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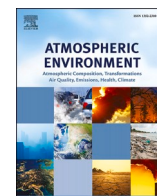
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Per- and polyfluoroalkyl substances (PFASs) in urban PM_{2.5} samples from Curitiba, Brazil

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HIGHLIGHTS

- First observation of PFASs i.e., PFOS, PFOA in PM_{2.5} and 6:2 FTS in PM in Brazil.
- Identified PFASs included those restricted by Stockholm convention.
- PFASs found in PM_{2.5} at low levels, but can accumulate in human tissues over time.
- PFASs were observed during Covid when most of the industrial activities were reduced.
- Research needed to confirm links between observed PFOS and pesticide-treated plantations.

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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs), also known as “forever chemicals” received significant attention during recent years due to their environmental persistence and emerging evidence on their toxicity to humans. In this work we present the first measurements of PFASs in inhalable fraction of airborne particles PM_{2.5} (particulate matter that has a diameter $\leq 2.5 \mu\text{m}$) in Brazil collected during Covid restriction period. Three PFASs that included perfluorooctanesulfonic acid (PFOS), a restricted by Stockholm convention perfluorooctanoic acid (PFOA), and 6:2 fluorotelomer sulfonate (6:2 FTS) were detected at concentrations up to 0.3 pg/m^3 . These values do not include uncertainties associated with potential adsorption of gas phase PFASs on the filters but may be lower than those generally occurring at Curitiba, Brazil due to an abrupt reduction in industrial activities and a major decrease in the use of transport during Covid lockdown. Although current air quality regulations do not set inhalable limits for PFASs, there is a concern that these substances can accumulate in human body.

The detection of 6:2 FTS in PM_{2.5} samples is a cause for concern due to its persistence in the atmosphere and emerging evidence that FTS could have health effects comparable with those of PFOA and PFOS. Multiple pollution sources of PFAS in Curitiba were considered based on air mass trajectories and wind roses.

Our results raise the question of whether the observed PFOS in Curitiba is linked to sulfluramid, a pesticide that is permitted for use in Brazil.

1. Introduction

Particulate matter (PM) specifically with an aerodynamic diameter $\leq 2.5 \mu\text{m}$ (PM_{2.5}) is of a great concern because it is small enough to penetrate deeply into the lungs and can cause a variety of health problems, including respiratory and cardiovascular diseases, as well as lung cancer. The World Health Organization (WHO) has established guidelines for PM_{2.5} concentration not to exceed $5 \mu\text{g/m}^3$ annually and $15 \mu\text{g/}$

m^3 daily (World Health Organization WHO, 2021). However, the potential health risks associated with exposure to PM_{2.5} cannot be fully represented by PM_{2.5} mass concentration alone, as the toxicity of fine particles may vary depending on their sources and composition (Lanphear, 2017; Park et al., 2018; Thurston et al., 2021; Kourtchev et al., 2022; Flanagan et al., 2023). When considering specific pollution components of PM_{2.5}, current Air Quality Standards Regulations require monitoring important but very small number of organic pollutants, e.g.,

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polycyclic aromatic hydrocarbons (PAHs), benzo(a)pyrene (Directive 2004/107/EC, 2004). In recent years, it became apparent that other harmful organic chemicals can be present in PM_{2.5}, which can be as toxic (or even more toxic) as currently monitored pollutants. These include a range of so-called persistent organic pollutants (POPs) and new and emerging pollutants (NEPs). For example, perfluoroalkyl and polyfluoroalkyl substances (PFASs) represent a group of thousands of chemicals some of which can belong to either POPs or NEPs. Due to unique PFAS' chemical and physical properties, such as resistance to heat, being water and oil repellents, they are used for a range of applications, e.g., to make non-stick coatings for cookware (such as Teflon), stain and water-resistant fabrics, food packaging and personal care products. PFAS, also known as "forever chemicals," are highly stable compounds because of their strong carbon-fluorine bond that is resistant to degradation from heat, light, and chemical reactions. These properties make PFAS persistent in the environment and challenging to eliminate once they are released. Therefore, they have been found in a variety of environments including surface waters, soil, sediment, and air (Kurwadkar et al., 2022; Wang et al., 2023; Lenka et al., 2021; Faust, 2023). Exposure to PFASs has been associated with a range of adverse health effects in humans, including altered immune and thyroid function, liver disease, lipid and insulin dysregulation, kidney disease, adverse reproductive and developmental outcomes, and cancer (e.g., Fenton et al., 2021).

Some steps have been taken to control and restrict the production of certain PFAS. For example, perfluorooctane sulfonic acid (PFOS) and its derivatives have been included in the list of restricted substances of the Stockholm Convention since 2009. Moreover, PFOS has been restricted under Annex I of the EU's Persistent Organic Pollutants (POPs) regulation. Another important and widely used PFAS, perfluorooctanoic acid (PFOA), its salts and related compounds, have also been included in the Stockholm Convention to eliminate their use. Since 2020, PFOA has been banned in Europe under the POPs regulation. Several countries beyond Europe supported the Stockholm convention related to PFAS initiative. For example, in 2021, the Government of Canada nominated long-chain perfluorocarboxylic acids (LC-PFCAs) for consideration under the Stockholm Convention on POPs. In the US, several states including California, New York, Maine, Vermont, Washington, Connecticut, and Minnesota adopted laws to ban the use of PFAS in food packaging starting from 2022/2023 (depending on the state). With regards to Brazil, in 2015, it launched the national implementation plan of the Stockholm Convention with the aim to guide national regulation and legislation, decision making and effective actions to address POPs throughout the supply chain and their lifecycle. However, according to several sources, Brazil still widely uses the pesticide sulfluramid (active ingredient n-ethylperfluorooctansulfonamid (EtFOSA)) for controlling leaf-cutting ants, which can degrade to PFOS. An extensive study of EtFOSA, PFOS, and other per- and polyfluoroalkyl substances (PFASs) in soil, eucalyptus leaves, water (ground, riverine, and coastal (estuarine/marine)) and coastal sediment from an agricultural region of Bahia State, Brazil, suggested that sulfluramid use contributes to the occurrence of PFASs in the Brazilian environment (Nascimento et al., 2018). Based on the observation of other than PFOS and EtFOSA PFAS compounds in studied environmental samples, Nascimento et al. (2018) suggested that other PFAS sources (in addition to sulfluramid) may be important in the studied region. Most of the current studies on PFAS are related to water, sediment, and wastewater (Kurwadkar et al., 2022; Wang et al., 2023; Lenka et al., 2021). However, compared to other environmental matrices there are fewer studies related to PFAS in PM (Faust, 2023), especially in South America including Brazil (Rauert et al., 2018; Saini et al., 2023). Moreover, to the authors' knowledge there are no literature data on PFAS in PM_{2.5} from Brazil, the fraction that is associated with increased mortality even at very low concentration (Vodanos and Schwartz, 2021; Di et al., 2017; Wei et al., 2020).

The aim of this work is to get preliminary insights on whether PFAS (including toxic PFOA and PFOS) are present in urban PM_{2.5} aerosol in

Brazil. To achieve this, a highly sensitive analytical technique, namely on-line solid phase extraction liquid chromatography high resolution mass spectrometry (online SPE-LC-HRMS) allowing screening 17 PFASs at the trace level in PM_{2.5} (Kourtchev et al., 2022) was applied to screen PM_{2.5} samples collected in Curitiba, the eighth most populous city in Brazil with population >1.9 million people (Brazilian Institute for Geography and Statistics (IBGE) estimate in 2021 (IBGE, 2023). On-line SPE allows simultaneous sample clean-up from interfering matrices and lower limits of detection (LODs) by injecting a large volume of sample (1 mL compared to a few μ L in conventional LC/MS methods) into the LC system without compromising chromatographic efficiency and resolution (Sanan and Magnuson, 2020; Kourtchev et al., 2022; Folorunsho et al., 2022; El Ouahabi et al., 2022).

2. Method

2.1. Chemical reagents

The reagents and chemicals used in this study include EPA-533PAR native analyte primary dilution standard mixture containing 25 PFASs (i.e. perfluoroalkylcarboxylic acids (C4–C12), perfluoroalkanesulfonates (C4, C5, C7 linear, C6 & C8 linear and branched isomers), 4:2 FTS, 6:2 FTS, 8:2 FTS, HFPO-DA, NaDONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, PF4O-PeA (PFMPA), PF5OHxA (PFMBA), 3,6-OPFHpA (NFDHA), & PFEEESA) at concentrations of 0.5 μ g/mL and EPA-533ES isotope dilution standard mixture containing 16 mass labelled (¹³C) PFASs (i.e., M3PFBS, M3PFHxS, M8PFOS, MPFBA, M5PFPeA, M5PFHxA, M4PFHpA, M8PFOA, M9PFNA, M6PFDA, M7PFUDa, MPFDaA, M2-4:2FTS, M2-6:2FTS, M2-8:2FTS and M3HFPO) at concentrations 0.5–2.0 μ g/mL (Wellington laboratories Inc.; Optima™ LC/MS grade methanol, water, ammonium acetate and formic acid (99.0+%), (Fisher Chemical). The full names of listed above abbreviated PFAS and corresponding isotopically labelled compounds are shown in Table S1 of the Supporting Information (SI).

2.2. Aerosol sampling procedure

PM_{2.5} aerosol were collected on 37 mm Quartz fibre filters (PALL Life Sciences, Pallflex®, Tissuquartz) using a Harvard impactor (Marple et al., 1987) at a sampling flow rate of 10 L/min. Quartz filters were baked at 650 °C for 24 h to remove any potential organic contaminants. Prewashed with ethanol stainless steel tweezers and Petri glass dishes were used during the filter handling and preparation, along with caution to avoid contaminations. After sampling, Quartz filters were folded in half, keeping the collected content inside, individually wrapped into aluminium foils (prewashed with 70% ethanol), and stored in a freezer until shipment for analysis.

Several blanks were prepared to assess a potential contribution of PFAS contaminations during the filter handling. The blanks included baked filters, freezer blanks (baked filter stored in a freezer), travel blanks (baked filters taken to the sampling site) and procedural blanks (baked filters exposed to air sampling for 2 min). It must be noted that the use of quartz fibre filters for aerosol sampling is linked to positive sampling artifacts (e.g., adsorption of gas-phase organic compounds) (Turpin et al., 1994). This can be of relevance when sampling some of the PFASs, which can dissociate to their ionic forms when sorbed in aqueous films on "wet particles" or in aqueous aerosols (Ahrens et al., 2012). This process is driven by atmospheric pH, temperatures, relative humidity and chemical pKa values (Ahrens et al., 2012) and can vary from one sampling day to another. In this respect, several studies observed PFOA and/or PFOS not only in the particle phase, but also in a gas phase (e.g., Riedel et al., 2019; Ahrens et al., 2012; McMurdo et al., 2008). Moreover, it has been suggested that the PFOA branched isomers will tend to partition less to the gas phase than the linear ones (e.g., McMurdo et al., 2008). Therefore, the exact measured concentrations of these species taken from the filter samples only can be potentially overestimated or underestimated.

3. Sampling site

Sampling of ambient PM_{2.5} took place in Ouvidor Pardiniho square in the city centre of Curitiba (25°26'40.81"S 49°16'18.36"W), south of Brazil. The sampler was installed within 3 m from the main street with regular car traffic and bus routes. Near the sampling site there is a hospital and a fire department. The sampler's inlet was 2.80 m above ground level. Samples were collected over 24-h periods (starting at 9AM BRT) from 30 November to 27 December 2020.

3.1. Aerosol analysis for PFASs

Aerosol samples were extracted and analysed using an online SPE-LC-HRMS method described elsewhere (Kourtchev et al., 2022). Briefly, 1.5 cm² of filter sample was spiked with an internal standard (IS) containing a mixture of 16 mass labelled (¹³C) PFASs at concentrations of 5 pg/mL and three telomer sulfonates (M2-4:2 FTS, M2-6:2 FTS and M2-8:2FTS) at 20 pg/mL. The spiked filters were left to dry for 5 min and then extracted with 2 mL of Optima LC/MS grade methanol using ultrasonic agitation. The extracts were reduced by volume to 1 mL using a gentle nitrogen flow, filtered through a prewashed 0.45 µm polytetrafluoroethylene (PTFE) syringe filter (see details on potential PFAS leachables from PTFE filters in our previous study, Kourtchev et al., 2022), followed by addition of 4 mL of Optima LC/MS grade water to provide 80:20 water methanol ratio required for the SPE method. The samples were vortexed and analysed for PFAS using Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ mass spectrometer (Thermo Fisher, Bremen, Germany) equipped with an electrospray ionisation (ESI) source (Thermo Scientific). Acquisition was performed in the negative ionisation mode using selected ion monitoring (SIM) where data were collected at a resolving power of 70,000, quadrupole isolation 1 amu and Orbitrap selectivity of 5 ppm. A list of PFASs, internal standards and corresponding target ions and retention times are shown in Table S1. On-line SPE and chromatographic separation were carried out on EQUAN MAX Plus Thermo Scientific™ Vanquish™ UHPLC system using a Thermo Scientific™ TriPlus™ RSH autosampler as described in Kourtchev et al. (2022).

Hypersil GOLD aQ Column, 20 × 2.1 mm, 12 µm (Thermo Scientific™) and CORTECS C18 Column, 90 Å, 100 × 2.1 mm, 2.7 µm (Waters®) were used as the on-line SPE and LC columns, respectively. Prior to the analysis of the aerosol samples and analytical standards, the system was continuously flushed with mobile phases A:B (A-2 mM Ammonium acetate in water with 10% methanol, and B-methanol) at 40:60% and a low flow rate (0.01 mL/min and 0.03 mL/min, over the weekend and overnight, respectively) to prevent accumulation of potential PFAS leachables from the system. At least 10 system ("zero volume") blanks were injected before sample analysis, between samples, and at the end of the sequence, followed by filter blanks, resulting in insignificant amounts (below LOQ) for PFAS from the system after the system purge. Several blanks (including procedural blanks) were processed in a similar way as aerosol samples (e.g., spiked with IS and extracted) and analysed for PFAS. The samples and blanks extracts were injected in three replicates providing relative standard deviation (RSD) < 10% between replicate injections.

It has been reported that several laboratories had problems meeting quality control acceptance criteria for 6:2 FTS due to background contamination (USEPA, 2023). Method 8327 suggested that the presence of PFAS contamination has been linked to a range of laboratory equipment, including reagents, glassware, tubing, LC vial caps made of PTFE, disposable pipets, aluminium foil, glass disposable pipettes, filters, degassers, and other apparatus that release PFAS. Therefore, extra care was taken to monitor 6:2 FTS along with other PFASs through zero volume, solvent, and procedural blanks (see above) analyses as well as assessment of PTFE containing materials (e.g., syringe filters) as described in Kourtchev et al. (2022). The applied method targeted non-volatile and semi-volatile PFASs present in an ionic form. The

method provides LODs in the range 0.08–0.5 pg/mL of sample extract allowing detection of selected PFAS in aerosol particles at low fg/m³ level with a good tolerance to the PM matrix (Kourtchev et al., 2022).

3.2. Air mass trajectories and wind roses

48-h air mass back-trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) dispersion model (Stein et al., 2015; Rolph et al., 2017) at 500 and 1000 m a.g.l. (above ground level) over the previous 48 h. The results are shown in Figs. S1 and S3 of the SI.

Wind roses were created using wind speed and wind direction data obtained from National Institute of Meteorology (INMET). The results are shown in Figs. S4 and S6 of the SI.

4. Results

Three PFAS compounds were observed in PM_{2.5} samples from Curitiba at concentrations significantly above the method's detection limit and that of blanks. These include perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and 6:2 fluorotelomer sulfonate (6:2 FTS). The corresponding PFAS concentrations and trends are summarised in Fig. 1. While PFOA was observed in all analysed samples, PFOS was present in 9 samples and 5 samples contained 6:2 FTS. To the authors knowledge, these are the first reported observations of PFASs including PFOS, PFOA in PM_{2.5} and 6:2 FTS in PM of any size in Brazil. Previous studies have identified PFOA as one of the most prevalent PFAS in PM in Europe and Asia (Barber et al., 2007; Yao et al., 2017; Kourtchev et al., 2022). The PFOA and PFOS concentrations found in this work were generally lower than those reported in other studies shown in Table S2. It is worth noting that the majority of the studies that reported extremely high concentrations of PFOA and PFOS were done close to the period when the production and use of PFOS and PFOA and their derivatives were not restricted (e.g., Barber et al., 2007) or the sampling was taken in highly industrialised regions (e.g., China, Yao et al., 2017). However, the concentrations of PFOS in the Curitiba samples were within the range of the PM_{2.5} concentrations observed in the US, i.e., Charlotte, Wilmington but higher than those found in Research Triangle Park in North Carolina (Zhou et al., 2021). More recent work by Zhou et al. (2022) found that PFOS was higher in total airborne samples collected near Chemours in Fayetteville, NC (i.e., 0.88–1.33 pg/m³ in quarterly averaged samples). The highest concentration of PFOS observed in Curitiba was almost 20 times higher than that recently observed in urban PM_{2.5} aerosol in Dublin, ROI (Kourtchev et al., 2022). The PFOA concentrations were within the lowest range of the observed concentrations in Wilmington and Research Triangle Park (Zhou et al., 2021) and those recently detected at Dublin and Enniscorthy, ROI (Kourtchev et al., 2022). 6:2 FTS was observed in aerosol samples in Curitiba at the range of 0.065–0.27 pg/m³. The average concentration of 6:2 FTS in Curitiba (0.14 pg/m³) samples was higher than the reported range in PM_{2.5} from Dublin and Enniscorthy (Kourtchev et al., 2022). Moreover, 6:2 FTS concentrations in Curitiba were higher than those reported more than a decade ago for a background aerosol in Mace Head, ROI and Hazlerigg, UK (Barber et al., 2007). It is worth noting that the aerosol from Hazlerigg was significantly influenced by PFAS pollution as suggested by high PFOA concentration peaking at the site at 552 pg/m³ (Barber et al., 2007). The PFAS concentrations in Curitiba were generally lower than those reported in the literature for aerosol measurements in Brazil and other countries in Central and South America (Table S2). For example, in 2017 PFOS and PFOA were observed in urban PM samples from São Luis do Maranhão, Brazil (13.2 and 24 pg/m³, respectively), background PM samples from São Jose dos Ausentes, Brazil (21.8 and 13.6 pg/m³) and Itatiaia, Brazil (22 and 17.8 pg/m³) (Saini et al., 2023). In another earlier study that performed sampling in Brazil in 2015 (Rauert et al., 2018), both PFOA and PFOS concentrations were also significantly higher than those observed at

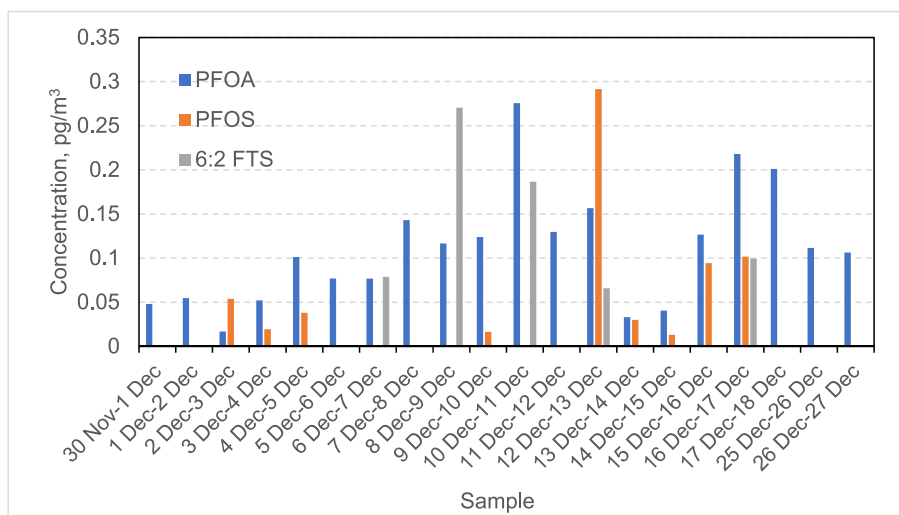


Fig. 1. Concentration of PFOA, PFOS and 6:2 FTS in 24h PM_{2.5} aerosol samples from Curitiba (Brazil) collected during 30 November – 27 December 2020.

Curitiba. Their reported concentrations for samples collected in São José dos Ausentes were 6.7 and < 15 pg/m³ for PFOS and PFOA, respectively. It must be noted that both reported studies by Saini et al. (2023) and Rauert et al. (2018) used a double-dome type passive air sampler, with sample collection interval over 90 days per sample. A direct comparison and assessment of an impact from the observations between the current work and the latter studies in Brazil are not possible as the PFAS concentrations were not only obtained from the different aerosol size fractions (approximately PM₅, see Markovic et al., 2015) but also had a chance to be influenced by multiple sources from local emissions and a long-range transport due to significantly longer sampling on a substrate where a single sample was taken over a three-month period.

4.1. PFAS sources

Considering that PFASs can have multiple potential sources and that none of the observed compounds can serve as a specific source tracer, linking our data to a single source is not possible. However, to understand the potential sources of the observed PFAS in Curitiba, air mass trajectories and wind roses were calculated and shown in Figs. S1–S3 and Figs. S4–S6, respectively. While wind roses can be used to understand the short term and local pollution transfer, the air mass trajectories are useful to understand the impact from long-range transport (Fleming et al., 2012). During the sampling period the sampling site was predominantly influenced by northerly winds (from North (N), Northeast (NE) and Northwest (NW)). There are several potential sources of PFASs located to the North of the sampling site. This includes Eucalyptus and Pine plantations located from the Northwest (NW) to NE of Curitiba (IFPRReSFB, 2023) that potentially might be treated with pesticide sulfluramid. In this respect, it has been previously reported that sulfluramid is used for the control of leaf-cutting ants (*Atta* spp. and *Acromyrmex* spp.), especially in Eucalyptus and Pine plantations (Nascimento et al., 2018). As per 2016 report by Löfstedt Gilljam et al. (2016), Brazil was permitted to manufacture and use sulfluramid, which can decompose into PFOS in the environment (Nguyen et al., 2013; Mejia Avendaño and Liu, 2015). The same study suggested that between 2004 and 2015, the production and import of sulfluramid in Brazil may have resulted in the release of between 167 and 487 tonnes of PFOS/FOSA into the environment.

Interestingly, samples that contained the highest PFOS concentrations corresponded to days with additional winds from North - NW direction (samples from 12 to 13 December, 15–16 December and 16–17 December).

One of the potential sources of PFOS, PFOA and 6:2 FTS observed at the site could be a wastewater treatment plant (WWTP), located to the

Northwest of the sampling site. It has been reported that WWTPs can give rise to PFASs (Ahrens et al., 2011). For example, the study by Ahrens et al. (2011) observed PFASs, i.e., fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs), sulfonamidoethanols (FOSEs), perfluoroalkyl sulfonic acids (PFASAs), and perfluoroalkyl carboxylic acids (PFCAs) with concentrations in air up to 15 times higher within the WWTP and 5–30 times higher at the landfill sites compared to the reference sites in Canada. Although their work didn't consider PFOS, PFOA and 6:2 FTS, these compounds can potentially be emitted by the latter sources. For example, PFOS and PFOA are shown to be produced during the WWTP biological treatment process, following degradation of polyfluoroalkyl precursors (Xiao, 2022). An additional potential source of PFASs at Curitiba may include fire stations that may still utilise the old stocks of firefighting foams containing PFOS. In this respect, the sampling site is located near fire station (less than 800m to the NW of the sampling site). It has been previously reported that the use of PFOS-based aqueous film forming foam (AFFF) from an old stock can lead to potential environmental contaminations (Young et al., 2021; Zhou et al., 2021). Interestingly, another compound 6:2 FTS observed in several Curitiba's samples, was previously linked to fire stations as well. A study conducted at a fire station in Massachusetts (USA) examined PFAS levels in dust and wipe samples. The findings, published by Young et al., in 2021, indicated the presence of three FTS, with 6:2 or 8:2 FTS being the most commonly observed species. However, in our work, PFOS and 6:2 FTS concentrations not only didn't correlate but also mainly occurred on different days (Fig. 1) which doesn't explain their common emission source at Curitiba. The occurrence of FTS has been observed previously in diverse environments, including drinking and surface waters, landfill leachate, influent and effluent of municipal wastewater treatment plants, and soil (Boiteux et al., 2017; Hamid et al., 2020; Houtz et al., 2016; Jarjour et al., 2022; Young et al., 2021). It must be noted that FTS have been found to be resistant to ozonolysis treatment in previous research (Boiteux et al., 2017). However, a study by Yang et al. (2014) discovered that 6:2 FTS can be fully degraded under ultraviolet (UV) irradiation with hydrogen peroxide. While the oxidation of hydrocarbons via ozone and hydroxyl radical reactions is a major atmospheric removal process, Yang et al. (2014) did not report the intensity of the lamps used in their photolysis study of 6:2 FTS. Another study reported successful photochemical degradation of 6:2 FTS at a wavelength of 254 nm (Jin et al., 2017), which has little relevance to lower tropospheric oxidative chemistry. As a result, it is difficult to generalise these findings to the potential atmospheric removal processes for FTS and link their presence to either fresh emissions or long-range transport. The PFOA was observed in all samples indicating a continuous emission

source of this pollutant, whether due to long range transport or from local emission source. A large fraction of sampling days corresponded to air masses either arriving or passing through the Atlantic Ocean and the second largest port of Brazil, Port of Paranaguá (Figs. S1–S3). A recent study by Sha et al. (2021) indicated that sea-spray can transport pollutants from contaminated waters (including oceans) into the atmosphere. Lab experiments with sea-spray showed that aerosol droplets can concentrate PFAS 1000s times higher than their levels in seawater (Sha et al., 2021). This study discovered a significant link between the sea spray tracer ion (Na^+) and the concentrations of PFAS (including legacy PFOA) in atmospheric samples from two coastal locations in Norway between 2018 and 2020. This finding suggests that sea spray aerosol might be a major contributor to atmospheric PFAS, particularly in coastal regions. Although there are no direct measurements of PFASs in Port of Paranaguá waters, PFASs have been detected through the Western Tropical Atlantic Ocean i.e., North, Equator, South Atlantic, and in the Brazilian coastal zone with the predominance PFOA along the transect (67%; 11 ± 8 pg/L) (Miranda et al., 2021). Therefore, a potential contribution of airborne PFOA in Curitiba from sea spray cannot be ruled out.

5. Conclusions

This study reports the first observations of PFASs including PFOS, PFOA in $\text{PM}_{2.5}$ and 6:2 FTS in PM of any size in Brazil. The concentrations of three PFASs in Curitiba were generally lower than those reported in the literature for limited aerosol measurements in Brazil, and other countries including Central and South America. Despite being detected at relatively low concentration in $\text{PM}_{2.5}$ in Curitiba, PFASs are known to accumulate in human tissues over time with lung tissues having the highest PFASs concentration (Pérez et al., 2013) and thus may increase the risk of acute lung toxicity and airway infections (Sorli et al., 2020). Considering that the current study was performed during Covid lockdown period, the range of detected PFAS species and concentrations observed during the studied period may have been lower or underestimated than the average levels either before or after the Covid restrictions. In this respect, it has been shown that Covid lockdown had a significant impact on air quality in other parts of the world because of reduced anthropogenic activities (Rives et al., 2023). As stated in the method section, the PFOA and PFOS concentrations taken solely from filter measurements may include potentially adsorbed fraction of PFASs from the gas phase. Our study suggests that the PFASs observed in Curitiba may originate from several sources, including industrial and domestic wastewater treatment plants as well as Eucalyptus and Pine plantations treated with PFOS precursor, sulfluramid pesticide, that is allowed for use in Brazil. Further work is needed to understand the PFOS and PFOA sources and extent of PFAS pollution in Curitiba to protect public health and the environment. Observation of fluorotelomer sulfonates 6:2 FTS (which is used as alternatives for toxic PFOA and PFOS) in ambient $\text{PM}_{2.5}$ samples in Curitiba raises a concern about its persistence in the atmosphere and impact on human health considering emerging evidence that it could be as toxic as PFOA and PFOS.

CRedit authorship contribution statement

Ivan Kourtchev: Conceptualization, Project administration, Methodology, Investigation, Resources, Formal analysis, Writing – original draft, Writing – review & editing, Data curation. **Bruna G. Sebben:** Investigation, Resources, Formal analysis, Writing – original draft, Writing – review & editing. **Anna Bogush:** Conceptualization. **Ana Flavia L. Godoi:** Conceptualization, Writing – review & editing. **Ricardo H.M. Godoi:** Conceptualization, Project administration, Methodology, Investigation, Resources, Writing – original draft, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2023.119911>.

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