

# Emissions of per- and polyfluoroalkyl substances (PFAS) by fluoropolymer production plants

Joost Dalmijn





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## Abstract

Per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals of environmental and human health concern due to their persistence, potential toxicities, and potential to bioaccumulate. Fluoropolymers, a subset of polymeric PFAS, consist of a carbon backbone that is fully or partially fluorinated. This structure confers unique properties such as chemical and thermal resistance, as well as hydrophobicity and lipophobicity and has led to diverse industrial and consumer applications of fluoropolymers. As such, these materials are positioned as a significant component of the global fluorochemical industry and economy.

However, fluoropolymer production has raised concerns due to the use, formation, and emission of various non-polymeric PFAS. In response, industry has sought to mitigate its impacts by introducing alternative PFAS, implementing emission abatement technologies, and modifying production processes.

This thesis aimed to determine and characterize PFAS emissions from fluoropolymer production plants (FPPs) in Europe and China by gaining a holistic understanding of production processes to identify sources and emission pathways. Emissions were captured through emission data collection (Paper I) and environmental sampling near FPPs (Papers II-IV) and further characterized through an emission inventory (Paper I), targeted analyses, suspect screening (Papers II-IV), and atmospheric dispersion modelling (Papers II and IV). Differences in management of PFAS emissions by FPPs between China and Europe were investigated by comparing measured atmospheric concentrations and assessing the implications for human exposure.

Results indicated that despite recent emission reduction efforts in the UK and the Netherlands, FPPs remain point sources of various PFAS, including introduced alternatives (Papers I-III). Perfluorooctanoic acid (PFOA), which was listed in the Stockholm Convention on Persistent Organic Pollutants in 2019, was still in use and emitted in large quantities during the sampling period in China in 2019 (Paper IV). Other identified emissions included monomeric PFAS, by-products from monomer production and polymerization, and PFAS used in fluoropolymer processing (Paper I). Furthermore, due to the persistence of PFAS, historical emissions have turned some production sites into contamination hotspots (Paper III).

Atmospheric dispersion modelling (Papers II and IV) showed that part of the atmospheric PFAS emissions could be subject to long-range atmospheric transport and contribute to PFAS loads in remote locations. Thus, PFAS emissions by FPPs not only influenced the local environment, but possibly had global impacts. Measured median concentrations of atmospheric PFAS (Papers II-IV) exceeded guidance values for exposure through inhalation 30 km from the FPP in China. Before the implementation of emission abatement systems, a similar situation could have existed in the Netherlands and the UK, due to emissions of PFOA and its replacements.

Overall, this thesis underscored the need for a broader scope in future research and regulatory efforts, extending beyond specific well-known PFAS to encompass other PFAS emissions by FPPs. Additionally, addressing geographical disparities in PFAS management is crucial for effective global solutions.

**Keywords:** *PFAS, fluoropolymer production, emissions, environmental sampling, emission inventory, liquid chromatography, high-resolution mass spectrometry, atmospheric dispersion modelling, human exposure.*

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(PFAS) BY FLUOROPOLYMER PRODUCTION PLANTS

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Per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals of environmental and human health concern due to their persistence, potential toxicities, and potential to bioaccumulate. Fluoropolymers, a subset of polymeric PFAS, consist of fully or partially fluorinated carbon backbones. These structures confer unique properties such as chemical and thermal resistance, as well as hydrophobicity and lipophobicity and has led to diverse industrial and consumer applications of fluoropolymers. As such, these materials are positioned as a significant component of the global fluorochemical industry and economy.

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Results indicated that despite recent emission reduction efforts in the UK and the Netherlands, FPPs remain point sources of various PFAS, including introduced alternatives (**Papers I-III**). Perfluorooctanoic acid (PFOA), which was listed in the Stockholm Convention on Persistent Organic Pollutants in 2019, was still in use and emitted in large quantities during the sampling period in China in 2019 (**Paper IV**). Other identified emissions included monomeric PFAS, by-products from monomer production and polymerization, and PFAS used in fluoropolymer processing (**Paper I**). Furthermore, due to the persistence of PFAS, historical emissions have turned some production sites into contamination hotspots (**Paper III**).

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Overall, this thesis underscored the need for a broader scope in future research and regulatory efforts, extending beyond specific well-known PFAS to encompass other PFAS emissions by FPPs. Additionally, addressing regional disparities in PFAS management is crucial for effective global solutions.

## Sammanfattning

Per- och polyfluorerade alkylsubstanser (PFAS) är syntetiska kemikalier med egenskaper som ger anledning till oro på grund av deras persistens, potentiella toxicitet och bioackumulering. Fluorpolymerer, en delmängd av PFAS med hög molekylmassa, består av kol-fluor-kedjor som ger unika egenskaper, såsom kemisk och termisk resistens samt fett- och vattenavvisande egenskaper. Dessa egenskaper har lett till att fluorpolymerer används i olika industri- och konsumentapplikationer, vilket gör dem till en viktig del av den globala fluorkemiska industrin och ekonomin.

Användningen, bildandet och utsläppen av olika PFAS vid tillverkningen av fluorpolymerer har dock orsakat miljöproblem. Som svar på detta har industrin försökt bekämpa dessa effekter genom att introducera alternativa PFAS, tillämpa utsläppskontrolltekniker och modifiera produktionsprocesser.

Syftet med denna avhandling var att fastställa och karakterisera PFAS-utsläpp från produktionsanläggningar för fluorpolymerer (FPP) i Europa och Kina genom att få en helhetsförståelse för produktionsprocesserna för att identifiera källor och utsläppskanaler. Utsläppen undersöktes genom insamling av utsläppsdata (**Paper I**) och miljöprovtagning i närheten av FPP:er (**Paper II-IV**) och karakteriserades ytterligare genom en utsläppsinventering (**Paper I**), riktade analyser, screening av misstänkta utsläpp (**Paper II-IV**) och modellering av atmosfärisk spridning (**Paper II och IV**). Skillnaderna i reglering och policy för PFAS undersöktes mellan Kina och Europa genom att jämföra luftkoncentrationer av PFAS och deras effekter på människors exponering.

Trots insatser för att begränsa utsläppen i Storbritannien och Nederländerna visade sig FPP-anläggningar fortfarande vara punktkällor för flera PFAS, inklusive introducerade alternativ (**Paper I-III**). Perfluoroktansyra (PFOA), som lades till i Stockholmskonventionen 2019, användes fortfarande och släpptes ut och uppmättes i stora mängder i Kina under 2019 års provtagningsperiod (**Paper IV**). Andra identifierade utsläpp omfattar PFAS-monomerer, biprodukter från monomerproduktion och polymerisering samt PFAS som används vid bearbetning av fluorpolymerer (**Paper I**). Dessutom har persistensen av PFAS och historiska utsläpp lett till att produktionsanläggningar blivit förorenade hotspots (**Paper III**).

Modellering av atmosfärisk spridning (**Paper II och IV**) visade att en del av PFAS-utsläpp i atmosfären kan färdas långa sträckor och bidra till PFAS-belastningen på avlägsna platser. PFAS-utsläpp från FPP:er påverkar således inte enbart den lokala miljön, utan kan även ha globala effekter. Uppmätta mediankoncentrationer av PFAS i atmosfären (**Paper II-IV**) överskred gränsvärdena för exponering vid inandning 30 km från kraftverket i Kina. En liknande situation har troligen funnits i Nederländerna och Storbritannien historiskt under användningen av PFOA och dess alternativ.

Sammantaget har denna avhandling visat på behovet av en bredare referensram för framtida forskning och reglering. Referensramen bör utöver specifika kända PFAS inkludera andra PFAS-utsläpp från FPP:er. Skillnader i PFAS-policyer, till exempel den fortsatta användningen av reglerade PFAS i vissa regioner, måste lösas för att säkerställa effektiva lösningar på denna globala utmaning.

## Samenvatting

Per- en polyfluoralkylstoffen (PFAS) zijn synthetische chemicaliën met zorgwekkende eigenschappen vanwege hun persistentie en mogelijke toxiciteit en bioaccumulatie. Fluoropolymeren, een subset van PFAS, bestaan uit een volledig of deels gefluoreerde koolstofketen. Deze structuur geeft fluoropolymeren unieke kenmerken, zoals chemische en thermische resistentie en vet- en waterafstotende eigenschappen en heeft geleid tot diverse industriële- en consumententoepassingen. Hierdoor vormen deze materialen een belangrijk onderdeel van de wereldwijde fluorochemische industrie en economie. Het gebruik, de vorming en de emissie van verschillende PFAS tijdens de productie van fluoropolymeren heeft echter de nodige milieuproblemen veroorzaakt. Als reactie heeft de industrie geprobeerd deze problemen te bestrijden door alternatieve PFAS te introduceren, emissiebeperkende technologieën toe te passen en productieprocessen te veranderen.

Deze thesis had als doel PFAS-uitstoot van productielocaties van fluoropolymeren (FPP's) in Europa en China te bepalen en te karakteriseren. Dit werd bewerkstelligd door productieprocessen te analyseren om bronnen en emissiekanalen te identificeren. PFAS-uitstoot werd onderzocht door emissiegegevens te verzamelen (**Paper I**) en door monsternamen in het milieu in de nabij FPP's (**Papers II-IV**). De uitstoot werd verder gekarakteriseerd door middel van een emissie-inventarisatie (**Paper I**), gerichte analyses, suspect screenings (**Papers II-IV**) en modellering van atmosferische verspreiding (**Papers II en IV**). Ook werden de verschillen in PFAS-regulatie en beleid tussen China en Europa onderzocht door de luchtconcentraties van PFAS en de gevolgen voor menselijke blootstelling te vergelijken.

Ondanks recente emissiebeperkende maatregelen in het Verenigd Koninkrijk en Nederland, bleken FPP's nog steeds puntbronnen van verschillende PFAS te zijn, waaronder de geïntroduceerde alternatieven (**Papers I-III**). Perfluorooctaanzuur (PFOA), dat in 2019 toegevoegd werd aan het Verdrag van Stockholm, werd tijdens de bemonsteringsperiode in 2019 nog steeds gebruikt en in grote hoeveelheden uitgestoten en gemeten in China (**Paper IV**). Andere geïdentificeerde uitstoot omvatte PFAS-monomeren, bijproducten van monomeerproductie en polymerisatie en PFAS die werden gebruikt in de verwerking van fluoropolymeren (**Paper I**). Bovendien zijn sommige FPP's vervuiling-hotspots door de hoeveelheid historische emissies en de persistentie van PFAS (**Paper III**). Modellering van atmosferische verspreiding (**Papers II en IV**) toonde aan dat een deel van de PFAS-uitstoot zich over lange afstanden kan verplaatsen en mogelijk ook wereldwijde gevolgen heeft. Gemeten mediaanconcentraties van PFAS in de lucht (**Papers II-IV**) overschreden bovendien de toetsingswaarden voor blootstelling door inhalatie op 30 km van de FPP in China. In Nederland en het Verenigd Koninkrijk bestond in het verleden waarschijnlijk een vergelijkbare situatie tijdens het gebruik van PFOA en zijn alternatieven.

Al met al benadrukte deze thesis de noodzaak van een breder referentiekader in toekomstig onderzoek en regelgeving. Dit zou verder moeten gaan dan specifieke bekende PFAS en alle PFAS-emissies door FPP's moeten omvatten. Geografische verschillen in PFAS-beleid moeten worden aangepakt om effectieve oplossingen voor deze mondiale uitdaging te waarborgen.

## List of papers

I) Joost Dalmijn, Juliane Glüge, Martin Scheringer and Ian T. Cousins

Emission inventory of PFASs and other fluorinated organic substances for the fluoropolymer production industry in Europe

**Contributions:** As lead author, I contributed to the study design, conducted data collection and analysis, and wrote the manuscript, including drafting the initial version and revising it based on co-author feedback and peer-reviews.

II) Joost Dalmijn, Julia J. Schafer, Jonathan P. Benskin, Matthew E. Salter, Jana H. Johansson and Ian T. Cousins

HFPO-DA and other PFAS in air downwind of a fluoropolymer production plant in the Netherlands; measurements and modeling

**Contributions:** As lead author, I contributed to the study design, organized and conducted sampling campaigns in the Netherlands, performed sample extractions and chemical analyses, processed and interpreted data, and wrote the manuscript, including drafting and revising it in collaboration with co-authors and based on peer-reviews.

III) Joost Dalmijn, Jonathan P. Benskin, Matthew E. Salter, Andrew J. Sweetman, Crispin J. Halsall, Jack Garnett and Ian T. Cousins

Perfluoro(2-ethoxy-2-fluoroethoxy)-acetic acid (EEA) and other target and suspect PFAS in the vicinity of a fluoropolymer production plant

**Contributions:** As lead author, I contributed to the study design, performed sample extractions and chemical analyses, processed data, and prepared the manuscript, including drafting the initial version and revising it in response to co-author input and based on peer-reviews.

IV) Bo Sha, Joost Dalmijn, Jana H. Johansson, Matthew E. Salter and Ian T. Cousins

Emission of perfluoroalkyl acids and perfluoroalkyl ether carboxylic acids to the atmosphere from a fluorochemical industrial park in China

**Contributions:** As a contributing author, I participated in data analysis and processing, contributed to the interpretation of results, and revised sections of the manuscript.

## Abbreviations

3M	Minnesota Mining and Manufacturing Corporation
6:2 FTS	6:2 Fluorotelomer sulfonic acid
9CI-PFO3NS	9-Chlorohexadecafluoro-3-oxanone-1-sulfonic acid
ADONA	Ammonium 4,8-dioxa-3H-perfluorononanoate
ADV	Mixture of chlorinated perfluoropolyether carboxylic acids used as FPA
AGC	Asahi Glass Company
APFN	Ammonium perfluorononanoate
APFO	Ammonium perfluorooctanoate
BPAF	Bisphenol AF
C6O4	Perfluoro ([5-methoxy-1,3-dioxolan-4-yl]oxy) acetic acid
CFC	Chlorofluorocarbon
CTA	Chain-transfer agent
CTR	Chain-transfer reaction
CTFE	Chlorotrifluoroethylene
DIOFB	1,4-diiodoperfluorobutane
DuPont	DuPont de Nemours Inc.
E	Ethylene
ECF	Electrochemical fluorination
ECHA	European Chemicals Agency
ECTFE	Ethylene-trifluorochloroethylene
EEA	Perfluoro(2-ethoxy-2-fluoroethoxy)-acetic acid
EFSA	European Food Safety Authority
EOF	Extractable organofluorine
E-PRTR	European Pollutant Release and Transfer Register
ETFE	Ethylene-tetrafluoroethylene
EU	European Union
FAVE	Perfluoroalkyl vinyl ether
FEP	Fluorinated ethylene propylene
FEVE	Fluoroethylene vinyl ether
FFKM/FFPM	Perfluoroelastomer
FKM	Fluorine kautschuk material
FLEXPART	FLEXible PARTicle dispersion model
FPA	Fluorinated processing aid
FPP	Fluoropolymer production plant
FTSA	Fluorotelomer sulfonic acid
GWP	Global warming potential
HFC-142b	1-Chloro-1,1-difluoroethane
HCFC	Hydrochlorofluorocarbon
HCFC-22	Chlorodifluoromethane
HF	Hydrogen fluoride
HFC	Hydrofluorocarbon
HFC-152a	1,1-Difluoroethane
HFC-23	Fluoroform
HFC-32	Difluoromethane
HFC-4310mee/Vertrel XF	1,1,1,2,3,4,4,5,5,5-Decafluoropentane
HFE	Hydrofluoroether
HFO	Hydrofluoroolefin
HFP	Hexafluoropropylene
HFPO	Hexafluoropropylene oxide
HFPO-DA	Hexafluoropropylene oxide dimer acid
HFPO-TA	Hexafluoropropylene oxide trimer acid
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory model
ICI	Imperial Chemical Industries
LC-HRMS	Liquid chromatography – high resolution mass spectrometry
MeOH	Methanol
NL	The Netherlands
ODP	Ozone depletion potential
OECD	Organisation for Economic Cooperation and Development
P	Propylene
PBT	Persistent, bioaccumulative and toxic
PBVE	Perfluorobutenyl vinyl ether
PCB	Polychlorinated biphenyl

PCTFE	Polychlorotrifluoroethylene
PDD	4,5-difluoro-2,2-bis(trifluoromethyl)-2H-1,3-dioxole
PEM	Proton exchange membrane
PEVE	Perfluoroethyl vinyl ether
PFA	Perfluoroalkoxyalkane
PFAA	Perfluoroalkyl acid
PFAC	Perfluoroallyl chloride
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFC-318	Octafluorocyclobutane
PFCA	Perfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoic acid
PFDoDA	Perfluorododecanoic acid
PFECA	Perfluoroalkyl ether carboxylic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFIB	Perfluoroisobutene
PFNA	Perfluorononanoic acid
PFO3DA	Perfluoro-3,6,9-trioxadecanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFPE	Perfluoropolyether
PFPeA	Perfluoropentanoic acid
PFPeOPA	2-Perfluoropentoxy-2,3,3,3-tetrafluoropropanoic acid
PFSA	Perfluoroalkyl sulfonic acid
PFTeDA	Perfluorotetradecanoic acid
PFTriDA	Perfluorotridecanoic acid
PFUnDA	Perfluoroundecanoic acid
PMVE	Perfluoromethyl vinyl ether
POP	Persistent organic pollutant
PPVE	Perfluoropropyl vinyl ether
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
QFF	Quartz fibre filter
R-12	Dichlorodifluoromethane
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RIVM	Dutch National Institute for Public Health and the Environment
SFVE	Sulfonyl fluoride vinyl ether
SPE	Solid-phase extraction
SSA	Sea spray aerosol
SVHC	Substance of very high concern
T-5	Fluorinated processing aid containing HFPO-TA
TFA	Trifluoroacetic acid
TFE	Tetrafluoroethylene
THV	Tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride (terpolymer)
TTD	2,2,4-trifluoro-5-(trifluoromethoxy)-1,3-dioxole
UK	United Kingdom
US-EPA	United States Environmental Protection Agency
VDF	Vinylidene fluoride
VE	Vinyl ether
VF	Vinyl fluoride
WAX	Weak anion exchange
WWII	World War II

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# 1. Introduction

## 1.1 Per- and polyfluoroalkyl substances (PFAS)

### 1.1.1 PFAS definition & properties

Per- and polyfluoroalkyl substances (PFAS) are a group of fluorinated organic substances that are defined by the European Chemicals Agency (ECHA) <sup>1</sup> and Organisation for Economic Co-operation and Development (OECD), <sup>2</sup> as chemicals having at least one perfluoroalkyl moiety ( $-\text{CF}_2-$ ) without chlorine, bromine, iodine or hydrogen attached (with a few exceptions noted).<sup>1</sup>

The unique physical-chemical properties of PFAS are derived from the carbon-fluorine (C-F) bond. Fluorine stands out among halogens and other substituents due to its exceptional electronegativity ( $\chi = 3.98$ , the highest of all reactive elements), small covalent radius (0.6 Å), small Van der Waals radius (1.47 Å), and extremely low polarizability ( $0.56 \times 10^{-24} \text{ cm}^3$ ). These attributes result in C-F bonds that are remarkably short ( $\sim 1.4 \text{ Å}$ ), strong ( $\sim 480 \text{ kJ/mol}$ ), and highly polar (dipole moment: 1.41 D).<sup>3</sup> Consequently, perfluoroalkyl moieties exhibit exceptional thermal and chemical stability, along with hydrophobic and lipophobic characteristics,<sup>4</sup> making them valuable in diverse applications but also contributing to their persistence in organisms and the environment.<sup>5</sup>

The term 'PFAS' emerged in the early 2000s as an umbrella term in order to categorize thousands of structurally similar compounds with similar chemical properties.<sup>6</sup> Categorization of these substances was favoured because it helped various stakeholders in identifying these related chemicals without having to specify each compound individually.<sup>7</sup> With the help of improved sensitivity of analytical measurement techniques scientists discovered during this period that synthetic compounds known as perfluoroalkyl acids (PFAAs), such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were ubiquitous in the environment, human blood and wildlife.<sup>8</sup> PFOA and PFOS have a concerning combination of persistent, bioaccumulative and toxic properties.<sup>9</sup>

PFAAs, as defined by Buck et al <sup>7</sup>, consist of a perfluoroalkyl chain ( $\text{C}_n\text{F}_{2n+1}$ ) and an acid functional group (R).<sup>ii</sup> Because these substances contain a hydrophobic perfluoroalkyl chain and a hydrophilic head group, PFAAs are strong and chemically stable surfactants.<sup>10</sup> The two most important PFAA subclasses in terms of production volume and environmental relevance are the perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs).<sup>7</sup> The OECD made a distinction between PFAAs based on the length of the perfluoroalkyl chain ( $\text{C}_n\text{F}_{2n+1}$ ). PFCAs with  $n \geq 7$  and PFSAs with  $n \geq 6$  are considered long-chain PFAAs, while shorter homologues are

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<sup>i</sup> The full PFAS definition in the ECHA PFAS restriction proposal states that substances that contain one fully fluorinated methyl ( $-\text{CF}_2-$ ) or methylene ( $\text{CF}_3-$ ) group, without any H/Cl/Br/I attached are PFAS, with the exception of  $\text{X}-\text{CF}_2-\text{X}'$  or  $\text{CF}_3-\text{X}$  "where  $\text{X} = -\text{OR}$  or  $-\text{NRR}'$  and  $\text{X}' = \text{methyl } (-\text{CH}_3)$ , *methylene* ( $-\text{CH}_2-$ ), *an aromatic group*, *a carbonyl group* ( $-\text{C}(\text{O})-$ ),  $-\text{OR}''$ ,  $-\text{SR}''$  or  $-\text{NR}''\text{R}''$ " and where  $\text{R}/\text{R}'/\text{R}''/\text{R}'''$  is a hydrogen ( $-\text{H}$ ), methyl ( $-\text{CH}_3$ ), methylene ( $-\text{CH}_2-$ ), an aromatic group or a carbonyl group ( $-\text{C}(\text{O})-$ ).

<sup>ii</sup>  $\text{R} = -\text{COO}^-$ ,  $-\text{COOH}$ ,  $-\text{SO}_3^-$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{SO}_2\text{H}$ ,  $-\text{P}(=\text{O})(\text{OH})_2$ ,  $-\text{P}(=\text{O})(\text{OH})(\text{C}_m\text{F}_{2m+1})$

considered short-chain PFAAs.<sup>11</sup> Thus, PFOA is a C<sub>8</sub> (long-chain) PFCA, and PFOS is a C<sub>8</sub> (long-chain) PFSA.

PFAAs differ from other persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) in that they are far less hydrophobic and lipophilic than these 'classical' contaminants.<sup>12</sup> Nevertheless, the presence of C-F bonds instead of e.g. C-Cl or C-Br bonds makes them more persistent than many traditional POPs, because the C-F bond is very resistant to degradation by heat, light, oxidation or microbial action.<sup>5</sup> This has several consequences for their environmental fate and bioaccumulation: PFAAs tend to partition into aqueous environments rather than sediments or fatty tissues, allowing them to travel long distances in groundwater and surface water.<sup>13</sup> This distinct behaviour affects their movement through ecosystems and their potential for long-term exposure in wildlife and humans.<sup>14</sup> Moreover, unlike classical POPs, which primarily bioaccumulate in fatty tissues, PFAAs bind to proteins in organisms, leading to accumulation in blood serum albumin and organs such as the liver and kidneys.<sup>15</sup>

Whereas early PFAS definitions focused primarily on PFAAs and their precursors, later definitions (such as the 2021 OECD definition) included all substances with a perfluoroalkyl moiety that are either persistent by themselves or are precursors to substances that are non-mineralizable in the environment (such as PFAAs; Figure 1).

<sup>1</sup> As such, substances such as fluoropolymers and certain fluorinated gases were included in the PFAS definition.<sup>1</sup> The chemical space covered by PFAS therefore shifted over time from covering a relatively minor part of the production volume of fluorinated organic chemicals (tens of thousands of tons per year) to a considerable proportion (millions of tons per year).<sup>16</sup>

PFAS can be sub-categorized into polymeric and non-polymeric substances based on their molecular weight and macromolecular structure.<sup>7</sup> Polymeric PFAS are high molecular weight compounds (ranging from thousands to hundreds of thousands of Daltons) composed of repeating subunits derived from small fluorinated organic monomers. In contrast, non-polymeric PFAS are lower molecular weight molecules (typically in the range of hundreds to a few thousand Daltons) with defined, discrete structures.<sup>7</sup> Due to their macromolecular nature, polymeric PFAS are generally considered to be inert, unable to penetrate cell membranes, and not biologically active.

<sup>17</sup> Non-polymeric PFAS, on the other hand, can exhibit biological activity.<sup>18</sup>

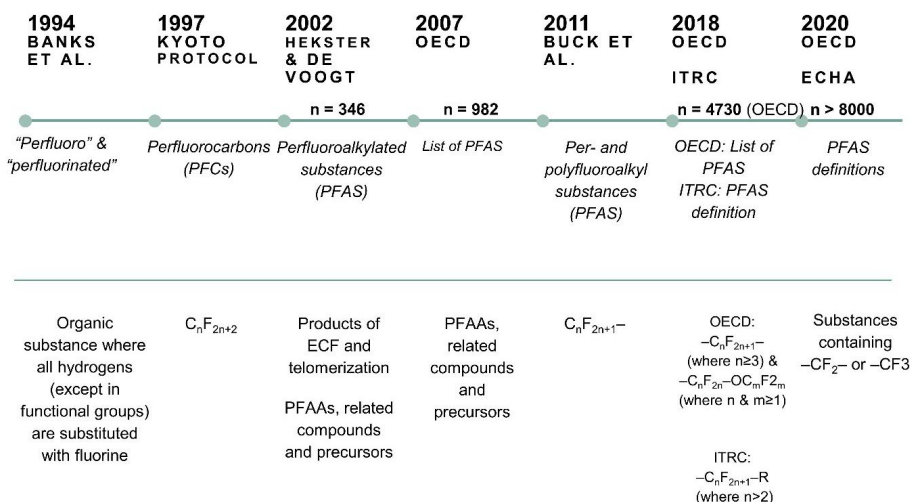


Figure 1. Timeline of PFAS definitions and chemical space covered, adapted from Buck et al. (2021).<sup>11</sup>

## 1.2 Fluoropolymers

### 1.2.1 Definition of fluoropolymers

Fluoropolymers are a category of polymeric PFAS which are characterized by having a carbon-only backbone that is fluorinated to different degrees depending on the monomers that make up the repeating sub-units.<sup>19</sup> Monomers are small and reactive organic substances with a double (alkene) bond which allows chain-forming polymerization when a radical is introduced (Figure 2). Well-known fluorinated monomers are tetrafluoroethylene ( $C_2F_4$ , TFE), vinylidene fluoride ( $C_2H_2F_2$ , VDF) and hexafluoropropylene ( $C_3F_6$ , HFP).<sup>20</sup> Monomers can be polymerized by themselves to form a homopolymer or combined with other monomers to form a copolymer.<sup>21</sup> As monomers can differ in their structure, composition and degree of fluorination, the resulting polymers have different physical and chemical properties that result in different uses and applications.<sup>22</sup>

### 1.2.2 Short history of fluoropolymer production

The first groundwork for the synthesis of fluoropolymers was laid in the industrial revolution. The current main inorganic feedstock for these materials and many other fluorinated organic substances, hydrogen fluoride (HF), was discovered in the mid-19<sup>th</sup> century by Edmond Frémy who was unsuccessfully trying to be the first to isolate elemental fluorine ( $F_2$ ).<sup>23</sup> Henri Moissan succeeded in this latter venture through Nobel Prize winning work in 1886.<sup>24</sup> However, elemental fluorine often reacts violently with organic compounds and therefore its use in the fluorochemical industry remains limited.

The Belgian chemist Frédéric Swarts synthesized the first chlorofluorocarbons (CFCs) in the 1890s.<sup>25</sup> These substances became the first fluorocarbons with commercial applications when a team of researchers from the General Motors Corporation and

DuPont de Nemours Inc. (DuPont) improved the synthesis of dichlorodifluoromethane (R-12) in the late 1920s and subsequently introduced this substance as an inert and non-toxic refrigerant in 1930.<sup>26</sup> From the beginning of the 1930s R12 and other CFCs were produced on an industrial basis by a joint venture of the two aforementioned companies called Kinetic Chemicals Inc. and were given the brand name Freon®.<sup>23</sup> Coincidentally, these substances would also be the first fluorocarbons for which an environmental impact became apparent as scientists discovered their depleting effects on the atmospheric ozone layer in the 1970s.<sup>27</sup>

In 1934, the first fluoropolymer polychlorotrifluoroethylene (PCTFE) was discovered by chemists at the German chemical company I.G. Farben.<sup>28</sup> Just a few years later, in 1938, Roy J. Plunkett, a chemist researching different Freon® refrigerants at DuPont, made a ground-breaking discovery of another fluoropolymer: polytetrafluoroethylene (PTFE).<sup>29</sup> While preparing for a reaction, Plunkett found that a canister of tetrafluoroethylene (TFE) gas had unexpectedly polymerized. When he opened the valve, instead of releasing gas, the canister contained a waxy layer of solid polymer. Upon further study, Plunkett and colleagues found that this material had many unique and potentially useful properties; it was inert, heat resistant and had a very low surface friction.<sup>30</sup>

Fluoropolymers and various other fluorocarbons found their initial applications during the Second World War (WWII), notably in the Manhattan Project, which aimed to develop the first nuclear weapons.<sup>31</sup> These materials were used extensively in order to handle highly reactive fluorine (F<sub>2</sub>) and uranium hexafluoride (UF<sub>6</sub>) and thus played an essential part in the uranium enrichment process that was used to build these weapons.<sup>23</sup>

Shortly after WWII the products and synthesis processes from the Manhattan Project were declassified and commercialized. These included fluoropolymer products such as PTFE and fluorination processes such as electrochemical fluorination (ECF, Simons process) and fluorination using cobalt trifluoride (CoF<sub>3</sub>, Fowler process).<sup>23,32,33</sup>

The 1950s saw further commercialization of various fully and partially fluorinated fluoropolymers, like polyvinylidene fluoride (PVDF), fluorinated ethylene propylene (FEP), fluoroelastomers (FKM) and processes such as telomerization by US-based companies like the Minnesota Mining and Manufacturing Corporation (3M) and DuPont.<sup>23</sup> Various fluoropolymer-producing processes were also established by companies in Europe (e.g. Imperial Chemical Industries; ICI, UK) and Japan (e.g. Daikin). The 1960s and 1970s saw the introduction of various functionalized fluoropolymers (e.g. ionomers) and perfluoropolyethers (PFPEs). The latter are not fluoropolymers, because of the interruption of their carbon chain by oxygen (ether-linkages). However, PFPEs are usually made by the same companies at the same facilities as fluoropolymers and not treated very differently from an industrial perspective.

The myriad of technological developments in e.g. electronic and (aero)space engineering since WWII combined with surging growth in world population led to expanding applications of- and increasing demand for fluorocarbons. As such, the fluorochemical industry has grown considerably since the commercialization of the first

fluorinated organic substances and is still experiencing growth.<sup>29</sup> Since the early 2000s, a significant amount of fluoropolymer production has been established in China.<sup>34</sup> This country has a strong manufacturing base and about 42 million tonnes (~15% of world reserves) of mineable deposits of the mineral fluorite (CaF<sub>2</sub>)<sup>35</sup>; which is the main feedstock for producing HF and fluorochemical production.<sup>36</sup> Consequently, China is currently the global lead producer of fluoropolymers and world's largest fluoropolymer producer, Shandong Dongyue, is based in China.<sup>19</sup>

The total production volume of the entire fluorochemical industry has grown from several tens of thousands of tonnes per year post-WWII to millions of tonnes per year currently.<sup>16</sup> Fluoropolymers are an important part of this production volume, with hundreds of thousands of tons produced annually. As such, these materials are in terms of production volume second only to fluorinated gases such as hydro(chloro)fluorocarbons (HCFCs), hydrofluoroolefins (HFOs) and hydrofluoroethers (HFEs), the production volume of which is in the millions of tons annually.<sup>16</sup> The 2024 fluoropolymer market is estimated to be worth around 4.6 billion US dollars (\$).<sup>37</sup>

### *1.2.3 Types and uses of fluoropolymers*

Fluoropolymers can be divided into a couple of categories depending on their physical-chemical properties (Table 1 and Figure 4). Fluorothermoplastics, or fluoropolymers which become pliable at elevated temperatures, account for more than 90% of fluoropolymer production. Key fluorothermoplastics include PTFE, PVDF, FEP, ETFE, and PCTFE.<sup>22</sup> PTFE alone represents over 50% of total fluoropolymer production, followed by PVDF (~16%) and FEP (~8%). Despite being the highest production volume fluoropolymer, PTFE is the only fluorothermoplastic that is not melt-processable.<sup>22</sup> Fluorothermoplastics have many different uses that include, but are not limited to, (non-stick) coatings, insulation materials and chemical-resistant binders for batteries.<sup>38</sup>

A category of amorphous curable fluoropolymers that are collectively known as fluoroelastomers or fluororubbers represent the second highest production volume of fluoropolymer categories (9%). These are used in applications such as chemical resistant seals, tubing and O-rings but also as extrusion processing aids in the production of other plastics.<sup>22</sup>

Furthermore, relatively minor fluoropolymer types are the amorphous fluoropolymers, which have a cyclic structure that provides them with good clarity and refractive indices. These are used in various optical and electronical applications.<sup>22</sup>

Lastly, functional fluoropolymers are polymers that are characterized by side chains with various functional groups. Examples include ionomers, which contain charged (e.g. perfluorosulfonate) side groups and find uses in the proton exchange membranes (PEM) of fuel cells or fluoroethylene-vinyl ether (FEVE) polymers used in various coatings or resins to e.g. weather-proof glass surfaces.<sup>22</sup>

Table 1. Non-exhaustive overview of fluoropolymers and example uses adapted from Améduri, 2018<sup>22</sup>

Category	Fluoropolymer	Abbreviation	Monomer(s)	Common trade names	~Market share (%)	First introduced	Uses
<i>Thermoplastic fluoropolymers</i>	Polytetrafluoroethylene	PTFE	TFE + PMVE (modified PTFE)	Teflon, Fluon, Algoflon, Polyflon, Hostafion	55	1948	Coatings, insulation, non-stick cookware
	Polychlorotrifluoroethylene	PCTFE	CTFE	Voltalef, Kel-F, Aclon,	3	1953	Cryogenic components
	Polyvinylidene fluoride	PVDF	VDF	Solef, Kynar, Hylar,	16	1950	Electronics, binder for Li-Ion batteries
	Fluorinated ethylene propylene	FEP	TFE + HFP	Teflon FEP	8	1959	Tubing & wiring
	Polyethylene-tetrafluoroethylene	ETFE	TFE + E	Fluon ETFE, Tefzel	3	1972	Weather-proof laminate building material
	Polyethylene chlorotrifluoroethylene	ECTFE	CTFE + E	Halar	<1	1970	Telecommunication cables
	Perfluoroalkoxy alkane	PFA	TFE + PMVE	Teflon PFA Hostafion PFA	3	1972	Tubing, liners
	Perfluoromethylalkoxy alkane	MFA	TFE + PPVE	Teflon PFA Hyflon PFA		1980s	
	Tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride	THV	TFE + HFP + VDF	Dyneon THV	<1	1980s	Automotive
Polyvinyl fluoride <sup>iii</sup>	PVF	VF	Tedlar	2	1961	Films & coatings	
<i>Fluoroelastomers</i>	Fluorine kautschuk material	FKM	VDF + HFP	Viton, Dai-el, Tecnoflon	9	1957	O-rings, gaskets, hoses, extrusion processing aid
	Perfluoroelastomer	FFKM/FFPM	TFE + PMVE	Kalrez		1960s	
	Tetrafluoroethylene-propylene	TFE-P	TFE + P	Aflas		1975	
<i>Perfluoropolyethers<sup>iv</sup></i>	Perfluoropolyethers	PFPEs	HFPO TFE + HFP + photooxidation	Krytox, Galden Fluorolink, Fomblin, Afluid	<1	1960s	Lubricants
<i>Amorphous fluoropolymers</i>	Tetrafluoroethylene and fluorinated dioxole polymer	-	TFE + PDD	Teflon AF	<1	1989	Optical and electrical uses
	Tetrafluoroethylene and fluorinated dioxole polymer	-	TFE + TTD	Hyflon AD		1990s	
	Perfluoro(3-butenyl vinyl ether) cyclopolymer	-	PBVE	Cytop		1990s	
<i>Functional fluoropolymers</i>	Fluoroethylene vinyl ether	FEVE	TFE/CTFE + VE	Lumiflon, Zeffie	<1	1982	Weather-proof coatings
	Ionomers	-	TFE + perfluoro vinyl ether sulfonyl or carbonyl fluoride monomers	Aquivion, Nafion, Flemion 3M Membranes, Aciplex	<1	1960s	Proton exchange membranes

<sup>iii</sup> Not considered PFAS

<sup>iv</sup> Not considered fluoropolymers

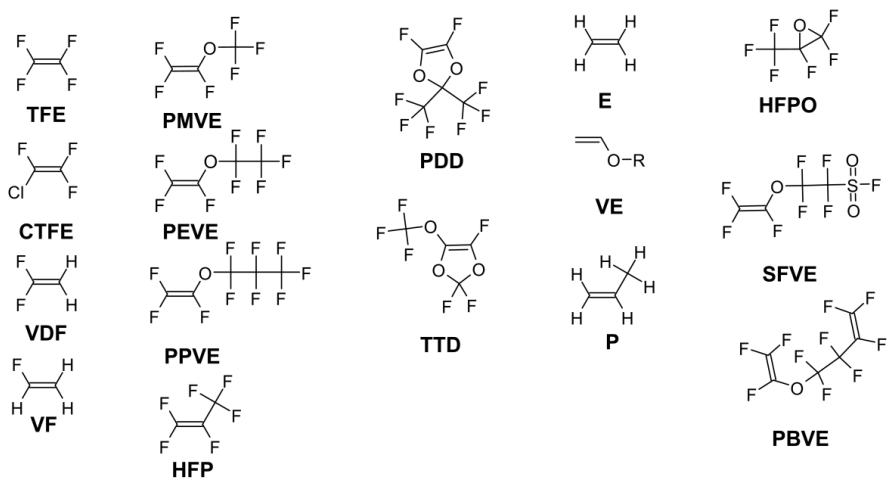


Figure 2. Examples of structures of monomers used in fluoropolymer production and their abbreviations

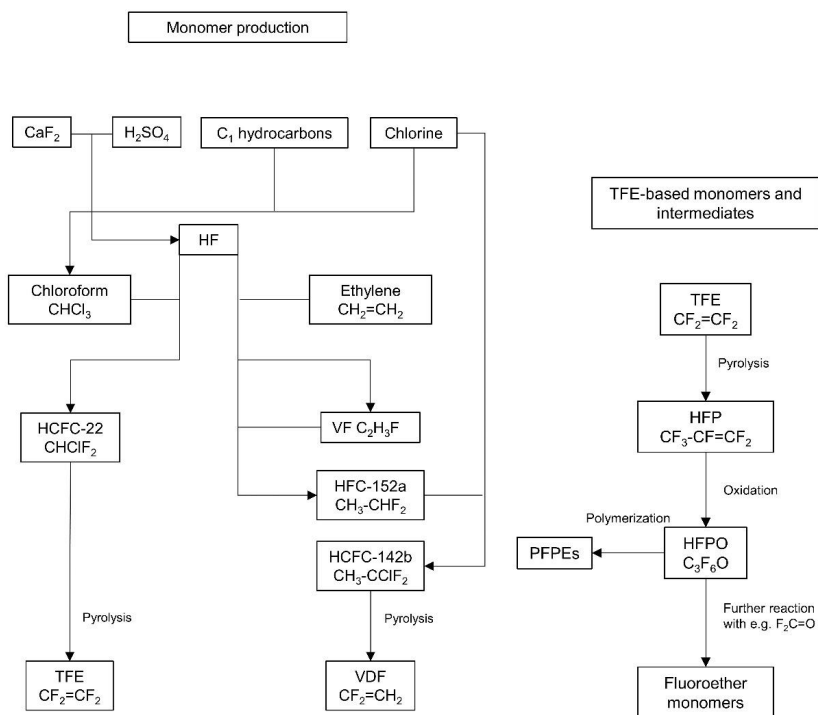


Figure 3. Flow chart for monomer production from **Paper I**, adapted from Hintzer et al., 2014





#### 1.2.4 Fluoropolymer production processes

The first process step in the production of fluoropolymers is the synthesis of the building blocks of which these materials consist; the monomers. The two most common monomers used in fluoropolymer production are TFE and VDF.<sup>40</sup> Both of these monomers are derived from the pyrolysis of hydrochlorofluorocarbon (HCFC) feedstock substances, in a reaction in which HCl leaves and a double bond is formed (Figure 3). For TFE, this feedstock is difluorochloromethane (HCFC-22) which is prepared by the reaction between chloroform ( $\text{CHCl}_3$ ) and HF.<sup>31</sup>

The production process of VDF ( $\text{C}_2\text{H}_2\text{F}_2$ ) starts at the synthesis of 1,1-difluoroethane (HFC-152a) from HF and acetylene ( $\text{C}_2\text{H}_2$ ). Subsequently, HFC-152 is chlorinated to produce 1-chloro-1,1-difluoroethane (HCFC 142b), which is then pyrolyzed into VDF.<sup>31</sup>

Other important fluoromonomers, such as HFP and perfluoroalkyl vinyl ethers (FAVEs), such as perfluoropropyl vinyl ether (PPVE), are mostly derived from TFE. HFP is produced through the pyrolysis of TFE and/or HCFC-22. Oxidation of HFP is used to produce hexafluoropropylene oxide (HFPO), an important building block in the synthesis of the FAVE monomers and PFPEs (Figure 3).<sup>39</sup>

Most fluoropolymers are produced by chain-growth polymerization using two main production processes: a) suspension polymerization; and b) emulsion polymerization.<sup>39</sup> In suspension polymerization, a medium is used in which the insoluble monomers are dispersed mechanically by e.g. stirring. The polymerization is then initiated in the monomer droplets by the addition of a monomer-soluble initiator molecule. A substance is sometimes added to stabilize the suspension and to prevent over-coagulation. Suspension polymerization yields a granular polymer that can be subsequently separated by e.g. sedimentation, filtration or spray drying.<sup>41</sup>

Emulsion polymerization uses an aqueous medium in which the monomers are emulsified using a surfactant. Polymerization is subsequently initiated in micelles by a water-soluble radical forming molecule such as a persulfate. This process yields a polymer latex or dispersion, which, when dried, can be processed into a fine-powder polymer.<sup>41</sup>

Surfactants used in the emulsion polymerization production process of fluoropolymers often have hydrophobic fluorinated tails and hydrophilic head groups and, as such, are fluorosurfactants.<sup>10</sup> As these surfactants are part of the fluoropolymer end-product, they are also called fluorinated processing aids (FPAs). There are two main reasons why the relatively expensive FPAs are used in the emulsion polymerization process as opposed to e.g. hydrocarbon surfactants. These reasons are mainly due to properties derived from the C-F bonds in the hydrophobic tails of these substances, which:

1. Inhibit unwanted chain transfer reactions (CTR) during the polymerization process. These reactions can reduce the average molecular weight of the polymer product through the formation of polymerization by-products.
2. Make FPAs very strong surfactants, with a surface tension below 25 mN/m in water. This makes them ideal for stabilizing solid-liquid interfaces, as

fluoropolymers typically have low surface energy (<40 mN/m), which requires strong stabilization energy.<sup>42</sup>

From the start of commercial fluoropolymer production until around the start of the 21<sup>st</sup> century, FPAs mainly used in the emulsion polymerization process were salts of long-chain PFAAs, such as ammonium perfluorooctanoate (APFO; C8; Figure 5) and ammonium perfluorononanoate (APFN; C9; Figure 5).<sup>43</sup> Because these substances were not intended to be part of the end-product, they were removed by processing steps such as washing and drying of fluoropolymer dispersions and emitted to the environment in dissociated form through liquid and gaseous waste streams.<sup>39</sup>

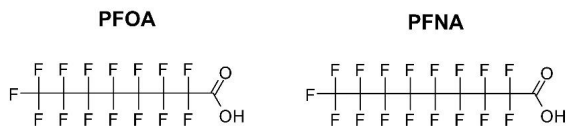


Figure 5. Structures of PFOA and PFNA; parent acids of FPAs used in fluoropolymer production.

### 1.2.5 The fluoropolymer-PFAS relationship

The production of fluoropolymers and their feedstock substances is intrinsically related with the use, formation and emissions of PFAS. This has led to increased PFAS exposure of workers and populations living nearby fluorochemical production sites. Large fluorochemical companies such as 3M and DuPont were reportedly aware of the toxicity of PFAA FPAs such as PFOA and the presence of fluorochemicals in the blood of workers by the 1970s.<sup>44,45</sup> However, it took about forty years for these findings to become public knowledge, as industry employed several strategies that aimed to influence science and regulation on PFAS.<sup>46</sup> In the meantime, substances such as PFOA continued to be used and emitted without much abatement, contaminating local environments around FPPs. Consequently, due to their mobility, persistence and emission volumes, PFAAs became ubiquitous environmental contaminants. Fluoropolymer production was and is one of the primary sources of PFCAs to the environment.<sup>43</sup>

### 1.2.6 Industrial solutions for PFAS-issues

In response to the (eco)toxicological and environmental issues associated with PFOA and its use as a FPA, a stewardship program was initiated in 2006 by the United States Environmental Protection Agency (US EPA), under which producers in the US, EU, and Japan voluntarily phased out (salts of) PFOA.<sup>47</sup> Subsequently, in 2019, most uses of PFOA were eliminated by the listing this substance on the Stockholm Convention on POPs.<sup>48</sup> To enable the continued production of fluoropolymers via emulsion polymerization, industry introduced replacement FPAs, which were primarily (ammonium salts of) perfluoroalkyl ether carboxylic acids (PFECAs; Figure 6).<sup>49</sup> Producers sourced these replacements from existing processes within their portfolios:

- **ADONA** from 3M/Dyneon was first introduced in 2002 and based on the monomer MV31 used in ionomer production processes.<sup>39</sup>
- **HFPO-DA/GenX**, introduced around 2011 by Chemours, was derived from the feedstock HFPO and their PFPE and FAVE production processes.<sup>50</sup>

- **EEA**, developed by AGC around 2008, was synthesized using a direct fluorination process introduced around 2005, which was already used to produce various perfluorinated building blocks and PFPEs.<sup>51</sup>
- **C6O4**, introduced by Solvay around 2011, was based on the chemistry of the amorphous fluoropolymer Hyflon AD.
- **ADV**, a mixture of long-chained chlorinated PFECAs also introduced by Solvay around 1996, was based on their Galden/Fluorolink PFPEs.<sup>52</sup>

Evidence suggests that most short-chain replacement FPAs retained toxicity and persistence when compared to long-chain PFAAs but were less bioaccumulative and more water-soluble.<sup>53,54</sup> Consequently, these replacements did not meet the PBT (Persistence, Bioaccumulation, and Toxicity) criteria employed in chemical risk assessments e.g. under REACH in the EU, thereby appearing as suitable alternatives.<sup>55</sup> However, these substances have raised concerns over regrettable substitution due to their persistence, mobility, and toxicity.<sup>56</sup> These properties cause the replacement FPAs to spread more readily through the aquatic environment and make them more difficult to remove from aqueous matrices with e.g. sorption techniques compared to long-chain PFAAs.<sup>57</sup> Moreover, the introduction and emission of replacement FPAs has significantly complicated the overall environmental PFAS profile, making it more challenging for scientists, regulators, and other stakeholders to fully understand their environmental impact. This added complexity has resulted in the need for additional resources to conduct studies on exposure pathways, toxicity, and other critical factors, thereby increasing the workload for ongoing risk assessments and regulatory efforts. This contributed to regulation following the introduction of alternatives; e.g. HFPO-DA was classified as a substance of very high concern (SVHC) by ECHA in 2019.<sup>58</sup>

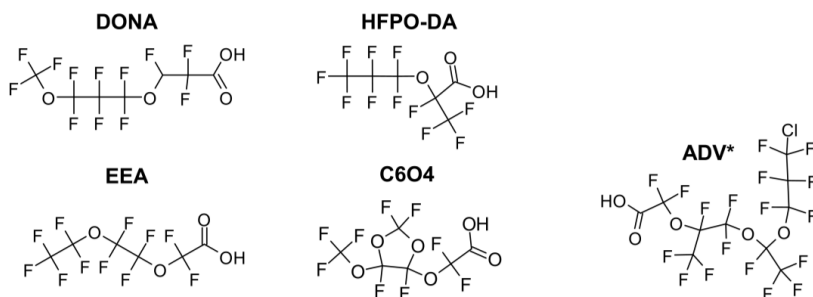


Figure 6. An overview of the structures of the parent acids of various replacement FPAs. \*ADV has multiple homologs with different chain lengths.

In addition to developing replacement FPAs, the industry also explored FPA-free polymerization methods. This approach was first applied to the production of PVDF in the early 2000s and is currently also being explored for other fluoropolymers.<sup>59</sup> While this method may seem like a suitable solution, some evidence suggests that these techniques rely on telogenic activity (chain transfer reactions) to intentionally generate a complex mixture of additional polymerization residuals of varying chain lengths in-situ.<sup>60</sup> These residuals are structurally similar to FPAs and could serve a similar

function after in-situ formation and are therefore present in similar quantities and could be emitted to the environment following the same pathways as FPAs.

Additionally, several companies implemented measures to reduce PFAS emissions through emission abatement techniques.<sup>39</sup> These included technologies designed to capture PFAS, such as activated carbon or ion exchange systems, as well as methods for their destruction, such as thermal oxidation. These advancements highlight the ongoing efforts of the industry to address environmental concerns and regulatory requirements, while maintaining fluoropolymer production.<sup>59</sup>

### *1.2.7 Previous studies and knowledge gaps*

Since the start of the 21<sup>st</sup> century, when fluoropolymer production was identified as a significant contributor to global PFAA levels,<sup>43</sup> multiple researchers have investigated the PFAS emissions of FPPs. Early studies focused on the emissions and environmental concentrations of long-chain PFAA FPAs, such as PFOA, at specific sites.<sup>61,62,63</sup> In the 2010s, when PFOA was gradually replaced by producers in the EU, US and Japan, its replacements and multiple other ionic PFAS were first detected around FPPs. This development was assisted by increasing availability of high-resolution mass spectrometry techniques and the expansion of studies to additional FPPs in the US, Europe and Asia.<sup>64,65,50</sup>

Despite these advancements, several knowledge gaps remain. Research on PFAS emissions has primarily focused on specific locations, meaning that not all FPPs have been investigated to the same extent. As a result, emission estimates and characterizations for atmospheric and aqueous releases remain incomplete. Additionally, relatively few studies have systematically compared multiple FPPs across different countries, limiting insights into regional variations in emissions and regulatory effectiveness.

Another limitation is that current analytical methods do not fully capture the diversity of PFAS emitted by FPPs, as some compounds fall outside the scope of both targeted and non-targeted analyses. Given the expanding definition of PFAS, broadening sampling and analytical approaches to include other classes—such as volatile neutral PFAS, (ultra)short-chain PFAAs, and polymeric PFAS—is necessary. Additionally, while research has largely focused on FPAs used in emulsion polymerization and commonly detected ionic PFAS, many other emission sources and production processes remain insufficiently characterized. The links between detected PFAS and specific production steps are often unclear, making it difficult to e.g. assess the effectiveness of emission control measures. A more comprehensive approach—integrating analytical methods with complementary data sources such as environmental permits, regulatory reports, and industrial disclosures and insights into applied production chemistries—would help bridge this gap.

Finally, PFAS emissions from FPPs are dynamic, influenced by regulation, emission abatement technologies, shifts in production processes, and alternative chemistries. While some of these changes are intended to reduce environmental impacts, their effectiveness and potential consequences remain insufficiently characterized. Addressing these knowledge gaps is essential for improving the understanding of PFAS emissions from FPPs and developing more effective mitigation strategies.

## **2. Research objectives**

### **2.1 Study aims & hypotheses**

The overarching aim of this research was to address the environmental challenges posed by PFAS emissions from FPPs. Specifically, this thesis aimed to identify and quantify the types and volumes of PFAS emitted during monomer production, polymerization, and further processing by applying complementary top-down and bottom-up approaches based on environmental measurements and documented data collection, respectively. It also sought to elucidate the environmental fate of atmospheric PFAS emissions and assess the impact of industrial solutions, such as replacement chemistries and emission abatement techniques. Finally, the research highlighted regional differences in PFAS management, comparing Europe and China, and examined the implications for human exposure and local and global PFAS concentrations.

The main hypothesis was that FPPs are significant sources of PFAS emissions, with different stages of production—monomer synthesis, polymerization, and processing—releasing PFAS into the environment. Furthermore, it was expected that certain PFAS detected through environmental sampling and analysis may not have been accounted for in regulatory documents such as environmental permits, particularly if they were unknown, unregulated, or not explicitly reported. Conversely, some PFAS emissions identified in regulatory data were expected to not have been previously detected through sampling and analysis due to limitations in analytical methods, environmental dispersion, or sampling design.

It was further hypothesized that atmospheric PFAS emissions from FPPs undergo long-range transport, contributing to contamination at remote locations. While industrial solutions such as replacement chemistries and abatement technologies were expected to reduce the impact of PFAS emissions, they were hypothesized to be insufficient to prevent environmental contamination entirely. Additionally, the research anticipated that regional disparities in regulatory frameworks and enforcement, particularly between Europe and China, would result in significant variations in PFAS emissions and their impacts on environmental concentrations and resulting human exposure. Finally, it was hypothesized that historic emissions and legacy contamination at FPP sites act as persistent sources of re-emission, prolonging environmental exposure.

### **2.2 Research questions**

Building on the study aims and hypotheses, this research aimed to answer the following research questions:

- ❖ Which specific PFAS are emitted during the production of fluoropolymers?
- ❖ What are the mechanisms and pathways of PFAS emission during fluoropolymer production?
- ❖ How do PFAS emissions relate to specific fluoropolymer production processes?
- ❖ What is the environmental fate of PFAS emissions from FPPs?

- ❖ What are the consequences of atmospheric PFAS emissions by FPPs for human exposure to these substances?
- ❖ How do industrial solutions, such as replacement chemistries and abatement techniques impact PFAS emissions from fluoropolymer production?
- ❖ How do PFAS concentrations measured in the environment near FPPs compare between geographic regions?

### 3. Materials & methods

This section briefly summarizes the methodology followed in the studies included in this thesis (Figure 8). More detailed descriptions of the applied methodology can be found in the papers and their supporting information.

#### 3.1 Research scope and locations

##### 3.1.1 Study sites

**Papers I-III** focused on PFAS emissions by the European fluoropolymer production industry. In **Paper I**, all six FPPs located within the EU and the UK, were investigated simultaneously, while **Papers II** and **III** studied individual FPPs in the Netherlands (Chemours, Dordrecht) and the UK (AGC Chemicals Europe, Hillhouse), respectively. **Paper IV** went outside of the European context and investigated PFAS in the environment near a major FPP operated by Shandong Dongyue in Zibo, China (Table 2).

Table 2. Locations and characteristics of study sites and sampling dates

Company	Location	Paper	Polymers (production capacity x10 <sup>4</sup> tonnes)	Sampling campaigns	Sampling sites
AGC Chemicals Europe	Hillhouse, Thornton-Cleveleys, United Kingdom	I and III	PTFE (0.4), ETFE (0.2)	11-06-2021 – 24-09-2021 (air) 12-02-2023 (water)	Hazelrigg Meteorological Station (air) Several discharges to the River Wyre (water)
Arkema France and Daikin Chemical	Pierre-Bénite, France	I	PVDF (0.8), FKM (0.365)	-	-
Chemours	Dordrecht, the Netherlands	I and II	PTFE (0.8), FEP (0.35), FKM (0.68)	02-06-2021 – 28-10-2021 (air)	Cabauw Meteorological Station
Dyneon (3M subsidiary)	Bürgkirchen a/d Alz, Germany	I	PTFE, PFA, ETFE, THV, FKM, ionomers, PFPEs (Σ1.7)	-	-
Solvay/Syensqo	Tavaux, France	I	PVDF (3.4)	-	-
Solvay/Syensqo	Spinetta-Marengo, Italy	I	PTFE, PFA, FKM, PFPEs, Hyflon AD, ionomers (unknown)	-	-
Shandong Dongyue	Zibo, China	IV	PTFE (4.5), PVDF (1.0), FEP (0.5), FKM (0.3)	20-03-2019 – 16-04-2019 (air)	Rooftop of apartment complex 30 km downwind

##### 3.1.2 Substance scope

In terms of substance scope and covered chemical space, **Paper I** focused on the emissions of PFAS and all other fluorinated organic substances by the fluoropolymer production industry (Figure 7). **Papers II-IV** investigated specific alternative chemistries introduced by different companies, such as HFPO-DA/GenX (**Paper II**), EEA (**Paper III**) and PFOA and a mixture of different PFECAs (**Paper IV**). Additionally,

**Papers II-IV** studied a subset of emitted detectable ionic PFAS that were within the chemical space of the used sampling, extraction and analysis methods.

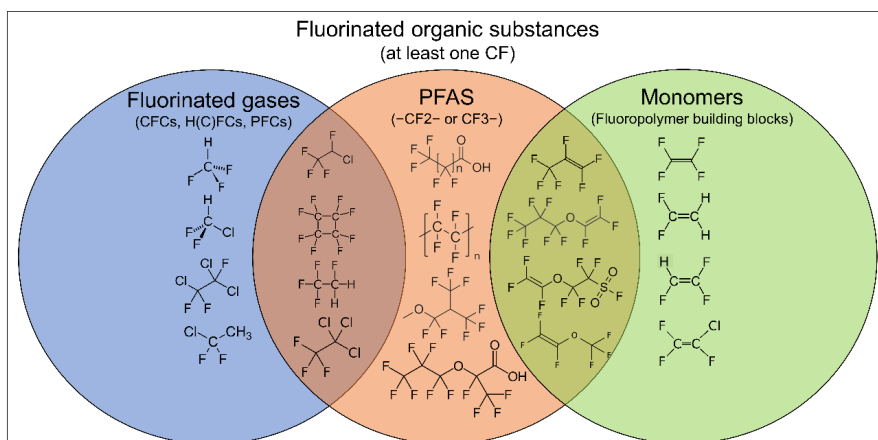


Figure 7. Substance scope diagram from **Paper I** showing example substances in each category.

### 3.2 Data collection and sampling

#### 3.2.1 Desk-based data collection

Methodologies to capture PFAS emissions from FPPs included a ‘bottom-up’ desk-based approach which consisted of the extensive investigation of multiple documents and databases that contained information on FPPs and their PFAS emissions. The goal of this approach was to identify, quantify, compare and summarize the known and regulated PFAS emissions by FPPs. This was the main methodology followed in **Paper I** and used to create an emission inventory for the European fluoropolymer production industry. Investigated data sources included FPP environmental permits, emission databases (such as the European Pollutant Release and Transfer Register – E-PRTR) and emission monitoring reports. These data were obtained through inquiries to the responsible authorities or acquired from publicly available data.

#### 3.2.2 Environmental sampling

The second applied approach to capture emissions was a ‘top-down’ field-based method and was followed in **Papers II-IV**. The goal of this approach was to capture PFAS emissions by collecting environmental (air and surface water) samples in the vicinity of FPPs through sampling campaigns (Table 2). In **Paper II** and **III**, samples of airborne particulates were collected on quartz fibre filters (QFFs) using high volume active air samplers, while in **Paper IV** a cascade impactor was employed to collect different size fractions of airborne particulates on membranes. Air sampling flow rates ranged from about 200 L/min (**Paper IV**) to 1000 L/min (**Paper II**). These samplers were located 20-30 km downwind of the FPPs and collected samples over fixed time periods (e.g. 24 hours), so that emission plumes could be sampled periodically, depending on the meteorological conditions such as wind speed and direction. This allowed for the study of the transport of atmospheric PFAS emissions on a regional



scale. Data were also collected in parallel to the sampling campaigns, so that the influence of meteorological conditions on ambient PFAS concentrations could be investigated. Sampling campaigns for **Papers II and III** were therefore carried out at meteorological observatories. Additionally, air sampling campaigns were chosen because PFAS air emissions have been characterized less than aqueous emissions.

Additionally, grab surface water samples were collected in the vicinity of discharges of the AGC Chemicals Europe FPP studied in **Paper III**. This work was done because relatively little data was available on environmental PFAS emissions of this plant at the time. Multiple discharges around the industrial site were sampled, including the main discharge of process water effluent, but also surface water runoff and tidal discharges and old pipes.

### **3.3 Aggregation and extraction**

#### *3.3.1 Data aggregation*

The emission data collected using the desk-based approach in **Paper I** were reported in varying formats and levels of detail across different authorities. In environmental permits, some agencies set limits for individual substances, while others regulated emissions of substance groups, such as fluorinated organic substances. These permits varied from including only limit values to also providing reported or estimated yearly emissions. In some cases, data included detailed parameters such as concentrations ( $\text{mg}/\text{m}^3$ ) and flow rates ( $\text{m}^3/\text{h}$ ), enabling the calculation of permitted emissions, while others reported annual limits directly (e.g., in  $\text{kg}/\text{year}$ ). For consistency of the emission inventory, all emission data were converted to tonnes per year ( $\text{t}/\text{year}$ ). Most permits identified emission points (e.g., stacks) or processes (e.g., production activities). These were aggregated into total FPP emissions by summing emissions across points. Where available, actual reported emissions were used for accuracy, while permitted emissions served as worst-case estimates if reporting data were unavailable.

#### *3.3.2 Extraction of air and water samples*

For **Papers II-IV** lab work was carried out in order to prepare the environmental samples for instrumental analysis (Section 3.4.1). For the particulate air samples collected both on QFFs and cascade impactor membranes using high-volume air sampling, an extraction of PFAS was carried out based on the ultrasonication of these collection media in organic solvent, i.e. methanol (MeOH). After ultrasonication, the sample extracts were concentrated using evaporation and cleaned by filtration and centrifugation.

Due to the proximity of the sampling sites in the Netherlands (**Paper II**) and the UK (**Paper III**) to the coast, small punches were taken of the QFFs before extraction to assess the potential contribution of sea spray aerosol (SSA). These were extracted using ultrapure water and analysed to determine the concentrations of the sodium ( $\text{Na}^+$ ) tracer ion, a proxy for SSA influence, using ion chromatography. The results were used to investigate the relation between SSA and ambient PFAS concentrations at these sampling sites.

The surface water samples (**Paper III**) were extracted and concentrated using a method for PFAS based on weak anion-exchange (WAX) solid-phase extraction (SPE).

### 3.4 Characterization of PFAS emissions

#### 3.4.1 Analytical methodology

In **Papers II-IV** the presence and concentrations of different PFAS in environmental samples was determined by analysing injected sample extracts using liquid chromatography coupled with Orbitrap high-resolution mass spectrometry (LC-HRMS). This approach allowed for: a) 'targeted' PFAS analysis in which the presence and concentrations of PFAS in samples was determined by comparison to calibration standards with known PFAS concentrations and; b) PFAS 'suspect screening' in which the high mass accuracy and resolution of the Orbitrap were used to screen the full-scan ( $MS^1$ ) spectrum of the sample injections for features that were potential PFAS.

The relevance of the targeted analysis relied heavily on the availability of the appropriate analytical standards for the studied PFAS emissions, such as HFPO-DA/GenX (**Paper II**), EEA (**Paper III**) and various PFECAs (**Paper IV**). Some of these substances were not readily available from standard catalogues and were therefore synthesized by vendors specifically for this research (EEA) or acquired from other study groups (PFECAs). Additionally, the analyte list of all conducted studies in this thesis consisted of  $C_4$ - $C_{14}$  PFECAs,  $C_4$ ,  $C_6$  and  $C_8$  PFASs and FTASs.

In the suspect screening methodology followed in **Papers II-IV**, the LC-HRMS isolated precursor ions in a scan range between 150-1800 Da by using a so-called 'data-dependent acquisition' (DDA) which is based on the presence of their masses ( $m/z$ ) in a mass inclusion list containing about 5000 PFAS suspects or when their instrumental response was above a certain intensity threshold (in the Top 5 per scan). These isolated precursors were then fragmented in order to collect a molecular 'fingerprint' through an  $MS^2$  scan. The detected features could subsequently be compared with various sources (e.g. spectral libraries or in-silico fragmentation) and diagnostic evidence such as the presence of homologous series and isotopic patterns. This analysis was not only used to determine whether suspects could possibly be PFAS, but also to assess the confidence in these determinations.

#### 3.4.2 Modelling of environmental fate

The environmental fate of FPP PFAS emissions to the atmosphere was modelled in **Papers II** and **IV**. This was achieved by running simulations using Lagrangian atmospheric dispersion and transport models such as FLEXPART (**Paper II**) and HYSPLIT (**Paper IV**). These models were used in forward mode, which allows for the modelling of transport of pollutants from point sources, using pollutant emission rates as input. These simulations were used to validate measured ambient PFAS concentrations at the downwind sampling site (**Paper II**) and to model the long-range atmospheric transport of the PFASs HFPO-DA (**Paper II**) and PFOA (**Paper IV**).

#### 3.4.3 Consolidation of approaches

To comprehensively assess PFAS emissions from FPPs, both bottom-up and top-down approaches were applied in a complementary manner. The bottom-up approach, based on emission reports and permit data (**Paper I**), was used to inform instrumental analyses (Section 3.4.1) and model inputs (Section 3.4.2) in **Papers II-IV**. Conversely, top-down methods, including previous environmental sampling and analysis, provided concentration data that were compared to reported PFAS emissions in **Paper I**. This

integration not only improved the overall assessment of PFAS emissions but also allowed for direct comparisons between PFAS identified through regulatory data and those detected via environmental sampling, highlighting potential discrepancies or overlooked emissions.

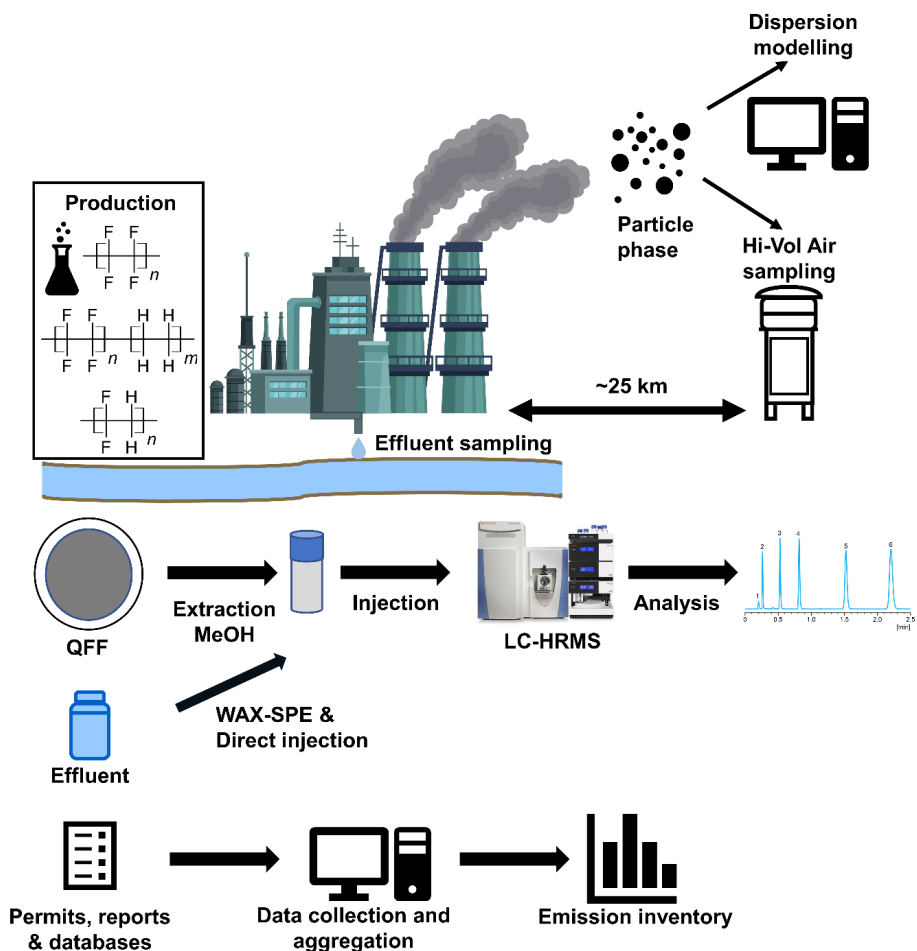


Figure 8. Overview of the applied methodology in this thesis research

## 4. Results & Discussion

### 4.1 Sources, types and volumes of FPP PFAS emissions

#### 4.1.1 Monomers and their production

Results from the emission inventory for the European fluoropolymer production industry (**Paper I**) showed that FPPs emit considerable amounts of the monomeric starting materials and substances related to their production. Because monomers are the primary feedstock for fluoropolymers, their emissions were generally well-documented in environmental permits and could largely be effectively captured by the 'bottom-up' approach of **Paper I**. Unfortunately, these substances were not within the chemical space of the sampling and analysis methods of **Papers II-IV**.

In **Paper I** emissions of monomers were estimated to be around 75 tonnes per year for European fluoropolymer production. This was shown to occur during on-site monomer production and after polymerization, when residual unreacted monomers were purged. Monomers are small, volatile and reactive and preventing fugitive emissions might be difficult. That said, not all monomers can be classified as PFAS. The main feedstocks of e.g. PTFE and PVDF, small C<sub>2</sub> fluoroalkene monomers, such as TFE and VDF, are not PFAS and mineralizable in the environment.<sup>66,67</sup> However, this property is not without potential issues, because substances like the toxic carbonyl fluoride (COF<sub>2</sub>) and highly acidic and corrosive HF can be formed when these monomers mineralize.

Larger (co)monomers, typically with more than three carbons ( $\geq C_3$ ) such as HFP, FAVEs and the functional monomers used in e.g. ionomers are PFAS. Their emissions could lead to the formation of small persistent ionic PFAS, such as trifluoroacetic acid (TFA), e.g. through acyl fluoride formation and hydrolysis.<sup>68, 69, 70</sup> Especially HFP is used and possibly emitted in high volumes; results of **Paper I** indicated that emissions of this PFAS monomer in Europe were almost 36 tonnes/year for three out of six FPPs. Although data was scarce, emission volumes of other  $\geq C_3$  (co)monomers were smaller than that of e.g. TFE and HFP, but not insignificant. Around 4 tonnes of FAVEs (PMVE, PPVE and PEVE) were reportedly emitted yearly by Chemours, Dordrecht.

Furthermore, the production of the monomers through the pyrolysis of HCFC feedstocks could also lead to the emissions of PFAS and other fluorinated organic substances. This occurs through the formation and release of various pyrolysis by-products that are a result of oligomerization, incomplete leavening of chlorine from the feedstock HCFC or a combination of these two processes. For e.g. TFE production, PFAS by-products include (the highly toxic) perfluoroisobutene (PFIB), perfluorocyclobutane or TFE-dimer (PFC-318) and perfluoroallyl chloride (PFAC). Data collected in **Paper I** on the emissions of pyrolysis by-products from fluoropolymer production in Europe were limited, but shown to be in the tens to potentially hundreds of tons per year.

Due to their physical chemical properties, HCFC feedstocks, monomers and pyrolysis by-products are mainly emitted to the atmosphere. Although the HCFC feedstocks for TFE and VDF production -HCFC-22 and HCFC-142b respectively- are not PFAS they are regulated under the Montreal Protocol due to their ozone depleting potential (ODP) and actually phased out as end-use chemicals.<sup>71</sup> However, their use as feedstock chemicals is an exemption for this protocol<sup>72</sup> and considerable amounts are still

emitted by the fluoropolymer production industry; about 52 tonnes by the European producers in 2021 (**Paper I**). Additionally, various HFCs and PFCs such as fluoroform (HFC-23) and difluoromethane (HFC-32), both by-products of HCFC-22 production and PFC-318, a pyrolysis by-product, have high global warming potentials (GWPs). Global atmospheric concentrations of gases such as PFC-318 and HCFC-22 have been increasing over the last decades.<sup>73</sup>

#### 4.1.2 Polymerization

The main production process carried out at FPPs, polymerization, inherently produces polymeric PFAS; i.e. the fluoropolymers themselves. Although production volumes of FPPs studied in **Papers I-IV** were mostly well-known, relatively little data could be collected on fluoropolymer emissions. Due to the high molecular weight and inert nature of these polymers, emissions might be difficult to detect and monitor but nevertheless possible, especially if these materials are not properly managed. Potential emissions could include polymer dust generated during or after drying dispersions or when handling fine powder polymers as well as aqueous emissions of colloidal fluoropolymers from polymer dispersions.

Other PFAS featured in polymerization depended on the type of process that was used. Emulsion polymerization was associated with the emissions of FPAs. Results of both the emission inventory (**Paper I**) and the environmental sampling (**Papers II-IV**) showed that fluoropolymer production plants remained sources of these substances to the environment. Emissions of the FPAs HFPO-DA (used for PTFE and FEP production) and 6:2 FTSA (used for FKM production) to air were reported in the environmental permit and these substances were also detected in air downwind of the Chemours plant in Dordrecht, the Netherlands (**Paper II**). Similarly, emissions of EEA (used for PTFE production) were reported in the environmental permit of the AGC Chemicals Europe plant and measured in air and water in the vicinity of this FPP in the UK (**Paper III**). In China, multiple FPAs were reportedly used at the Shandong Dongyue facility in Zibo, these included (the regulated) PFOA and T-5, of which the main component is hexafluoropropylene oxide trimer acid (HFPO-TA). These were detected in samples taken downwind of this FPP, along with various additional PF(E)CAs, such as HFPO-DA and EEA. (**Paper IV**).

Impurities that stemmed from the production of FPAs or other fluorochemical production processes were also detected in the environmental samples in **Papers III and IV**. Examples included branched isomers that were formed during the ECF process used to produce PFOA and various suspect classes linked to this process, such as cyclical PFECAs (**Paper III and IV**).<sup>74</sup>

Additionally, studies have shown that some fluoropolymer polymerization processes inherently lead to the formation of oligomeric by-products through the telogenic (chain-forming) polymerization reaction. These by-products can form due to premature termination of the chain forming reaction through chain transfer and e.g. through interactions with impurities present in the reactor.<sup>60</sup> Like fluoropolymers, these substances consist of chains of repeating monomer derived sub-units, but differ from these materials due to their lower molecular weight and the presence of charged head groups. Thus, polymerization by-products could have similar structures as FPAs and

potentially similar concerning properties. For PTFE, for instance, hydrogen-substituted PFCAs (H-PFCAs) have been described as inherent polymerization by-products. Polymerization by-products are not well monitored and regulated. The emission inventory could find little data on these PFAS and their emissions (**Paper I**). However, the suspect screening approaches applied in **Papers II-IV** showed that substances such as H-PFCAs were present in the environment close to all studied FPPs.

Lastly, the emission inventory (**Paper I**) found that PFAS other than FPAAs could also be used in polymerization reactions. These included fluorinated solvents that were used as polymerization media and subsequently partially emitted to the environment. For instance, AGC Chemicals Europe emitted more than 30 tonnes of the fluorinated solvent 1-H PFHx used in granular ETFE production to the atmosphere per year. Other PFAS used in polymerization reactions included chain-transfer agents (CTAs). These are substances added during polymerization to control the molecular weight of the polymer by transferring the chain-forming reaction to their structures. Emissions of iodinated PFAS; e.g. 1,4-diiodoperfluorobutane (DIOFB) used as chain transfer agent were reported for Solvay Specialty Polymers (currently named Syensqo) in Italy. Similar to PFAS monomers and their by-products, these substances were not within the chemical space of the methods of **Papers II-IV**.

#### 4.1.3 Further processing

Some fluoropolymers are processed further after production and PFAS can be used in these processing steps. Fluoroelastomers, for example, can be crosslinked or cured/vulcanised in order to harden these materials. A common crosslinking agent for FKM is Bisphenol AF (BPAF), which is both a PFAS and a possible endocrine disruptive compound.<sup>75</sup> Although BPAF was not mentioned on the environmental permit of Chemours (**Paper I**), it is used at this facility for curing FKM and traces of this curing agent were detected downwind of this FPP (**Paper II**).

Other on-site processing steps, such as the compounding of different fluoropolymers and PFPEs could use fluorinated solvents, that are emitted when the compounded material is dried or extruded and the solvent evaporated. The Chemours FPP in Dordrecht, for example, reportedly emitted 900 kg/year of the fluorinated solvent Vertrel XF or HFC-4310mee through compounding of fluoropolymers. The global concentrations of this high GWP substance have been increasing over the last decade.

<sup>76</sup>

#### 4.1.4 Historical emissions

It has to be noted that the FPPs investigated in the Netherlands (**Paper II**) and the UK (**Paper III**) have been in operation for a relatively long time period. Chemours' predecessor DuPont started producing PTFE in Dordrecht in 1967, while the former operator of the AGC Chemicals Europe plant, ICI, started using the Hillhouse site in the early 1950s. Since the start of production at these plants until its phaseout in 2012, APFO was used and emissions of PFOA to the local environment were considerable; in total around 145 tonnes in the UK between 1955 and 2012 and yearly emissions in the Netherlands were in the tens of tons per year.<sup>77,78</sup> Because of this historical use pattern and the persistency of PFOA, local background levels are elevated and reservoirs of PFOA and related compounds still exist on-site, which could lead to

(re)emissions of these substances. These factors, along with continued use in China, may have contributed to the detection of PFOA in all but one of the environmental samples analysed in this research (**Papers II-IV**).

## **4.2 Environmental PFAS concentrations and impact of industrial solutions**

### *4.2.1 Air concentrations*

The peak concentrations of total detected  $\Sigma$ PFAS in air downwind of FPPs measured during the sampling campaigns of **Papers II-IV** ranged from about 5 pg/m<sup>3</sup> in the UK, up to about 100 pg/m<sup>3</sup> in the Netherlands and more than 3000 pg/m<sup>3</sup> in China. Individual PFAS with the highest peak concentrations were PFOA (2.50 pg/m<sup>3</sup>), HFPO-DA (98.66 pg/m<sup>3</sup>) and PFOA (2952 pg/m<sup>3</sup>) for the UK, the Netherlands and China respectively. In all cases, the peak ambient PFAS concentrations were associated with wind blowing from the direction of the FPPs (Figure 9).

The differences in measured average PFAS air concentrations (Figure 10) between countries were attributed to multiple factors. Firstly, the size and production capacity of the facilities differed between FPPs. Total production capacities for the UK, Dutch and Chinese plants were 0.60 x 10<sup>4</sup> tonnes (PTFE and ETFE), 1.88 x 10<sup>4</sup> tonnes (PTFE, FEP and FKM) and at least 6.3 x 10<sup>4</sup> tonnes (PTFE, PVDF, FEP and FKM) respectively (Table 2). Although with higher fluoropolymer production volumes higher PFAS emissions were also expected, this difference could not fully explain the multiple orders of magnitude difference in measured PFAS concentrations between sites.

Other important considerations are differences in regulation and enforcement between China and Europe. PFOA, which is listed in the Stockholm Convention on POPs, was still produced and used and had the highest concentrations of all PFAS measured in China during sampling. PFOA was fully phased out in the UK and the Netherlands as of 2012. This might indicate that the Chinese plant is not as strictly regulated as its European counterparts and higher relative emissions are possibly also permitted by the local authorities. Moreover, after regulatory pressure, the FPPs in both the UK and the Netherlands have implemented abatement techniques that aimed to reduce PFAS emissions by over 90%. These might not have been implemented in China before or during the sampling campaign.

An additional explanatory factor for the relatively high PFAS and PFOA levels in China could be that PFOA was actually produced on-site through ECF, while in the UK and the Netherlands, the used FPAs were produced off-site.

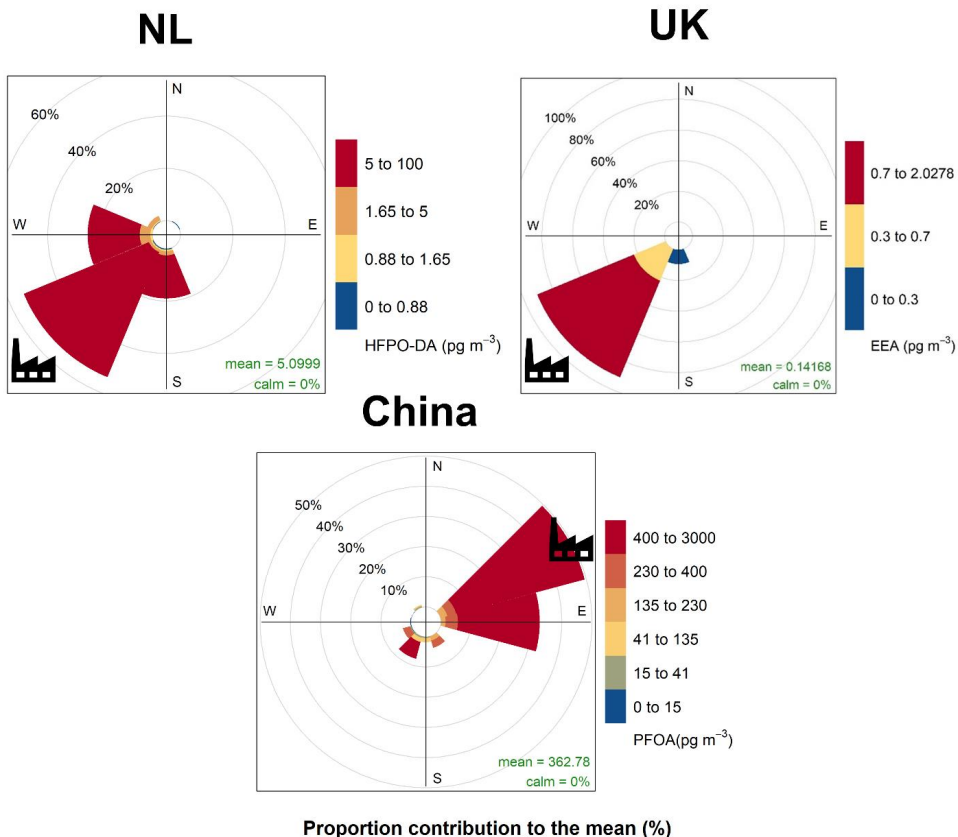


Figure 9. Pollution roses for HFPO-DA, EEA and PFOA ambient concentrations at the sampling sites in the Netherlands (NL, **Paper II**), United Kingdom (UK, **Paper III**) and China (**Paper IV**), respectively. The plots show which wind directions contributed most to mean concentrations of the FPAs. The location of the FPPs relative to the sampling site is shown using the factory icon.



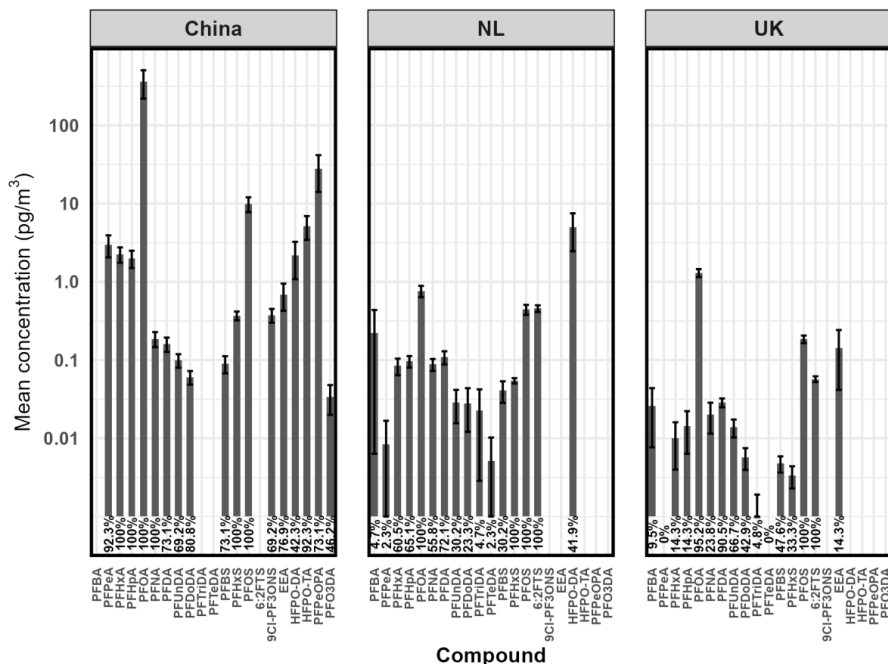


Figure 10. Mean detected PFAS concentrations ( $\text{pg}/\text{m}^3$ ) at the sampling sites during air sampling campaigns of **Papers II-IV**. Error bars show the standard errors and detection frequencies are shown beneath the bars. Values below MDL have been replaced by 0. Note the logarithmic scale.

#### 4.2.2 Water concentrations

The water concentrations of PFAS measured in **Paper III** showed that the site of AGC Chemicals Europe was a source of both legacy and scarcely monitored PFAS to the local environment. Notably, PFOA concentrations from a discharge near a lagoon that was used by AGCs predecessor ICI as a collection pond for effluent were around 20000 ng/L. These concentrations were around 4600 times higher than the surface water limit (AA-EQS) of 4.4 ng/L proposed in the EU.<sup>79</sup> The levels of their replacement processing aid, EEA, were highest in the surface water runoff discharge (~1700 ng/L). Compared to these levels, concentrations in the main discharge for process water effluent were relatively low with the sum of detected  $\Sigma$ PFAS around 30 ng/L. These results showed that emissions from on-site PFAS reservoirs and e.g. re-emissions of atmospherically deposited PFAS via runoff water can potentially occur. This emphasized that the process water effluent is not the sole contributor to aqueous PFAS emissions from FPPs and that other emission pathways should be considered when assessing FPP emissions.

#### 4.2.3 Alternative chemistries

Samples from the environment around the FPPs in the UK and the Netherlands (**Paper II and III**) showed that the PFOA alternatives EEA and HFPO-DA were emitted to the atmosphere. HFPO-DA was the PFAS with the highest measured concentration (98.66  $\text{pg}/\text{m}^3$ ) downwind of Chemours, Dordrecht while EEA had the second-highest

measured concentration (2.03 pg/m<sup>3</sup>) after PFOA (2.50 pg/m<sup>3</sup>) downwind of AGC Chemicals Europe. Although PFOA dominated the PFAS concentrations downwind of the Shandong Dongyue plant in China (**Paper IV**), peak concentrations of substances that could potentially be used as replacement surfactants, such as HFPO-DA (26 pg/m<sup>3</sup>), EEA (5 pg/m<sup>3</sup>) and HFPO-TA (33 pg/m<sup>3</sup>) were also detected in the air samples. However, it remains unclear to what extent these substances were actually used as FPAs at Shandong Dongyue and to what extent they are by-products of other fluorochemical production processes. HFPO-DA and oligomers, for instance, have been measured around plants producing, HFPO, FAVEs and PFPEs.<sup>50,80</sup>

PFOA is currently also being phased out in China and is reportedly being replaced by the shorter-chained perfluorohexanoic acid (PFHxA) at the Shandong Dongyue plant (**Paper IV**). Additionally, there is evidence of Chinese producers in the area switching to PFECA alternatives such as T-5 (HFPO-TA).<sup>81</sup> Environmental concerns with both these replacements remain, especially if emission volumes and environmental concentrations stay at similar levels as found in this research. Long-chain replacements, such as HFPO-TA, are concerning due to their possible PBT properties; HFPO-TA is potentially more bioaccumulative than PFOA.<sup>82,83</sup> Short-chain replacements could have persistent, mobile and toxic properties that prompted regulation in other parts of the world.<sup>57,84</sup>

#### 4.2.4 Emission abatement

The FPPs studied in **Papers II** and **III** had implemented emission abatement technologies during and before the sampling campaigns respectively. This was apparent in the measured environmental concentrations. The AGC Chemicals Europe plant has applied emission abatement shortly after a study conducted in 2007 measured a peak PFOA concentration of 823 pg/m<sup>3</sup> at Hazelrigg (the same sampling site as used in **Paper III**).<sup>61</sup> Similarly, the Chemours FPP in Dordrecht installed abatement technology for their atmospheric emissions while the sampling campaign at Cabauw was carried out. The HFPO-DA peak of 98.66 pg/m<sup>3</sup> was measured early during this period, at the start of the second week of sampling.

The peak concentrations of PFOA (2.50 pg/m<sup>3</sup>) and EEA (2.02 pg/m<sup>3</sup>), measured in the same sample in the UK and the peak level of HFPO-DA (12.22 pg/m<sup>3</sup>) showed that these systems are effective in reducing environmental PFAS concentrations. However, they fall short of eliminating these emissions entirely, as environmental concentrations were not reduced to non-detectable levels.

It is also noteworthy that these abatement efforts have primarily focused on reducing emissions of FPAs. Other PFAS, including e.g. monomers or neutral volatiles mentioned earlier and in **Paper I**, remain less targeted, highlighting a significant gap in the scope of current emission reduction strategies.

### 4.3 Fate of- and exposure to PFAS emissions

#### 4.3.1 Environmental fate of PFAS emissions

Although the deposition fluxes and concentrations of atmospheric ionic PFAS have been shown<sup>62,81,85</sup> and modelled<sup>86</sup> to be highest close (within 0-1 km) to the FPPs, results of the modelling work performed in **Papers II** and **IV** also showed that part of the atmospheric HFPO-DA and PFOA emissions respectively could be subject to long-

range atmospheric transport due to the partial partitioning to the accumulation mode of the particle phase.

Thus, part of the FPP stack emissions of ionic PFAS such as PFOA and HFPO-DA could directly be transported to- and subsequently deposited in remote areas and lead to detectable concentrations hundreds of kilometres from their sources. Considering the past and current emission volumes of PFCAs by FPPs, this process could possibly explain the ubiquitous presence of PFOA and other PFCAs in the global environment and at remote locations, such as the arctic.<sup>87</sup>

Furthermore, results of **Paper I** showed that FPPs are not only sources of ionic PFAS to air, but emit various volatile fluorinated organic substances, such as H(C)FCs, monomers, pyrolysis by-products and fluorinated solvents that mainly partition to the atmosphere. Their persistence and presence in the gas phase enables them to remain airborne for long periods and be transported over vast distances.<sup>88</sup> Some of these substances have ozone depletion potentials (ODP) and can exhibit high global warming potentials (GWP), contributing to climate change. Additionally, some of these volatile PFAS can possibly undergo atmospheric degradation, leading to the formation of persistent short-chain PFAS, such as trifluoroacetic acid (TFA). TFA is highly water-soluble and can accumulate in aquatic ecosystems and drinking water sources, raising concerns about their long-term environmental and human health impacts.<sup>89,90</sup>

The total aqueous emissions of ionic PFAS (e.g. FPAs or polymerization by-products) by FPPs are assumed to exceed atmospheric emissions.<sup>91</sup> Moreover, most atmospheric emissions of these substances eventually partition to the aqueous phase. Due to their solubility and persistence these substances are prone to long-range transport through water bodies.<sup>92</sup> Whereas long-chain PFAAs bioaccumulate, short-chain replacements such as HFPO-DA are more soluble and mobile and can therefore threaten to contaminate water systems. Additionally, the higher solubility means that short-chained ionic PFAS have the potential to accumulate in vegetation through capillary uptake<sup>93</sup> and are harder to remove using water treatment systems.<sup>57</sup>

Furthermore, results also indicated that long-chain PFAS in the marine environment could be potentially be resuspended in the air and deposited near coastal sites through enrichment on SSA.<sup>94</sup> Associations between  $\text{Na}^+$  and PFAS concentrations measured in **Paper III** indicated that resuspension of various PFAS emitted by AGC through SSA in the Morecambe Bay area could potentially contribute to atmospheric concentrations at the Hazelrigg Meteorological Station.

#### 4.3.2 Exposure to PFAS emissions

The atmospheric PFAS levels measured and modelled in **Papers II-IV** could be compared with published guidance values for chronic atmospheric exposure through inhalation based on European Food Safety Authority (EFSA) guidance values.<sup>95</sup> Results showed that at the sampling site 30 km downwind of the FPP of Shandong Dongyue, the peak concentration of PFOA ( $\sim 3 \text{ ng/m}^3$ ) exceeded the guidance value ( $0.3 \text{ ng/m}^3$ ) by approximately ten times, while median concentrations ( $0.38 \text{ ng/m}^3$ ) were just above this guidance value. PFOA concentrations decrease with increasing distance to the plant; additional measured median atmospheric concentrations  $0.451 \text{ ng/m}^3$  within 10 km and  $0.887 \text{ ng/m}^3$  within 5 km close to this FPP also exceeded the

guidance value.<sup>96, 82</sup> Emissions of PFOA from this plant were estimated to be around 1890 kg to the atmosphere and 7560 kg to surface water during 2021.<sup>81</sup>

Concentrations measured ~25 km downwind of the FPPs in the Netherlands and the UK were well below the guidance values for HFPO-DA (1.4 ng/m<sup>3</sup>) and PFOA. For EEA no guidance value is available. However, modelled mean daily concentrations of HFPO-DA in Dordrecht (**Paper II**) before the installation of the abatement system were 10 ng/m<sup>3</sup> between the source and 556m of the FPP and decreased to 1.8 ng/m<sup>3</sup> between 556 and 1.7 km and further decreased to 0.5 ng/m<sup>3</sup> between 1.7 and 2.8 km. Thus, before installation of the abatement system mean HFPO-DA levels could have exceeded the guidance value within a radius of approximately 2 km of the plant.

Historical air emissions of HFPO-DA (660 kg/year from 2012-2016) and its predecessor PFOA (up to 3532 kg/year in 2000) were higher than that used in the emission scenario for the modelled concentration (95 kg/year) and atmospheric PFOA concentrations up to 100 ng/m<sup>3</sup> (assuming emissions during 2000) were previously modelled at the source.<sup>85</sup> Similarly, atmospheric PFOA concentrations between 120 ng/m<sup>3</sup> and 900 ng/m<sup>3</sup> were measured near the fence line of a Chemours plant in the US in 2006. Thus, atmospheric PFAS exposure could have exceeded guidance values in a wider radius in the past, possibly affecting the towns of Sliedrecht and Dordrecht and the wider region.

A similar assessment was made for the PFOA levels in the UK (**Paper III**); the historic peak level of 0.823 ng/m<sup>3</sup> measured during 2005-2006<sup>61</sup> at the Hazelrigg Meteorological Station (~25 km downwind) also exceeded the guidance value of 0.3 ng/m<sup>3</sup>. Mean concentrations of PFOA measured during the two sampling periods of this study (0.552 and 0.101 ng/m<sup>3</sup>) were around this value. Thus, mean ambient concentrations of PFOA near the plant (within 0-2 km) at the time probably were orders of magnitude higher. Given that the AGC Chemicals Europe is located in an urban environment, the local population around the plant and in the region might have been exposed to levels above guidance values for prolonged periods of time.

Considering the modelled and measured current and historic atmospheric concentrations of PFAS at or near all these point sources, exposure assessments for FPP workers and people living in the direct vicinity of these sites could be particularly relevant.

Furthermore, deposition of atmospheric PFAS around the FPPs could impact local environments, increasing the potential for contamination of food and water sources. The Dutch National Institute for Public Health and the Environment (RIVM) advised people not to eat fruit or vegetables from vegetable gardens within 1 km of the Chemours FPP in Dordrecht.<sup>97</sup>

With increasing distance from the point source, however, other exposure routes become more significant and could potentially contribute to even higher cumulative exposures.<sup>98</sup> These pathways include aqueous emissions, which may contaminate local drinking water supplies, and the bioaccumulation of PFAS in the food chain.<sup>99, 100</sup> The consumption of locally sourced fish, meat, and dairy products is of particular concern, as PFAS have been shown to bioaccumulate in aquatic organisms and

livestock exposed to contaminated water and feed.<sup>101</sup> Drinking water contamination, often stemming from leaching into groundwater and surface water, represents another critical pathway of exposure for communities further downwind or downstream of these facilities.<sup>102</sup>

These multiple exposure routes highlight the importance of comprehensive assessments that consider the combined contributions of atmospheric, aqueous, and dietary pathways. Such evaluations are necessary to accurately determine the risks posed by PFAS emissions from FPPs and to develop effective mitigation strategies to protect both local, regional and global populations.

## **4.4 Limitations**

### *4.4.1 Data gaps*

Despite significant efforts to compile an emission inventory in **Paper I**, considerable data gaps remain. These gaps primarily stem from the limited availability of information on specific PFAS uses and emissions at fluoropolymer production plants (FPPs). The bottom-up method could be significantly improved with greater transparency and a regulatory level playing field across facilities and jurisdictions.

One of the main challenges in interpreting the results of the inventory is the inconsistent level of detail in emission permits. Some permits regulate emissions on a substance-specific level, providing detailed information on individual PFAS. In contrast, others regulate emissions as grouped categories, which can obscure the contribution of individual compounds. For instance, cumulative emission limits may include broad categories such as “fluorinated organic substances”, which encompasses PFAS, fluorinated gases, and monomers. These inconsistencies create difficulties in data collection and comparability, as overlapping or undefined substance categories complicate the attribution of emissions to specific PFAS or European Pollutant Release and Transfer Register (E-PRTR) reportable groups (Figure 7).

Additionally, the frequency and quality of permit updates vary widely. While some permits are regularly updated and provide recent data, others remain outdated. This irregularity complicates the direct comparison of emission figures between plants. Consequently, companies with more comprehensive public reporting and detailed permit applications may appear to be major emitters, not necessarily because of higher emissions but due to superior data availability relative to less transparent operators.

The analysis of environmental permits revealed that companies are required to monitor emission flux concentrations and report these values to regulators and permitting authorities. However, these data are often not made publicly available, even after formal inquiries. This lack of transparency further hampers the creation of a comprehensive and comparable emission inventory.

To address these issues, it is recommended that emission data in e.g. the EU be made publicly available and reported in a consistent and transparent manner. Such improvements would enable more accurate assessments of PFAS emissions, better facilitate comparisons between facilities, and enhance regulatory oversight and accountability.

#### 4.4.2 Chemical space covered

It must be emphasized that the chemical space of the PFAS emissions captured by the top-down methodology applied in **Papers II-IV** was constrained by several factors such as a) sampling methods: the high-volume air sampling of airborne particulates and surface water grab sampling focused primarily on ionic PFAS associated with particulate matter and water matrices; b) extraction: ultrasonication in MeOH for QFFs and WAX SPE for surface water were also optimized for specific ionic PFAS; and c) instrumental analysis: liquid chromatographic separation using a column with a C18 stationary phase and detection via mass spectrometry with electrospray ionization in negative mode (ESI<sup>-</sup>) limited the study to ionic PFAS with carbon chain lengths between  $\geq C_4$  and  $\leq C_{18}$ .

These methodological limitations may have resulted in inadequate capture or identification of additional PFAS emissions, particularly volatile, neutral, polymeric, and ultrashort-chain PFAS. For instance, certain volatile neutral PFAS such as pyrolysis by-products, fluorinated solvents and (co)-monomers reportedly emitted in substantial amounts by FPPs (**Paper I**) could not be measured using these methods.

Furthermore, although ionic PFAS such as PFOA and HFPO-DA have low  $pK_a$  values (around 2.02 and 0.77-2.84 respectively),<sup>50,103,104</sup> a portion of the emitted ionic PFAS might have partitioned into the gas phase, particularly under conditions of low aerosol pH. This potential partitioning could lead to underrepresentation of specific PFAS species in particulate samples and further highlights the need for future studies to consider both particulate and gas-phase sampling.

As the definition of PFAS has expanded considerably, broadening both the understanding and analytical coverage of their chemical space remains a crucial focus for future research on PFAS emissions from FPPs. This will require research, regulatory, and emission abatement efforts to extend beyond FPAs and include processes such as suspension polymerization and feedstock production, as well as substances like (ultra)short-chain PFAS, (semi)volatile neutral PFAS, polymeric PFAS, and transformation products. Additionally, methods such as fluorine mass balance techniques, gas-phase sampling and gas chromatography coupled with advanced high-resolution analytical approaches will be necessary to comprehensively identify and characterize PFAS emissions and inform more effective mitigation strategies.

#### 4.4.3 Sampling strategies

The sampling strategies from **Papers II-IV** were subject to several constraints that may have impacted the scope and representativeness of the results. First, the number of samplers deployed was limited, which restricted spatial coverage and the ability to capture potential emission variability at finer scales. Deploying additional samplers at multiple locations, including fence line sites or areas upwind of the FPPs, could have provided more detailed information on the identities of PFAS emissions and their spatial distribution. Second, the duration of sampling periods was relatively short in comparison to the timescales of emission variability. For example, longer-term sampling campaigns, particularly for effluent discharges, would have allowed for a more robust assessment of temporal trends, including daily or seasonal fluctuations in emissions.

## 5. Conclusions and outlook

In addressing the challenges associated with PFAS emissions by the fluoropolymer production industry, significant progress has been made, but critical gaps remain. This thesis demonstrated that a complementary approach combining top-down and bottom-up strategies was effective in capturing, measuring and characterizing PFAS emissions by FPPs. Notably, some substances were detected by one approach and not the other and vice versa, underscoring the importance of integrating these methodologies for future research to achieve a more comprehensive understanding and regulation of PFAS and the fluoropolymer production industry.

Overall, this research confirmed the hypothesis that FPPs are significant sources of PFAS emissions, with various stages of production—including monomer synthesis, polymerization, and processing—contributing to these emissions. Furthermore, the hypothesis that atmospheric PFAS emissions by FPPs can undergo long-range transport was supported, with dispersion modelling revealing contributions to contamination at remote locations.

Despite these advancements, much remains unknown about the properties of various PFAS identified in this research, particularly their toxicity, persistence, and environmental fate. While industry has applied innovations such as non-fluorinated processing aids (NFPAs) and emission abatement, they can potentially introduce other issues such as additional by-product formation and waste management constraints. Although abatement technologies were shown to reduce emissions, the findings of this research corroborate the hypothesis that these measures alone are insufficient to entirely prevent environmental contamination. Additionally, industrial solutions such as alternative chemistries have often further complicated regulation, research and policy-making efforts.

Although a PFAS restriction following a grouping approach has been proposed to address these issues in the EU,<sup>1</sup> it will be difficult to entirely phase out PFAS due to their various uses and ingrained role in technologies and society. While the essential use concept provides a framework to determine which uses of fluoropolymers are vital, its implementation poses significant challenges and is dependent on arguments by various stakeholders, including industry and end-users.<sup>105</sup> Fluoropolymer producers are arguing for an exemption for these PFAS on the basis of their inertness and lack of biological activity.<sup>106</sup> Furthermore, arguments for this exemption from the production perspective focus mostly on the abatement of FPA emissions or their replacement by NFPAs.<sup>59</sup> This thesis showed that a broader scope than fluorosurfactants is necessary to fully capture the chemical space and environmental implications of FPP emissions.

Furthermore, the use and emissions of regulated PFAS such as PFOA in regions such as China aligned with the hypothesis that regulatory frameworks and enforcement significantly influence emissions and their impacts. This underscores the importance of addressing global disparities in PFAS-management. Finally, it is important to move beyond the focus on the production stage of fluoropolymers. Assessments and investigations should cover the entire life cycle; from production to disposal. This will be critical to ensure that fluoropolymers do not introduce new environmental or health concerns.<sup>107</sup>

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 **PERFORCE** 

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