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Occurrence of a “forever chemical” in the atmosphere above pristine Amazon Forest

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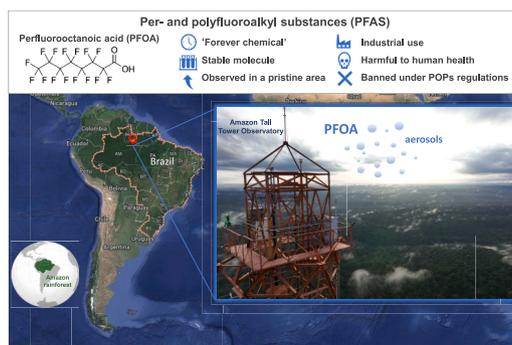
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HIGHLIGHTS

- First measurements of PFAS in atmosphere above pristine Amazon Forest
- Perfluorooctanoic acid (PFOA) concentrations reached up to 2 pg/m³.
- Strong dependency of PFOA levels with the measurement heights
- PFOA spikes coincided with long range polluted air masses from urban area.
- Results raise concerns over potential impact on endangered Amazon biota.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS), often referred to as “forever chemicals”, are a class of man-made, extremely stable chemicals, which are widely used in industrial and commercial applications. Exposure to some PFAS is now known to be detrimental to human health. By virtue of PFAS long residence times, they are widely detected in the environment, including remote locations such as the Arctics, where the origin of the PFAS is poorly understood. It has been suggested that PFAS may be transported through contaminated waters, leading to accumulation in coastal areas, where they can be aerosolised via sea spray, thereby extending their geographical distribution far beyond their original source regions.

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The aim of this work is to investigate, for the first time, whether “forever chemicals” could be transported to areas considered to be pristine, far from coastal sites. This study was performed at the Amazonian Tall Tower Observatory (ATTO), a unique remote site situated in the middle of the Amazon rainforest, where a restricted PFAS, perfluorooctanoic acid (PFOA), was observed with concentrations reaching up to 2 pg/m^3 . A clear trend of increasing concentration with sampling height was observed and air masses from the south over Manaus had the highest concentrations. Atmospheric lifetime estimations, removal mechanisms supported by measurements at two heights (320 and 42 m above the rainforest), and concentration spikes indicated a long-range transport of PFOA to pristine Amazon rainforest. Potential sources, including industrial activities in urban areas, were explored, and historical fire management practices considered.

This research presents the first measurements of PFAS in the atmosphere of Amazon rainforest. Remarkably, even in this remote natural environment, appreciable levels of PFAS can be detected. This study provides valuable insights into the long-range transport of the anthropogenic “forever chemical” into a remote natural ecosystem and should raise awareness of potential environmental implications.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of man-made, extremely stable chemicals. Accordingly, they are colloquially referred to as “forever chemicals”. Due to the ability of PFAS to repel water and oil, withstand high temperatures and other chemicals, they are widely used in industrial, consumer and commercial applications (Glüge et al., 2020). As stated in the recent review on PFAS toxicity and human health: “widespread human exposure to PFAS in water, food, and air coupled with the lengthy environmental persistence and biological half-lives of some PFAS have led to measurable PFAS in the blood of nearly the entire population in developed countries, with health effects reported globally” (Fenton et al., 2021). Exposure to PFAS is suggested to be associated with a range of human health effects, including liver damage, reduced immune response, thyroid disease, and endocrine-disruption (Fenton et al., 2021; Bartell and Vieira, 2021; US Department of Health and Human Services, 2016).

Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been the most extensively produced and studied PFAS compounds (US EPA, 2024a). The majority of environmental studies on PFAS, and thus local or governmental regulations, are generally associated with water pollution as the ingestion is considered the largest exposure route to humans, dominating over dermal and inhalation uptake rates (Chambers et al., 2021). PFOA and its salts were included in the Stockholm Convention on Persistent Organic Pollutants and were banned in 2020. In the US, the EPA issued health advisories in 2016, specifying that the recommended limit for PFOA and PFOS in drinking water should not exceed 70 parts per trillion (ppt). It must be noted that those advisories were limited to drinking water and none of the other matrices were considered. In April 2024, the US EPA announced the final National Primary Drinking Water Regulation (NPDWR) for six PFAS with enforceable levels of 4 ppt for PFOA and PFOS in drinking water (US EPA, 2024b). From the regulatory side, significantly less attention, if any, has been given to air pollution by PFAS. However, the PFAS analysis of autopsy tissues (brain, liver, lung, bone, and kidney) has shown that lung tissues accumulate the highest concentration of “forever chemicals” (Pérez et al., 2013). PFOA alone is shown to induce airway inflammation and alter airway function (Ryu et al., 2014; Dragon et al., 2023). Both PFOA and PFOS have relatively low vapour pressure, 3.16×10^{-1} and 2.00×10^{-3} mmHg at 25°C , respectively, and thus can partition onto aerosol particles. It should be noted that PFOA, in its acidic form, may also exist in the gas phase at typical ambient temperatures (McMurdo et al., 2008; Sinclair et al., 2007). Although, PFOS and PFOA have been phased out in certain countries and substituted by less toxic alternatives, they can still be widely detected in atmospheric samples (see review by Faust, 2023). For example, PFOA has been previously identified as one of the dominant PFAS in PM collected in several European countries (e.g., Barber et al., 2007; Kourtchev et al., 2022), US (e.g., Zhou et al., 2021) and Asia (e.g., Lin et al., 2020).

The highest concentrations of PFOA were generally observed near, or

linked to, industrial activities (e.g., Barber et al., 2007; Wang et al., 2021). For example, extremely high concentrations of PFOA (up to 552 pg/m^3) were observed in total suspended particles (TSP) in the semi-rural area of Hazlerigg, Lancaster, England (in February–March 2005) and attributed to the proximity of the sampling sites to a fluoropolymer production plant (Barber et al., 2007). In a more recent study, in China, PFOA was found as a predominant PFAS near a fluorochemical manufacturer with alarming concentrations, up to 9730 pg/m^3 (Wang et al., 2021). Furthermore, PFOA was identified as the major species in dust near fire stations or airports, where firefighting exercises have led to PFAS contamination of soil, groundwater, and surface water in the surrounding areas (Young et al., 2021; Mesfin et al., 2022; Mazumder et al., 2023). PFAS were used as components of aqueous film forming foam (AFFF), a fire suppressant that has been manufactured and used in firefighting applications since the late 1960s (Leeson et al., 2021; US Government Accountability Office, 2018).

Due to their extreme stability, PFAS have been previously observed in remote locations that were considered pristine, e.g., Mace Head, Republic of Ireland (Jahnke et al., 2009), the Arctic (Xie et al., 2015) and High Arctic (Young et al., 2007) areas; however, the exact transfer mechanism for these substances in the atmosphere remains unclear. It has been suggested that perfluoroalkyl acids found in the environment may originate from the degradation of volatile precursors e.g., fluorotelomer alcohols (FTOHs) or oxidation of perfluorooctane sulfamido alcohols, including perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs) (Ellis et al., 2004; Martin et al., 2006). A recent study by Sha et al. (2022) suggested that PFAS can be transported through contaminated waters, influenced by the widespread use of “forever chemicals,” and ultimately accumulate in coastal zones. The chemicals can then be aerosolised via sea spray, expanding the geographical reach of PFAS far beyond their initial point of release (Johansson et al., 2019).

In this study, we selected a unique, remote but instrumented measurement site in the Amazon Forest, the Amazonian Tall Tower Observatory (ATTO), situated ≥ 800 km from the coastal areas, to investigate, for the first time, whether “forever chemicals” can be transported to natural areas in the continental interior far from coastal sites.

The sampling site is located 150 km northeast from Manaus, the 7th most populous city in Brazil. Due to its geographical position, the site generally experiences North-Easterly winds (especially during “wet” season – April–May) with minimal impact from local human activities (Pöhlker et al., 2019). This makes it an ideal place to study a potential transfer of pollutants to pristine area. The sampling tower is 325 m tall, extending well above the surface roughness layer (canopy height ~ 40 m), and allowing the study of air masses transported over several hundred kilometres of rainforest. Understanding how PFAS reach, and impact remote environments is crucial for assessing their global environmental implications and potential risks.

2. Experimental section

2.1. Site description

ATTO is situated in a pristine rainforest region within the central Amazon Basin, Brazil, approximately 150 km northeast of Manaus city with coordinates S 2° 08' 45.13" W 59° 00' 20.12". Full description of the sampling site can be found in [Andreae et al. \(2015\)](#).

2.2. Meteorological data

The meteorological data was obtained from the ATTO Tower at the measurement heights 40 and 316 m. Air temperature and relative humidity (RH) parameters were measured by a compact and precise sensor (I-Series, GALLTEC MELA Ltd., Germany). Precipitation was recorded using a EML ARG100 sensor, installed at 81 m at the Instant Tower. Wind speed and wind directions were recorded using a CSAT3B - Campbell sensor, installed at 316 m of the ATTO Tower. Meteorological data (i.e., temperature, relative humidity, precipitation and wind speed) from Manaus were acquired from National Institute of Meteorology (INMET, 2024). The overall meteorological conditions in the central Amazon during May 2022 were not marked by any anomalies (Fig. S1), except 19 and 20th May 2022 which were marked by a sudden change in the typical temperature (Fig. S2) and wind patterns (Fig. S3) in the region. It is known that the Amazon region can be impacted by the incursion of cold waves (called in literature as Friagem) from the high latitudes of the Southern Hemisphere, with a relatively common occurrence ([Marengo et al., 1997](#); [Camarinha-Neto et al., 2021](#)).

2.3. Air mass trajectories

Air mass back-trajectories (48 h) were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) dispersion model ([Stein et al., 2015](#); [Rolph et al., 2017](#)) with starting heights 42, 316 and 320 m above ground level. The results are shown in Figs. S4-S9 of the SI.

2.4. Sample collection

Total suspended particles (TSP) were collected on 150 mm glass fibre filters (Type MN-85/90BF; Macherey-Nagel GmbH & Co. KG, Düren, Germany) with retention capacity $\geq 0.5 \mu\text{m}$. Prior to sampling, the filters were baked at 400 °C for 10 h and mounted on a precleaned filter holder. The Teflon ring from the filter holder was removed to avoid potential contaminations with PFAS.

TSP was collected using two high-volume aerosol samplers (Digital DHA-80, Switzerland) running in parallel at 1000 L/min, at two heights (42 and 320 m) and over 24-hour intervals allowing collection of sufficient organic mass from the pristine environment. 29 samples in total (15 at 42 m and 14 at 320 m) were collected between 7 and 21 May 2022. May belongs to the cleanest months at ATTO with generally very low pollution levels and episodes that can be regarded as atmospherically pristine ([Pöhlker et al., 2018](#); [Holanda et al., 2023](#)).

After sampling, glass filters were split into two halves, individually wrapped into baked aluminium foils, and stored at -20 °C until shipment for analysis.

Due to the requirements related to another project, the lab bench, interior of the sampler, and the surfaces of tools were precleaned, before handling each filter, using Bacillol® AF (an alcohol-based rapid disinfectant with an extensive spectrum of activity that dries without leaving residues).

Several types of blanks were prepared to assess potential PFAS contaminations from filter handling. These include: (1) baked filters, (2) baked filters contacted with scissors and tweezers, (3) baked filters that were placed into the sampler filter holder (at two heights) for 2 min, (4) baked filters held in the sampler (at two heights) and air drawn at 1000

L/min for 5 min.

2.5. PFAS analysis

Aerosol filter samples were extracted and analysed using an online solid-phase extraction (SPE)-LC-HRMS method described in [Kourtchev et al. \(2022\)](#). Briefly, a filter portion (area of 5.9 to 7.4 cm²) was spiked with internal standard (IS) mixture containing 16 mass labelled (¹³C) PFAS at 5 pg/mL and three telomer sulfonates (M2-4:2 FTS, M2-6:2 FTS and M2-8:2 FTS) at 20 pg/mL. After allowing the spiked filters to air-dry for 5 min, they were subjected to extraction with 5 mL of Optima® LC/MS grade methanol using ultrasonic agitation for 20 min. The procedure was repeated two times. The resulting extracts were then combined, reduced by volume to 1 mL under a gentle nitrogen flow, and filtered through a prewashed 0.45 μm polytetrafluoroethylene (PTFE) syringe filter. The details on PTFE filter conditioning and assessment for PFAS leachables are discussed in our earlier study, [Kourtchev et al. \(2022\)](#). It has been demonstrated that PTFE filters can be a source of PFOA, PFNA, PFHpA and PFDA; however, purging the filters 3 times with 5 mL of Optima LC/MS Grade methanol (total volume 15 mL) reduces PFAS contaminations to a background level ([Kourtchev et al., 2022](#)).

4 mL of Optima LC/MS grade water was added to each methanolic extract to provide 80:20 water methanol ratio required for the SPE method. The samples then were vortex mixed and subjected to an online SPE. The chromatographic separation was achieved using the EQUAN MAX Plus Thermo Scientific™ Vanquish™ UHPLC system, with a Thermo Scientific™ TriPlus™ RSH autosampler. The details on the mobile phase, LC gradient parameters, and system conditioning are described in [Kourtchev et al. \(2022\)](#) and [Kourtchev et al. \(2023\)](#) and summarised in Table S1. The method validation parameters are summarised in Table S2. The samples were screened for 17 PFAS; however, only PFOA was observed significantly above the method's LOD (0.18 pg/mL, [Kourtchev et al., 2022](#)).

Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ mass spectrometer (Thermo Fisher, Bremen, Germany) was fitted with heated electrospray ionisation (HESI) source (Thermo Scientific). MS analysis was performed in negative ionisation mode using selected ion monitoring. The instrument was operated at 70,000 (at m/z 400) mass resolving power and mass accuracy (≤ 5 ppm). Table S3 provides details on target PFAS, internal standards, corresponding target ions and chromatographic retention times. The PFOA concentration in the blanks was below the method's LOD.

Screening of samples for traces of 8:2 fluorotelomer alcohol (8:2 FTOH), a potential precursor of PFOA, not amenable to the method listed above, was done using a direct infusion analysis as described in [Kourtchev et al. \(2020\)](#). Briefly, the aerosol sample extracts were directly infused into the MS at a flow rate of 7 $\mu\text{L}/\text{min}$, spray voltage 3.5 kV (negative mode), AGC target 1e6, maximum inject time 50. The authentic standard solution of 8:2 FTOH was used to check if the compound can be ionised by the applied technique and then aerosol samples were screened for a presence of the deprotonated ion of 8:2 FTOH (m/z 463.000) within 5 ppm mass error.

3. Results and discussion

Fig. 1 shows the distribution of PFOA during the sampling period measured at two heights (42 and 320 m). The average 24-hour concentrations of PFOA varied between 0.01 and 2.0 pg/m³. Overall, higher concentrations of PFOA were detected at 320 m compared to that at 42 m (**Fig. 1**). PFOA (in the conjugated form) has a very low vapour pressure and thus is expected to be mainly found in particle phase ([Kaiser et al., 2005](#)). However, in the acid form, PFOA is more volatile and can be also present in the gas phase ([McMurdo et al., 2008](#); [Sinclair et al., 2007](#)). Owing to PFOA's water solubility ($\sim 3.4 \text{ g/L}$ and $26 \mu\text{g/L}$, in the conjugated and acid form respectively ([McMurdo et al., 2008](#))), one could expect that the RH difference at 42 m (just above the canopy) and

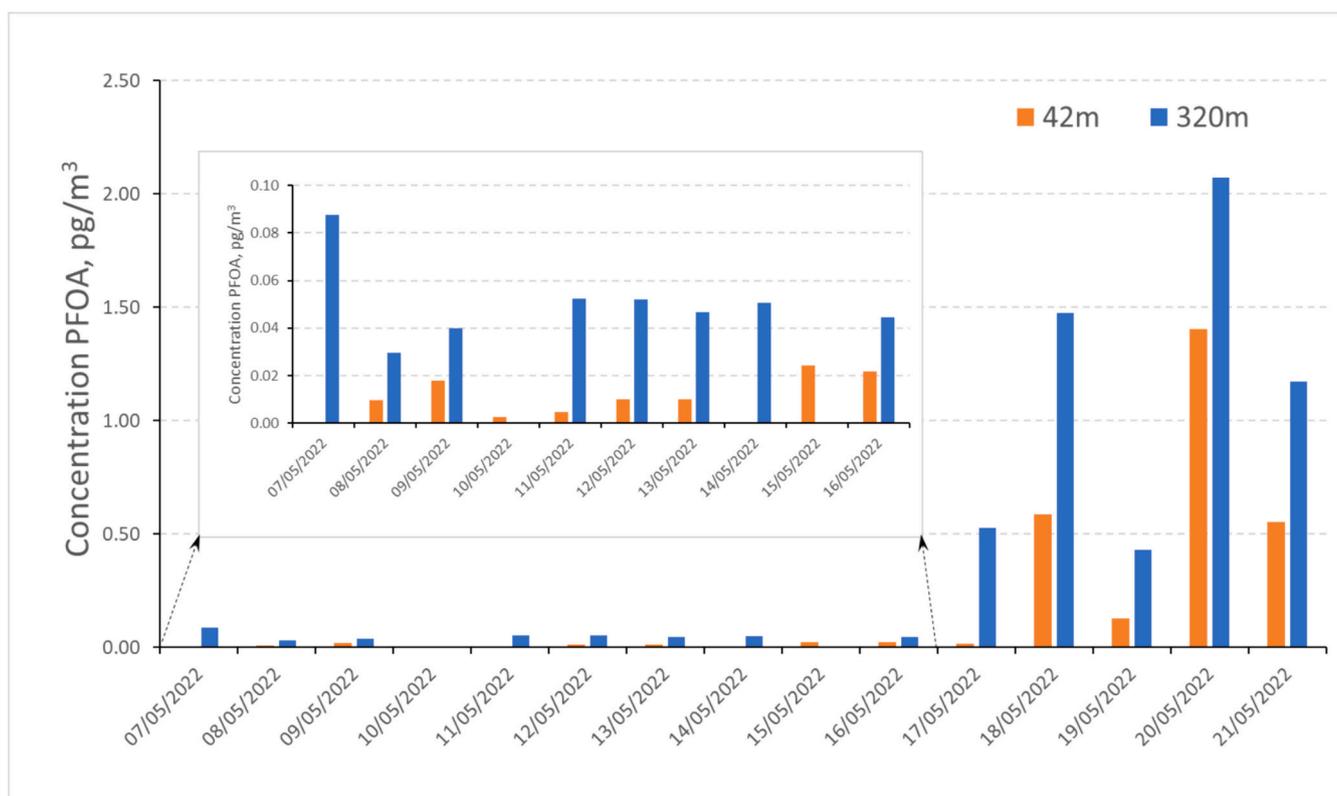


Fig. 1. Perfluorooctanoic acid (PFOA) 24-h average concentrations at ATTO measured at 42 m and 320 m. PFOA concentration at 42 m on 14th May 2022 was below method LOD, whereas on the 15th May no sample was collected at 320 m.

at 320 m may be the reason for the observed differences in the PFOA concentrations. Although the RH was generally higher at 42 m than that at 320 m during the night (reaching up to 100 %), an opposite compensating trend was observed during the day (Fig. S10) giving a rather small RH difference (average 0 to 6.8 %, depending on the day) when averaged over 24-hour sample collection period. There is currently no consensus over the atmospheric lifetime of PFOA in the literature. However, with respect to reaction with OH radicals, PFOA atmospheric lifetime is estimated to be approximately 130 days (Hurley et al., 2004). The main removal mechanism of PFOA in the atmosphere is through either wet or dry deposition, with estimated lifetimes of approximately 10–12 days (Hurley et al., 2004; Wallington et al., 2006). In general, concentration of a pollutant emitted from the surface is expected to decrease with height due to dispersion and dilution effects as the pollutants are transported away from their sources (Watson et al., 1988). Considering that the concentration of PFOA at 320 m was significantly greater than that observed just above the canopy, it is unlikely that these pollutants were emitted from the local or immediate source. Although the sampling was done during the wet season, the particular sampling period was not marked by extensive local precipitation (Fig. S11) showing no correlation with PFOA concentration trends.

Owing to the long atmospheric lifetime of PFOA, it potentially can be transported long distances away from its emission sources. In this respect, PFOA along with other PFAS e.g., fluorotelomer alcohols (FTOHs) and perfluorobutanoic acid (PFBA) were previously found in the Arctic atmosphere during the measurements between 2006 and 2014 (Muir et al., 2019). The spikes in PFOA concentrations, determined in this study, coincided with air mass trajectories coming from the south of Brazil, passing through Manaus (a large city with population of 2.2 million) and Manacapuru (population 98.5 K) (Figs. S5, S7 and S9). As mentioned in the introduction section, PFOA can have multiple sources in the environment, including industrial processes, firefighting foam,

consumer goods, landfills, biosolids (Glüge et al., 2020) and municipal landfill leachate (Capozzi et al., 2023).

Manaus hosts several industrial chemical plants with a known history of PFAS production or use; however, there is no available information indicating whether they are still manufacturing or use PFOA related products or their precursors. It has been shown previously that PFOA can be transported away from chemical plants through air emissions and subsequently deposited in the adjacent landscape (Brandsma et al., 2018; Gerardu et al., 2023). Although, to the authors' knowledge, this is the first study that reports PFOA in ambient air of the State of Amazonas, PFOA (along with other 11 PFAS) has been detected in surface waters of the Amazon River indicating Manaus and Belem as pollution hot-spots (Gonzalez-Gaya et al., 2021). Substantially lower PFOA concentrations were observed from 7 May to 15 May 2022 (Fig. 1) when the air masses arrived from northeast and east (Figs. S4, S6 and S8). To the northeast, the closest area with significant human activity lies in the coastal regions of the Guyanas and Amapá State, approximately 1100 km away from the ATTO site. To the east of ATTO there are sparse smaller towns and the cities of Santarém and Belém at distances of around 500 and 900 km, respectively (Andreae et al., 2015).

One of the well-recognised sources of PFOA pollution includes PFAS-containing AFFF (East et al., 2021; Reinikainen et al., 2022). It must be noted that the Amazon Forest is still impacted by forest fires. However, according to National Institute for Space Research-Fire Monitoring Portal, during the sampling period, most of the fires were recorded to the South (>500 km to the Southeast and Southwest) of ATTO (Fig. 2), which coincided with the air mass trajectories when the highest concentration of PFOA was detected. Also, it is important to mention that between May 19 and 20, 2022, a Friagem event occurred in the Manaus region and at the ATTO site. One of the main characteristics of this phenomenon is the abrupt drop in temperature (Fig. S2) and the change in wind direction from northeast/southeast to southwest/west (Fig. S3) i.e., air masses arriving to ATTO from the direction of Manaus.

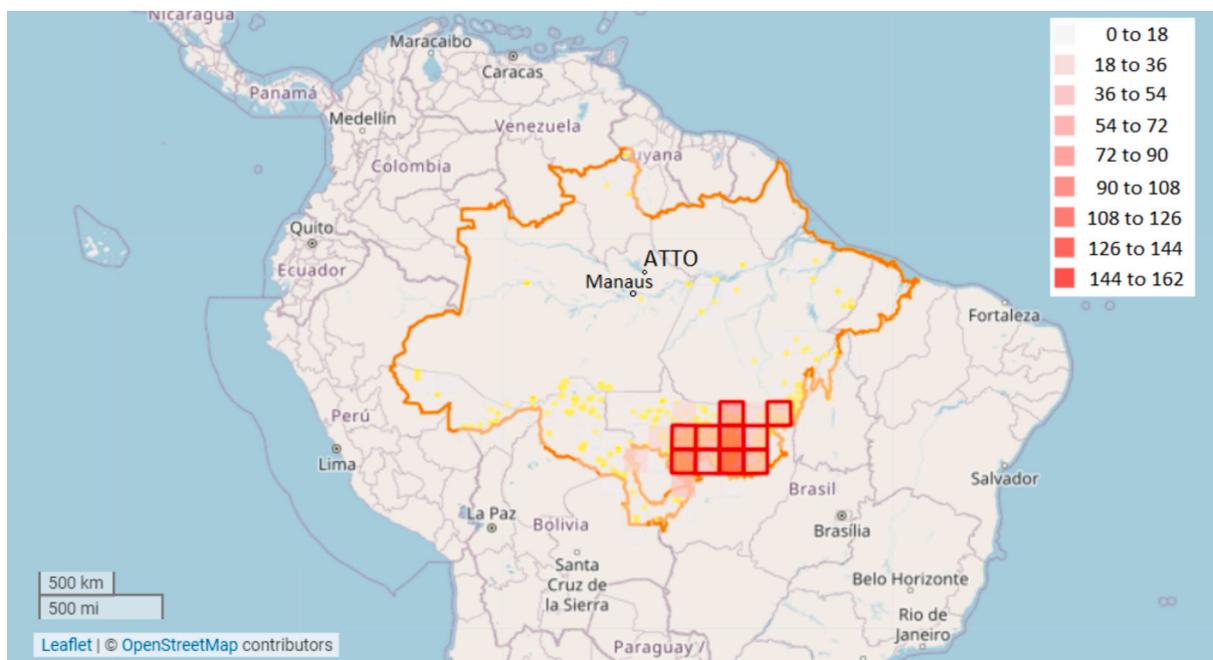


Fig. 2. Occurrence of fires in Amazon Basin during the sampling period (between 7 May and 15 May 2022). The sampling site is marked as ATTO (Amazon Tall Tower Observatory). The affected by fires areas are marked as red square and the number of wildfire outbreaks are indicated on the color-coded legend. Data and map source: <http://terrabrasilis.dpi.inpe.br/queimadas/portal/>.

[Camarinha-Neto et al. \(2021\)](#) investigated a Friagem event at the ATTO site. They showed that the Friagem arriving to ATTO from the southwest carried the air mass with a higher concentration of pollutants, compared to the air masses present at the ATTO site.

Although, there are no open-source reports on the use of PFAS-containing AFFF near the site, there is a history of using unspecified flame retardants to put out fires in the Amazon Forest ([Spring, 2021](#)) and other protected areas in Brazil, e.g., a national park Chapada dos Veadeiros, located in state of Goiás ([Menegassi, 2021](#)). PFAS-containing AFFF have been linked to several cases of environmental contamination of soil and drinking water across the US and EU ([East et al., 2021](#), [Reinikainen et al., 2022](#)).

To the authors' knowledge, this is the first measurement of PFAS above the Amazon Forest; therefore, no direct comparison of observed concentration with previous studies at the site could be made.

However, the observed concentrations ($0.01\text{--}2.0\text{ pg/m}^3$) in the current study are in line with those reported for other pristine areas, e.g., the Arctic atmosphere. For example, PFOA was detected at Alert Canada, 2006–2014 ($<0.0063\text{--}1.3\text{ pg/m}^3$), Zeppelin, Svalbard, Norway, 2006–2014 ($<0.12\text{--}4.0\text{ pg/m}^3$) and Andøya, Norway, 2010–2014 ($<0.12\text{--}5.5\text{ pg/m}^3$) ([Wong et al., 2018](#)). Based on the temporal, seasonal distribution and air mass trajectories, [Wong et al. \(2018\)](#) suggested that PFOA can be either formed from atmospheric oxidation of precursors or in sea spray aerosols under open water conditions in the summer. Sea spray has been recently linked to a global transfer of PFOA in the atmosphere. For example, using a sea-spray chamber [Johansson et al. \(2019\)](#) have observed a notable enrichment of PFAS in aerosols from fortified water. In the subsequent field study, based on the correlation between sea spray tracer Na^+ and perfluoroalkyl acids concentration at two Norwegian coastal locations, Andøya and Birkenes, sea spray was proposed as a source of the perfluoroalkyl acids (including PFOA) in the atmosphere ([Sha et al., 2022](#)). Although such a transfer route of the pollutant can be relevant to coastal areas, the ATTO site is located >800 km from Atlantic Ocean (to the Northeast) and 1000 km from South Pacific Ocean (to the West); therefore, sea spray is an unlikely source of PFOA at the measured site. Moreover, the highest PFOA concentration corresponds to inland trajectories.

In general, PFOA concentrations in the Amazon Forest were lower than those reported in limited studies for urban and background areas of Brazil. For example, [Saini et al. \(2023\)](#) detected PFOA in urban air samples from São Luis do Maranhão (24 pg/m^3), background samples from São Jose dos Ausentes (13.6 pg/m^3) and Itatiaia (17.8 pg/m^3). It must be noted that the latter study used a passive sampler with PUF as a substrate; therefore, their measured values could also include larger fraction of gas phase PFOA compared to that expected due to adsorption on the glass fibre filters (as sampling artifacts).

It should be noted that PFOA concentration in pristine Amazon Forest was higher than that observed recently in Curitiba, the 6th most populous city in Brazil ([Kourtchev et al., 2023](#)). Although, the latter study has looked at a different aerosol size fraction ($\text{PM}_{2.5}$) compared to that (TSP) in the current study, the difference in the aerosol fraction is unlikely to be the reason for such unexpected observations. In this respect, [Dreyer et al. \(2015\)](#) investigated particle-size distribution of PFAS and indicated that PFOA was predominantly observed in the smallest size fraction ($<0.14\text{ }\mu\text{m}$), which is a subset included in both $\text{PM}_{2.5}$ and TSP.

Given the comparable population sizes of Curitiba and Manaus (the city that was passed over by the southerly air mass trajectories), it is reasonable to propose that variations in industrial activities between these cities could be a contributing factor to the observed differences. However, more studies, especially in the urban areas (e.g., Manaus) are needed to support this suggestion.

Another potential route of PFOA formation in the environment, frequently discussed in the literature, is atmospheric oxidation of a gas phase 8:2 fluorotelomer alcohol (8:2 FTOH) by hydroperoxyl radical ([Ellis et al., 2004](#)) or biodegradation ([Dinglasan et al., 2004](#)).

In a later modelling study, [Wallington et al. \(2006\)](#) suggested that under typical atmospheric conditions, molar yields of PFOA (in the range of 1–10 %) initiated by reaction with OH radicals can explain the observed levels of the perfluorinated carboxylic acid in Arctic fauna (depending on location and season). Although appreciable OH levels have been detected over the Amazon ([Ringsdorf et al., 2023](#)), it is highly likely that, compared to the Arctic, there will be more competition with numerous very reactive biogenic volatile organic compounds (BVOCs)

emitted by the rich forest vegetation in the Amazon. Because of the high volatility of FTOH and its low ionisation efficiency, particularly in the presence of a complex matrix when using negative electrospray ionisation (ESI), the analysis of filter samples for 8:2 FTOH has not yielded any corroborating information to substantiate the mentioned above PFOA formation route in Amazon.

4. Conclusions

In this study we report the first measurements of PFOA, an anthropogenic “forever chemical”, in the atmosphere above an area of the Amazon rainforest that was considered pristine. Higher PFOA levels detected at 320 m compared to that at 42 m (canopy height ~40 m) suggest a long-range transport provenance rather than local sources. The peaks in PFOA concentrations coincided with polluted air masses from the south of the sampling site, likely originating from Manaus, the 7th largest city in Brazil located 150 km from ATTO. Manaus hosts several industrial activities that could potentially explain the observation of PFOA at Amazon.

While the observed PFOA concentrations at ATTO were similar to those in other remote environments, they surpassed levels recently detected in urban locations in Brazil. Based on the observations of PFOA at considerable distance from the coastline, our study suggests that transport mechanisms other than sea spray transfer of PFAS to remote environments should be explored. For example, understanding whether the PFOA gas phase precursor, 8:2 FTOH, is present in the atmosphere of the Amazon could provide insights into additional pathways of PFAS transport. The observation of PFOA in Amazon Forest atmosphere raises questions whether PFOA containing AFFFF are used to extinguish fires in Amazon. Due to PFOA's bioaccumulative and endocrine-disruptive properties, its presence poses potential adverse effects on the fragile Amazon ecosystem.

Further studies are warranted, potentially applying semi-targeted analytical methods, to investigate the presence of additional PFAS in the Amazon that are not amenable to the applied targeted method.

Our study provides valuable insights into “forever chemicals” distribution in a unique ecosystem, raising awareness of potential environmental implications to unique Amazon flora and fauna, health risks including those of indigenous groups and the need for further studies in the region.

CRedit authorship contribution statement

Ivan Kourtchev: Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Bruna G. Sebben:** Writing – review & editing, Visualization, Investigation, Data curation. **Sebastian Brill:** Writing – review & editing, Methodology, Investigation, Data curation. **Cybelli, G.G. Barbosa:** Writing – review & editing, Visualization, Investigation, Data curation. **Bettina Weber:** Writing – review & editing, Resources, Methodology. **Rosaria R. Ferreira:** Writing – original draft, Investigation, Formal analysis, Data curation. **Flávio Augusto Farias D'Oliveira:** Formal analysis. **Cléo Q. Dias-Junior:** Writing – review & editing, Investigation. **Olalekan A.M. Popoola:** Writing – review & editing, Software. **Jonathan Williams:** Writing – review & editing. **Christopher Pöhlker:** Writing – review & editing. **Ricardo H.M. Godoi:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.173918>.

References

- Andreae, M.O., Acevedo, O.C., Araújo, A., Artaxo, P., Barbosa, C.G.G., Barbosa, H.M.J., Brito, J., Carbone, S., Chi, X., Cintra, B.B.L., da Silva, N.F., Dias, N.L., Dias-Júnior, C. Q., Ditas, F., Ditz, R., Godoi, A.F.L., Godoi, R.H.M., Heimann, M., Hoffmann, T., Kesselmeier, J., Könemann, T., Krüger, M.L., Lavric, J.V., Manzi, A.O., Lopes, A.P., Martins, D.L., Mikhailov, E.F., Moran-Zuloaga, D., Nelson, B.W., Nölscher, A.C., Santos, Nogueira D., Piedade, M.T.F., Pöhlker, C., Pöschl, U., Quesada, C.A., Rizzo, L. V., Ro, C.-U., Ruckteschler, N., Sá, L.D.A., de Oliveira Sá, M., Sales, C.B., dos Santos, R.M.N., Saturno, J., Schöngart, J., Sörgel, M., de Souza, C.M., de Souza, R.A. F., Su, H., Targhetta, N., Tóta, J., Trebs, I., Trumbore, S., van Eijck, A., Walter, D., Wang, Z., Weber, B., Williams, J., Winderlich, J., Wittmann, F., Wolff, S., Yáñez-Serrano, A.M., 2015. The Amazon Tall Tower Observatory (ATTO): overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols. *Atmos. Chem. Phys.* <https://doi.org/10.5194/acp-15-10723-2015>.
- Barber, J.L., Berger, U., Chaemfa, C., Huber, S., Jahnke, A., Temme, C., Jones, K.C., 2007. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Environ. Monit. Assess.* <https://doi.org/10.1039/b701417a>.
- Bartell, S.M., Vieira, V.M., 2021. Critical review on PFOA, kidney cancer, and testicular cancer. *J. Air Waste Manag. Assoc.* <https://doi.org/10.1080/10962247.2021.1909668>.
- Brandtsma, S.H., Koekkoek, J.C., van Velzen, M.J.M., de Boer, J., 2018. The PFOA substitute GenX detected in the environment near a fluoropolymer manufacturing plant in the Netherlands. *Chemosphere.* <https://doi.org/10.1016/j.chemosphere.2018.12.135>.
- Camarinha-Neto, G.F., Cohen, J.C., Dias-Júnior, C.Q., Sörgel, M., Cattanio, J.H., Araújo, A., Wolff, S., Kuhn, P.A.F., Souza, R.A.F., Rizzo, L.V., Artaxo, P., 2021. The frigate event in the Central Amazon and its influence on micrometeorological variables and atmospheric chemistry. *Atmos. Chem. Phys.* <https://doi.org/10.5194/acp-21-339-2021>.
- Capozzi, S.L., Leang, A.L., Rodenburg, L.A., Chandramouli, B., Delistraty, D.A., Carter, C. H., 2023. PFAS in municipal landfill leachate: occurrence, transformation, and sources. *Chemosphere.* <https://doi.org/10.1016/j.chemosphere.2023.138924>.
- Chambers, W.S., Hopkins, J.G., Richards, S.M., 2021. A review of per- and polyfluorinated alkyl substance impairment of reproduction. *Front. Toxicol.* <https://doi.org/10.3389/ftox.2021.732436>.
- Dinglasan, M.J.A., Ye, Y., Edwards, E.A., Mabury, S.A., 2004. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environ. Sci. Technol.* <https://doi.org/10.1021/es0350177>.

- Dragon, J., Hoaglund, M., Badireddy, A.R., Nielsen, G., Schlezinger, J., Shukla, A., 2023. Perfluoroalkyl substances (PFAS) affect inflammation in lung cells and tissues. *Int. J. Mol. Sci.* <https://doi.org/10.3390/ijms24108539>.
- Dreyer, A., Kirchgörs, T., Weinberg, I., Matthias, V., 2015. Particle-size distribution of airborne poly- and perfluorinated alkyl substances. *Chemosphere.* <https://doi.org/10.1016/j.chemosphere.2014.06.069>.
- East, A., Anderson, R.H., Salice, C.J., 2021. Per- and polyfluoroalkyl substances (PFAS) in surface water near US air force bases: prioritizing individual chemicals and mixtures for toxicity testing and risk assessment. *Environ. Toxicol. Chem.* <https://doi.org/10.1002/etc.4893>.
- Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Sulbaek Andersen, M.P., Wallington, T.J., 2004. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* <https://doi.org/10.1021/es049860w>.
- Faust, J.A., 2023. PFAS on atmospheric aerosol particles: a review. *Environ. Sci. Process. Impacts.* <https://doi.org/10.1039/d2em00002d>.
- Fenton, S.E., Ducatman, A., Boobis, A., DeWitt, J.C., Lau, C., Ng, C., Smith, J.S., Roberts, S.M., 2021. Per- and Polyfluoroalkyl substance toxicity and human health review: current state of knowledge and strategies for informing future research. *Environ. Toxicol. Chem.* <https://doi.org/10.1002/etc.4890>.
- Gerardu, T., Dijkstra, J., Beeltje, H., van Renesse van Duivenbode, A., Griffioen, J., 2023. Accumulation and transport of atmospherically deposited PFOA and PFOS in undisturbed soils downwind from a fluoropolymers factory. *Environ. Adv.* <https://doi.org/10.1016/j.envadv.2022.100332>.
- Glüge, J., Scheringer, M., Cousins, I.T., DeWitt, J.C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C.A., Trier, X., Wang, Z., 2020. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environ. Sci. Process. Impacts.* <https://doi.org/10.1039/d0em00291g>.
- Gonzalez-Gaya, B., Huarte, A., Prieto, A., Etxebarria, N., Oliveira, R., Nunes, G.S.S., Waichman, A., Rico, A., 2021. Presence and distribution of perfluorinated contaminants in the Amazon river. In: Abstract Book of SETAC Europe 31st Annual Meeting. Society of Environmental Toxicology and Chemistry - Europe, p. 222.
- Holanda, B.A., Franco, M.A., Walter, D., Artaxo, P., Carbone, S., Cheng, Y., Chowdhury, S., Ditas, F., Gysel-Beer, M., Klimach, T., Krempner, L.A., Krüger, O.O., Lavric, J.V., Lelieveld, J., Ma, C., Machado, L.A.T., Modini, R.L., Morais, F.G., Pozzer, A., Saturno, J., Su, H., Wendisch, M., Wolff, S., Pöhlker, M.L., Andreae, M.O., Pöschl, U., Pöhlker, C., 2023. African biomass burning affects aerosol cycling over the Amazon. *Commun. Earth Environ.* <https://doi.org/10.1038/s43247-023-00795-5>.
- Hurley, M.D., Sulbaek Andersen, M.P., Wallington, T.J., Ellis, D.A., Martin, J.W., Mabury, S.A., 2004. Atmospheric chemistry of perfluorinated carboxylic acids: reaction with OH radicals and atmospheric lifetimes. *J. Phys. Chem. A.* <https://doi.org/10.1021/jp036343b>.
- INMET - National Institute of Meteorology, 2024. BDMEP - Meteorological Database for Teaching and Research - Historical Series. Available at: <http://www.inmet.gov.br/portal/index.php?r=bdmep/bdmep>. (Accessed 15 May 2024).
- Jahnke, A., Barber, J.L., Jones, K.C., Temme, C., 2009. Quantitative trace analysis of perfluorinated alkyl substances (PFAS) in ambient air samples from Mace Head (Ireland): a method intercomparison. *Atmos. Environ.* <https://doi.org/10.1016/j.atmosenv.2008.10.049>.
- Johansson, J.H., Salter, M.E., Acosta Navarro, J.C., Leck, C., Nilsson, E.D., Cousins, I.T., 2019. Global transport of perfluoroalkyl acids via sea spray aerosol. *Environ. Sci. Process. Impacts.* <https://doi.org/10.1039/c8em00525g>.
- Kaiser, M.A., Larsen, B.S., Kao, C.-P.C., Buck, R.C., 2005. Vapor pressures of perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic acids. *J. Chem. Eng. Data.* <https://doi.org/10.1021/je050070r>.
- Kourtchev, I., Hellebust, S., Heffernan, E., Wenger, J., Towers, S., Diapoulis, E., Eleftheriadis, K., 2022. A new on-line SPE LC-HRMS method for the analysis of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in PM2.5 and its application for screening atmospheric particulates from Dublin and Enniscorthy, Ireland. *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2022.155496>.
- Kourtchev, I., Sebben, B.G., Bogush, A., Godoi, A.F., Godoi, R.H.M., 2023. Per- and polyfluoroalkyl substances (PFAS) in urban PM2.5 samples from Curitiba, Brazil. *Atmos. Environ.* <https://doi.org/10.1016/j.atmosenv.2023.119911>.
- Kourtchev, I., Szeto, P., O'Connor, I., Popoola, O.A.M., Maenhaut, W., Wenger, J., Kalberer, M., 2020. Comparison of Heated Electrospray Ionization and Nano-electrospray Ionization Sources Coupled to Ultra-High-Resolution Mass Spectrometry for Analysis of Highly Complex Atmospheric Aerosol Samples. *Anal. Chem.* <https://doi.org/10.1021/acs.analchem.0c00971>.
- Leeson, A., Thompson, T., Stroo, H.F., Anderson, R.H., Speicher, J., Mills, M.A., Willey, J., Coyle, G., Ghosh, R., Lebrón, C., Patton, C., 2021. Identifying and managing aqueous film-forming foam-derived per- and polyfluoroalkyl substances in the environment. *Environ. Toxicol. Chem.* <https://doi.org/10.1002/etc.4894>.
- Lin, H., Taniyasu, S., Yamazaki, E., Wei, S., Wang, X., Gai, N., Kim, J.H., Eun, H., Lam, P. K.S., Yamashita, N., 2020. Per- and polyfluoroalkyl substances in the air particles of Asia: levels, seasonality, and size-dependent distribution. *Environ. Sci. Technol.* <https://doi.org/10.1021/acs.est.0c03387>.
- Marengo, J.A., Nobre, C.A., Culf, A.D., 1997. Climatic impacts of "friagens" in forested and deforested areas of the Amazon basin. *J. Appl. Meteorol. Climatol.* [https://doi.org/10.1175/1520-0450\(1997\)036<1553:CIOFIF>2.0.CO;2](https://doi.org/10.1175/1520-0450(1997)036<1553:CIOFIF>2.0.CO;2).
- Martin, J.W., Ellis, D.A., Mabury, S.A., Hurley, M.D., Wallington, T.J., 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environ. Sci. Technol.* <https://doi.org/10.1021/es051362f>.
- Mazumder, N.U., Hossain, M.T., Jahura, F.T., Girase, A., Hall, A.S., Lu, J., Ormond, R.B., 2023. Firefighters' exposure to per- and polyfluoroalkyl substances (PFAS) as an occupational hazard: a review. *Front. Mater.* <https://doi.org/10.3389/fmats.2023.1143411>.
- McMurdo, C.J., Ellis, D.A., Webster, E., Butler, J., Christensen, R.D., Reid, L.K., 2008. Aerosol enrichment of the surfactant PFO and mediation of the water-air transport of gaseous PFOA/Environ. Sci. Technol. <https://doi.org/10.1021/es703202642>.
- Menegassi, D., 2021. Ibama abre licitação para compra de retardante de chamas questionado pelo próprio Ibama. <https://oeco.org.br/reportagens/ibama-abre-licitacao-para-compra-de-retardante-de-chamas-questionado-pelo-proprio-ibama/>. (Accessed 15 May 2024).
- Mesfin, Tefera Y., Gaskin, S., Mitchell, K., Springer, D., Mills, S., Pisaniello, D., 2022. Food grown on fire stations as a potential pathway for firefighters' exposure to per- and polyfluoroalkyl substances (PFAS). *Environ. Int.* <https://doi.org/10.1016/j.envint.2022.107455>.
- Muir, D., Bossi, R., Carlsson, P., Evans, M., De Silva, A., Halsall, C., Rauert, C., Herzke, D., Hung, H., Letcher, R., Rigét, F., Roos, A., 2019. Levels and trends of poly- and perfluoroalkyl substances in the Arctic environment – an update. *Emerg. Contam.* <https://doi.org/10.1016/j.emcon.2019.06.002>.
- Pérez, F., Nadal, M., Navarro-Ortega, A., Fàbrega, F., Domingo, J.L., Barceló, D., Farré, M., 2013. Accumulation of perfluoroalkyl substances in human tissues. *Environ. Int.* <https://doi.org/10.1016/j.envint.2013.06.004>.
- Pöhlker, M.L., Ditas, F., Saturno, J., Klimach, T., Hrabě de Angelis, I., Araújo, A.C., Brito, J., Carbone, S., Cheng, Y., Chi, X., Ditz, R., Gunthe, S.S., Holanda, B.A., Kandler, K., Kesselmeier, J., Könemann, T., Krüger, O.O., Lavric, J.V., Martin, S.T., Mikhailov, E., Moran-Zuloaga, D., Rizzo, L.V., Rose, D., Su, H., Thalman, R., Walter, D., Wang, J., Wolff, S., Barbosa, H.M.J., Artaxo, P., Andreae, M.O., Pöschl, U., Pöhlker, C., 2018. Long-term observations of cloud condensation nuclei over the Amazon rain forest – part 2: variability and characteristics of biomass burning, long-range transport, and pristine rain forest aerosols. *Atmos. Chem. Phys.* <https://doi.org/10.5194/acp-18-10289-2018>.
- Pöhlker, C., Walter, D., Paulsen, H., Könemann, T., Rodríguez-Caballero, E., Moran-Zuloaga, D., Brito, J., Carbone, S., Degrendele, C., Després, V.R., Ditas, F., Holanda, B.A., Kaiser, J.W., Lammel, G., Lavric, J.V., Ming, J., Pickersgill, D., Pöhlker, M.L., Praß, M., Löbs, N., Saturno, J., Sörgel, M., Wang, Q., Weber, B., Wolff, S., Artaxo, P., Pöschl, U., Andreae, M.O., 2019. Land cover and its transformation in the backward trajectory footprint region of the Amazon Tall Tower Observatory. *Atmos. Chem. Phys.* <https://doi.org/10.5194/acp-19-8425-2019>.
- Reinikainen, J., Perkola, N., Äystö, L., Sorvari, J., 2022. The occurrence, distribution, and risks of PFAS at AFFF-impacted sites in Finland. *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2022.154237>.
- Ringsdorf, A., Edtbauer, A., Vilà-Guerau de Arellano, J., Pfannerstill, E.Y., Gromov, S., Kumar, V., Pozzer, A., Wolff, S., Tsokankunku, A., Soergel, M., Sá, M.O., Araújo, A., Ditas, F., Poehlker, C., Lelieveld, J., Williams, J., 2023. Inferring the diurnal variability of OH radical concentrations over the Amazon from BVOC measurements. *Sci. Rep.* <https://doi.org/10.1038/s41598-023-41748-4>.
- Rolph, G., Stein, A., Stunder, B., 2017. Real-time environmental applications and display systems. *Environ. Model. Software.* <https://doi.org/10.1016/j.envsoft.2017.06.025>.
- Ryu, M.H., Jha, A., Ojo, O.O., Mahood, T.H., Basu, S., Detillieux, K.A., Nikoobakht, N., Wong, C.S., Loewen, M., Becker, A.B., Halayko, A.J., 2014. Chronic exposure to perfluorinated compounds: impact on airway hyperresponsiveness and inflammation. *Am. J. Phys. Lung Cell. Mol. Phys.* <https://doi.org/10.1152/ajplung.01000.2014>.
- Saini, A., Chinnadurai, S., Schuster, J.K., Eng, A., Harner, T., 2023. Per- and polyfluoroalkyl substances and volatile methyl siloxanes in global air: spatial and temporal trends. *Environ. Pollut.* <https://doi.org/10.1016/j.envpol.2023.121291>.
- Sha, B., Johansson, J.H., Tunved, P., Bohlin-Nizzetto, P., Cousins, I.T., Salter, M.E., 2022. Sea (SSA) as a source of perfluoroalkyl acids (PFAAs) to the atmosphere: field evidence from long-term air monitoring. *Environ. Sci. Technol.* <https://doi.org/10.1021/acs.est.1c04277>.
- Sinclair, E., Kim, S.K., Akinleye, H.B., Kannan, K., 2007. Quantitation of gas-phase perfluoroalkyl surfactants and fluorotelomer alcohols released from nonstick cookware and microwave popcorn bags. *Environ. Sci. Technol.* <https://doi.org/10.1021/es062377w>.
- Spring, J., 2021. Brazil's military fails in key mission: defending the Amazon. <https://www.reuters.com/investigates/special-report/brazil-environment-military/>. (Accessed 14 March 2024).
- Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA's HYSPLIT atmospheric transport and dispersion modeling system. *Bull. Am. Meteorol. Soc.* <https://doi.org/10.1175/BAMS-D-14-00110.1>.
- US department of Health and Human Services, 2016. National Toxicology Program. 2016. Immunotoxicity Associated With Exposure to Perfluorooctanoic Acid (PFOA) or Perfluorooctane Sulfonate (PFOS). Research Triangle Park, NC. Available from: https://ntp.niehs.nih.gov/ntp/ohat/pfoa_pfos/pfoa_pfosmonograph_508.pdf. (Accessed 14 March 2024).
- US EPA, 2024a. Our Current Understanding of the Human Health and Environmental Risks of PFAS. <https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas>. (Accessed 6 October 2024).
- US EPA, 2024b. <https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas>. (Accessed 15 May 2024).
- US Government Accountability Office, 2018. Status of DOD efforts to address drinking water contaminants used in firefighting foam. Available from: <https://www.gao.gov/assets/700/694759.pdf>. (Accessed 14 March 2024).
- Wallington, T.J., Hurley, M.D., Xia, J., Wuebbles, D.J., Sillman, S., Ito, A., Penner, J.E., Ellis, D.A., Martin, J., Mabury, S.A., Nielsen, O.J., Sulbaek Andersen, M.P., 2006. Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the

- atmospheric oxidation of 8:2 fluorotelomer alcohol. *Environ. Sci. Technol.* <https://doi.org/10.1021/es051858x>.
- Wang, P., Zhang, M., Li, Q., Lu, Y., 2021. Atmospheric diffusion of perfluoroalkyl acids emitted from fluorochemical industry and its associated health risks. *Environ. Int.* <https://doi.org/10.1016/j.envint.2020.106247>.
- Watson, A.Y., Bates, R.R., Kennedy, D. (Eds.), 1988. *Atmospheric Transport and Dispersion of Air Pollutants Associated with Vehicular Emissions*. National Academies Press (US), Air Pollution, the Automobile, and Public Health. Washington (DC) (doi:10.17226/1033).
- Wong, F., Shoeib, M., Katsoyiannis, A., Eckhardt, S., Stohl, A., Bohlin-Nizzetto, P., Li, H., Fellin, P., Su, Y., Hung, H., 2018. Assessing temporal trends and source regions of per- and polyfluoroalkyl substances (PFASs) in air under the Arctic Monitoring and Assessment Programme (AMAP). *Atmos. Environ.* <https://doi.org/10.1016/j.atmosenv.2017.10.028>.
- Xie, Z., Wang, Z., Mi, W., Möller, A., Wolschke, H., Ebinghaus, R., 2015. Neutral poly-/perfluoroalkyl substances in air and snow from the Arctic. *Sci. Rep.* <https://doi.org/10.1038/srep08912>.
- Young, C.J., Furdul, V.I., Franklin, J., Koerner, R.M., Muir, D.C., Mabury, S.A., 2007. Perfluorinated acids in Arctic snow: new evidence for atmospheric formation. *Environ. Sci. Technol.* <https://doi.org/10.1021/es0626234>.
- Young, A.S., Sparer-Fine, E.H., Pickard, H.M., Sunderland, E.M., Peaslee, G.F., Allen, J. G., 2021. Per- and polyfluoroalkyl substances (PFAS) and total fluorine in fire station dust. *J. Exposure Sci. Environ. Epidemiol.* <https://doi.org/10.1038/s41370-021-00288-7>.
- Zhou, J., Baumann, K., Mead, R.N., Skrabal, S.A., Kieber, R.J., Avery, G.B., Shimizu, M., DeWitt, J.C., Sun, M., Vance, S.A., Bodnar, W., Zhang, Z., Collins, L.B., Surratt, J.D., Turpin, B.J., 2021. PFOS dominates PFAS composition in ambient fine particulate matter (PM_{2.5}) collected across North Carolina nearly 20 years after the end of its US production. *Environ. Sci. Process Impacts.* <https://doi.org/10.1039/d0em00497a>.