filters is expected to be the dominant sampling artifact, leading to IPA Campaign measurements on front QFF that are upper-bound values for particulate PFAS. It is also worth noting that we expect the backup QFFs to experience substantial breakthrough of gases, at least for most targeted ionic PFAS. However, loadings of adsorbed gases on the backup QFFs can be expected to co-vary with the gas phase concentration. As a result, variations in the concentration of particle-phase PFAS normalized by $PM_{2.5}$ mass and divided by the concentration of PFAS on the backup QFF filter (κ_P) could be used as an indicator of variations in the particle–gas partition coefficient. This approach has been used in some exploratory statistical analyses below. In a few select cases where breakthrough of gases is low, the sum of front and backup filter concentrations might provide a reasonable estimate of total (gas + particle) concentrations. See Section S8† for results and discussion of sampling artifacts.

$PM_{2.5}$ characterization

Fig. 3 provides compositional information for indoor $PM_{2.5}$ for time periods corresponding to ionic PFAS measurements. We provide $PM_{2.5}$ compositional measurements because the form of ionic PFAS (acid or anion) and ionic PFAS gas–particle partitioning are expected to depend on aerosol properties (*e.g.*, composition, LWC, pH) and environmental conditions. Surface partitioning of short-chain PFAAs is expected to preferentially occur to water[19] while long-chain PFAAs are more likely to partition to carbonaceous materials,[91] including OM and EC, which can all be found associated with aerosol and soiled indoor surfaces.

OM dominated PM mass composition in all IPA Campaign homes (Fig. 3, S5, S6, Section S9, and Table S26†), in general agreement with previous residential indoor literature.[74,109] PM composition measurements were generally similar to one of the three cases shown in Fig. 3 (shown for Home 50), described as OM dominated (OM > 80% of sum of measured species), EC enriched (EC > 10%), or LWC enriched (LWC > 10%). Of the 19 sampling periods where PM species were measured, 13 samples were greater than 80% OM, three were still mostly OM but had greater than 10% EC, and three were mostly OM but had greater than 10% LWC. For all homes, OM contributed over 64% of mass, EC contributed <1–20%, and LWC contributed up to 20% of total measured PM mass. The mean (±standard deviation; σ) concentrations for the 19 sampling periods were 7.6 ± 6.4 μg m^{-3} for OM, 0.067 ± 0.058 μg m^{-3} for nitrate, 0.20 ± 0.11 μg m^{-3} for sulfate, 0.33 ± 0.43 μg m^{-3} for EC, and 0.37 ± 0.29 μg m^{-3} for LWC.

EC-enriched $PM_{2.5}$ samples (EC > 10%; Fig. S5†) were measured during sampling periods when participants noted fireplace use (Home 10), breadmaking (Home 43), large gatherings (Home 35), and hair dryer use (Home 65). LWC accounted for a larger percentage of PM mass (LWC > 10%; Fig. S5†) when nitrate concentrations were elevated in the home. Findings regarding aerosol composition are consistent with past indoor studies, although sulfate and OM concentrations in this study are lower than mean residential indoor values reported in earlier studies,[74,111] as discussed in Section S9.†

Estimated pH (see Table S26†) values ranged from −1.21 to −0.91. The pH of outdoor aerosols ranges from −1 to 5, and values are on the lower end of that range in NC.[112] Indoor pH has been reported to be lower than outdoors (by one unit) due to loss of ammonium nitrate and associated LWC from indoor aerosols as nitric acid is taken up by indoor surfaces.[113] This loss occurs despite higher indoor concentrations of ammonia (NH_3),[65] the dominant basic species indoors.[81,113] However, the pH of indoor aerosols is uncertain. The absolute numbers of our estimated pH values may be uncertain, particularly because we did not have gas-phase NH_3 concentrations to constrain the

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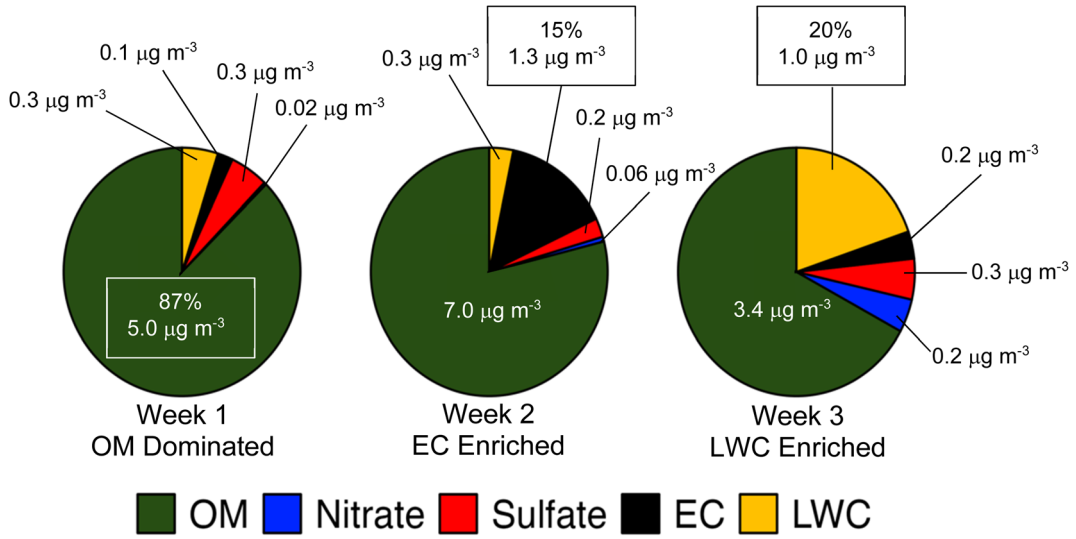

Fig. 3 Measured indoor PM species for Home 50 during Week 1, 2, and 3 sampling periods, representing the three compositional categories: OM dominated (OM > 80% of sum of measured species), EC enriched (EC > 10%), and LWC enriched (LWC > 10%) found in IPA Campaign homes. Shown are particulate OM (1.4 times particulate OC), nitrate, sulfate, EC, and aerosol LWC, which was calculated using E-AIM Model III.[80] Note: nitrate contribution in the OM dominated and EC enriched categories is negligible and the associated slice is not visible.

model, and we do not know to what extent indoor aerosol particle constituents are internally or externally mixed and whether individual aerosol particles are compositionally homogeneous or whether there is phase separation between an organic and inorganic/aqueous phase. However, we expect that the variations in these estimated values likely do reflect variations in aerosol pH. Since we are interested in examining how/whether variations in pH (and other PM features) correlate with variations in PFAS concentrations on indoor aerosols, we believe that there is merit in including these pH values into MLR analyses. Section S3† contains more information on LWC and pH estimations.

Predictors of PFAS concentrations and profiles

Below and in Section S10,† associations between ionic PFAS and characteristics of the aerosol and home environment are provided to stimulate further hypotheses regarding the fate and dynamics of ionic PFAS indoors. We would anticipate relationships with aerosol characteristics if PFAS are nearly equilibrated with the aerosol and the aerosol concentrations have been normalized by the gas-phase concentrations. However, equilibrium is not assured, and we did not measure gas-phase concentrations. Instead, we defined κ_p as a proxy for the equilibrium partitioning coefficient (eqn (2)); associations between κ_p and aerosol characteristics are discussed below. One complication is that PM species can be covariant. This is taken into consideration to greater degree by the MLR analyses than the single species Kendall's τ correlations. It is worth remembering as well, that interactions with indoor surfaces and surface grime can be a major driver of gas phase dynamics in buildings and thus can influence aerosol dynamics as well. Because of the complexity of the system, further research will be needed to test and refine any hypotheses suggested.

We found significant ($p < 0.05$; Kendall's τ) associations between the κ_p for ΣLong-chain PFCAs (Table S27†) and nitrate ($\tau = -0.69$) and OC ($\tau = -0.7$), while the κ_p for ΣShort-chain PFCAs was significantly ($p < 0.05$) and inversely associated with ammonium ($\tau = -0.71$) and sulfate ($\tau = -0.67$), as well as significantly ($p < 0.05$) and positively associated with both OC ($\tau = 0.53$) and EC ($\tau = 0.54$). The κ_p for ΣLong-chain PFSAs was significantly ($p < 0.05$) and positively associated with EC ($\tau = 0.55$) only, suggesting that increasing concentrations of EC are associated with a shift in long-chain PFSA concentrations into the particle-phase. Short-chain PFSAs and PAPs were excluded from analysis due their low DF on backup filters. No significant associations ($p < 0.05$) were found for κ_p of ΣPFAS, ΣPFSAs, and ΣPFCAs.

Significant associations between κ_p and particle species persisted in Stepwise MLR models ($p < 0.1$; Table 1) for the κ_p of ΣShort-chain PFCAs and ΣLong-chain PFSAs, but not for ΣLong-chain PFCAs. The κ_p for ΣShort-chain PFCAs was moderately (adj. $R^2 = 0.53$) associated with its predictors ($\beta_{OC} = 0.52$, $\beta_{EC} = 8.2$, $\beta_{Sulfate} = -0.8$, $\beta_{Ammonium} = -2.1$), while κ_p of ΣLong-chain PFSAs were weakly (adj. $R^2 = 0.23$) and significantly ($p < 0.1$) associated with EC ($\beta = 1.2$). Associations for κ_p for ΣShort-chain PFCAs with sulfate and ammonium were not significant in the MLR. Thus, the strongest evidence suggests that increased carbonaceous aerosol (OC and/or EC) is associated with a shift of short chain PFCAs and long chain PFSAs toward the particle phase.

For both MLR and Kendall's τ correlation results for short chain PFCAs, we found that when concentrations of OC and EC increased and ammonium and sulfate decreased, short chain PFCAs partitioned to a greater degree to the particle-phase (κ_p increased). Associations with OC and EC with κ_p were significant for both MLR and Kendall's τ, whereas associations with

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Table 1 Output from stepwise multiple linear regression results for κ_p (m^3 μg^{-1}) for different PFAS classes where indoor front filter PFAS concentrations were log-transformed but the auxiliary measurements were not[a]

κ_p (m^3 μg^{-1})	OC ($\mu g\ m^{-3}$)	EC ($\mu g\ m^{-3}$)	Nitrate ($\mu g\ m^{-3}$)	Sulfate ($\mu g\ m^{-3}$)	Ammonium ($\mu g\ m^{-3}$)	Int.	Adj. R^2	p
ΣLong PFCAs	−0.05	—	−0.01	—	—	0.94	−0.02	0.39
ΣShort PFCAs	0.52*	8.2*	—	−0.8	−2.1	−0.2	0.53	0.07
ΣLong PFSAs	—	1.2*	—	—	—	0.4	0.23	0.056

[a] Auxiliary measurements included in the model were particulate OC, EC, indoor RH (%) and T (°C), ammonium, sulfate, nitrate, and chloride in $\mu g\ m^{-3}$, and nitrate/sulfate ratio. ΣPAPs are not included in the table because no auxiliary measurements were predictors of ΣPAP concentration. Measurements marked with "*" are significant at $\alpha = 0.05$.

ammonium and sulfate were only significant for Kendall's τ. While associations with κ_p were significant, associations with the ΣShort-chain PFCAs concentrations themselves were not (Tables 2 and S28†). We propose that the observed shift in partitioning might be explained by increased sorption of short chain PFCAs to carbonaceous aerosol species. It is also plausible that the shift in partitioning is influenced by a change in particle-phase pH. Sulfate is a strong, low volatility acid. A decrease in the sulfate mass fraction might plausibly shift PFCA partitioning toward the particle phase by increasing aerosol pH, depending on the pK_a of the PFCAs relative to aerosol pH. Short chain and even long chain PFCAs are found, at least in part in the gas phase in the atmosphere, despite expectations that they are highly acidic (*i.e.*, have very low pK_a's).[57] Note that pK_a's of PFAAs are highly uncertain. Reported pK_a's have spanned several orders of magnitude; for example, from −0.5 (ref. 114) to 3.8 (ref. 115) for PFOA. Thus, the degree to which indoor aerosol (and indoor surface) pH affects PFCA partitioning is not yet clear.

For long chain PFCAs, Kendall's τ correlations (significant) suggest that when nitrate and OC concentrations are lower, more long-chain PFCAs partition to the particle-phase (Table S27†). MLR results were consistent but not significant (Table 1). Inverse (significant) associations with OC were also observed with the log-transformed ΣLong-chain PFCA concentrations themselves (Tables 2 and S28†). The inverse association of κ_p with OC for long chain PFCAs, not significant in MLR, differs from the findings for short chain PFCAs. Multiple factors could come into play here. The potential roles of acidity, water, and indoor surface dynamics are all worth exploring. These relationships may make sense with the following context. Homes with higher particulate OC concentrations may have also had higher indoor surface loadings of organics (*i.e.*, from cooking, which deposits long chain low volatility organics that persist on indoor surfaces). We expect the loading of surface-associated OC to be much larger than the mass of OC in aerosol. Since long chain PFCAs will more preferentially partition to long chain organic compounds, it is plausible homes with higher OC loadings may experience a shift of long-chain PFCAs from airborne particles to indoor surfaces.

There was also a significant inverse association of κ_p for long chain PFCAs with nitrate (Kendall's τ correlations); although an association with nitrate was not significant in MLR results. Nitrate/nitric acid can affect aerosol acidity in either direction. It can also affect aerosol partitioning by altering the chemistry and partitioning with indoor surfaces. It effects acidity directly because it is a weak acid and indirectly because it is the most hygroscopic aerosol component. Specifically, lower nitrate can mean less aerosol-associated water and lower aerosol pH. If the decrease in pH was sufficient to change κ_p, the shift would be toward the gas phase which is in the opposite direction than we observed. However, aerosol water can affect partitioning in other ways as well. Lower aerosol water might plausibly make carbonaceous aerosol components more accessible for partitioning of long chain PFCAs (*e.g.*, by inducing aerosol phase separation). If it did, this would help to explain the observed association. Additionally, it is well known that indoor surfaces (and associated surface grime) can have a major influence on the partitioning of semi-volatile species indoors, including nitrate/nitric acid and SVOCs. Upon transport indoors, loss of

Table 2 Output from stepwise multiple linear regression results for different PFAS classes where indoor front filter PFAS concentrations were log-transformed but the auxiliary measurements were not[a]

	Particulate OC	EC	ACH	RH_{Out}	Int.	Adj. R^2	p
Log(ΣPFAS)	0.071*	—	—	—	2.32	0.14	0.03
Log(ΣPFCAs)	0.077	—	—	—	1.52	0.069	0.1
Log(ΣPFSAs)	—	1.56*	2.58*	0.062	−5.05	0.33	0.007
Log(ΣLong PFCAs)	−0.096**	—	—	—	0.89	0.22	0.008
Log(ΣShort PFCAs)	0.11	—	—	—	0.73	0.093	0.063

[a] Auxiliary measurements included in the model were particulate OC, EC, and LWC (all in units of $\mu g\ m^{-3}$), ACH in units of h^{-1}, and indoor and outdoor RH (%) and T in °C. ΣPAPs are not included in the table because no auxiliary measurements were predictors of ΣPAP concentration. Measurements marked with "*" are significant at $\alpha = 0.05$ and those marked with ** are significant at $\alpha = 0.01$. Note that temperature and LWC did not improve the model for any PFAS and are thus not included in the table below.

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nitrate from aerosols is substantial along with its associated water. Ammonium nitrate transforms to ammonia and nitric acid, which are lost through deposition and sorption to indoor surfaces.[116] Furthermore, nitric acid is expected to partition to indoor surfaces, such as walls, more rapidly than ammonia, which exists preferentially in the gas-phase[113,116] (The pH of indoor surfaces is not well known, but is expected to be typically higher than aerosols). Nitric acid deposition to indoor surfaces might plausibly alter the partitioning of long chain PFCAs on aerosol by altering its partitioning on walls, due to changes in surface associated water or changes in surface pH. This example illustrates the complexity of the system. Our point is that there are a variety of ways that indoor surface dynamics may influence aerosol composition and the κ_p of ΣLong-chain PFCAs. However, to investigate this system further, concurrent measurements of gaseous nitric acid and ammonia, as well as indoor surface film composition are needed. Due to the high surface to volume ratio present indoors, the role that surfaces play in mediating indoor air quality warrants further investigation to better understand the fate and transport, as well as our exposure, to ionic PFAS.

For both MLR and Kendall's τ correlation results, increased EC was associated with a shift of ΣLong-chain PFSAs toward the particle phase, which most likely reflects partitioning of long chain PFSAs to carbonaceous aerosol. In addition, stepwise MLR models (Table 2) of log-ΣPFSAs concentrations themselves (adj. $R^2 = 0.33$) showed weak positive, but significant ($p < 0.05$) associations with the predictor variables EC, ACH, and outdoor RH. All adjusted R^2 values were <0.4. Regardless of the sources of PFSAs (indoor or outdoor), the positive associations between PFSA concentrations and EC and ACH might be explained by the fact that indoor EC mostly originates outdoors[101,117,118] (*e.g.*, automobile emissions[119,120]), and its indoor concentrations are higher when ACH is high. EC can also be emitted from solid fuel burning[120] (*i.e.*, fireplace use, used in one home), and sometimes cooking.[121] An association between EC and PFSAs might suggest a common origin for EC and PFSAs. PFSAs are used as additives in brake and hydraulic fluids to protect against corrosion,[122] and all homes were in suburban neighborhoods within 1 km of a major road. However, PFSA concentrations tended to be higher indoors, suggesting that there are significant indoor sources, such as carpeting and textiles.[123] Although PFSAs have been detected in food contact materials (*e.g.*, takeout containers and cookware[93]), the 6 days integrated samples collected in this study do not provide evidence for an association between cookware use and indoor PFSA concentrations (Table S29†). Most likely PFSAs emitted indoors partition to particulate EC which enters homes from outdoor sources.

Limitations

There are several limitations associated with this study. First, we recruited only 11 homes within a small geographic region in NC, and as a result, the profiles and concentrations may not be representative of the general population in the US, nor even within NC. Future studies should include more diverse homes, geographic regions, and participants from a wide range of socioeconomic statuses to provide a better understanding of PFAS in homes. Second, a larger sample size or finer time resolution may be able to identify the impact of activities (*e.g.*, showering, personal care product use, laundry frequency) on PFAS concentrations. Additionally, the varied nature of home floor plans, single *vs.* two-story homes, and proximity of the living room to the kitchen and bathroom, likely play a role in the variability of ionic PFAS concentrations in air, but the small sample size limited our ability to identify such associations. Third, while some gas-phase PFAS adsorbed on the QFFs, we did not measure total gas-phase PFAS, and because of sampling artifacts, we present upper-bound concentrations of particle-phase PFAS. Separate collection of gas- and particle-phase ionic PFAS may have been helpful in exploring the influence of aerosol composition on partitioning. However, separate collection of gas and particle phases remains challenging. Fourth, we did not assess the contributions of emissions to outdoor air compared to other emissions pathways, such as household sewage. Future studies should investigate other emissions pathways from homes to characterize the relative importance of various pathways to overall environmental emissions. Finally, this study investigated 26 ionic PFAS even though thousands of compounds exist.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts of interest to declare.

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