

Report

Investigating PFAS use and emissions to air in the refining sector – a literature review

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Executive summary

This report, commissioned by Concawe and prepared by Logika Group, presents the findings of a literature review to investigate and characterise the use and resultant potential emissions to air of per- and polyfluoroalkyl substances (PFAS) from the refining sector. The study aims to provide insights into the types and quantities of PFAS used in the sector, associated potential atmospheric emissions, available measurement techniques, and suitable dispersion modelling approaches for impact assessments. It does not consider use cases in other sectors or emissions to other environmental media e.g., to water or land. Full references supporting this executive summary are provided in the main body of the report.

Key findings on PFAS use and emissions

The literature review confirmed the refining sector is not a manufacturer of PFAS but, in common with many industrial sectors, identified multiple use categories of PFAS in the sector, predominantly involving fluoropolymers in applications such as seals and joints, piping and tubing, coatings and linings, electrical cabling, process equipment, membranes, and safety equipment. These fluoropolymers are generally considered "polymers of low concern" due to their stability (they do not biodegrade in the environment), low solubility, and low bioaccumulation potential.

The review also indicated potential use of non-polymeric PFAS in specific applications such as enhancing the efficiency of the alkylation process and in firefighting foams. These non-polymeric PFAS are of greater concern due to their higher mobility, potential for transformation, and bioaccumulation potential. However, there is a significant data gap regarding quantified emissions of PFAS from specific refinery processes, particularly non-polymeric PFAS in hydrocarbon processing and refining.

Potential release mechanisms have, however, been identified which, although applicable across multiple sectors, are nonetheless also of potential relevance to the refining sector. These include, for example, point source emissions resulting from thermolysis of fluoropolymers used in high temperature process equipment, fugitive emissions from the use of firefighting foams, and fugitive emissions associated with aerosolisation in wastewater treatment plants. However, whilst such mechanisms are considered plausible, there is a lack of evidence of these emissions in a specific refining context, particularly in terms of quantitative estimates, and this remains a significant data gap. There is no quantitative data to confirm, or otherwise, that these emissions occur.

That said, based on information supplied, and sectors covered, as part of the European Chemicals Agency's proposed "universal" PFAS restriction and, in particular, based on data in the background document, it is anticipated that use and emissions of non-polymeric PFAS from the refining sector would be insignificant in comparison to other sectors.

Key findings on PFAS emissions measurement techniques

Whilst an internationally standardised method for measuring PFAS emissions to air from stationary sources does not exist, measurement of PFAS stack emissions from significant emission sources e.g., from fluoropolymer production, has been performed in Europe and/or the United States for at least 20 years using non-standardised methods. More recently, the US EPA has developed Other Test Methods (OTMs) 45 and 50, which provide documented methodologies. These methods have also been used as a basis for developing domestic standards in some European countries/regions, including France and Flanders.

OTM-45 has been developed for polar, semi-volatile PFAS and involves isokinetic sampling of stack gas through a heated filter and adsorbent cartridges, followed by laboratory analysis using Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS). OTM-50 targets non-polar, volatile PFAS and involves collecting stack gas samples in passivated canisters, followed by laboratory analysis using Gas Chromatography Mass Spectrometry (GC/MS). Both OTM-45 and OTM-50 are periodic, extractive techniques, providing a snapshot of emissions at a specific point in time. Emerging techniques, such as Selected Ion Flow Tube-Mass Spectrometry (SIFT-MS), offer the potential for real-time, continuous monitoring of volatile PFAS (and those that can easily partition to the

vapour phase under conditions found in the analyser), providing a more comprehensive understanding of emission patterns. However, SIFT-MS cannot be used to measure PFAS adsorbed to the surfaces of particles.

Potential sample contamination is a significant challenge in PFAS emissions measurements due to the ubiquitous nature of these compounds in the environment and in standard equipment used to collect samples. Strict quality control procedures, including the use of various sample blanks and specialised sampling equipment, are essential to ensure data accuracy.

The number of laboratories with OTM-45 and OTM-50 within their schedule of accreditation is currently low, largely because of the recent introduction of these methods. For example, in France, as of 27 November 2025, there are only three stack testing laboratories that are accredited to OTM-45 (and four which are accredited to the domestic standard derived from OTM-45) and none to OTM-50, whilst, in the UK, only a single laboratory is accredited to OTM-45 and OTM-50 as of 25 February 2026. However, it is expected that the number of accredited laboratories will grow in time, reflecting the increasing importance and regulatory scrutiny being placed on PFAS emissions in general.

Key findings on dispersion modelling techniques

Given the uncertainty in actual emissions to air of PFAS from refining activities, impact assessments ultimately may not be relevant for the sector at this time and are a lower priority at the current juncture than establishing robust source term estimates through measurement or calculation. Additionally, as a general note, whilst the level of knowledge concerning the behaviour and fate of PFAS in the atmosphere is improving, application of dispersion models to this family of compounds is more limited, with many of the examples in literature focussing on emissions from fluoropolymer production, where the nature of the release and PFAS of relevance may be materially different to potential refinery emission sources

PFAS exhibit complex and variable behaviour in the atmosphere driven by the substance specific physicochemical properties. Some PFAS will readily and dynamically partition between the vapour and particle/aerosol phase, with resultant effects on the deposition of these compounds from the atmosphere to soil and surface water. Other PFAS will undergo transformation e.g., by reaction with hydroxyl and chlorine radicals, to form other types of PFAS. For example, fluorotelomer alcohols can undergo transformation in the atmosphere to form perfluorocarboxylic acids (PFCAs). Some PFAS are also conducive to long range transport as evidenced by previous research by the US EPA indicating different classes of PFAS compounds could be transported more than 150 km from an emission source.

Three classes of dispersion models – Gaussian plume models, Lagrangian models, and Chemical Transport Models (CTMs) – have been used to model the transport and fate of PFAS in the atmosphere from industrial emission sources. Each modelling approach has its inherent assumptions and limitations, which must be considered when selecting the most appropriate model for a specific impact assessment.

Gaussian plume models, such as ADMS and AERMOD, are computationally efficient and have been used for initial screening assessments of peak concentrations of PFAS in the vicinity of fluoropolymer manufacturing sites. However, they lack the complexity to accurately represent the dynamic partitioning and transformation of PFAS in the atmosphere, limiting their use for long-range transport and deposition predictions. Lagrangian models, such as CALPUFF and FLEXPART, can account for long-range transport and offer some basic functionality for simulating dynamic partitioning and chemical transformation. They are a more complex and computationally intensive model than Gaussian plume models but less so than CTMs. FLEXPART has been used to model the regional scale transport of PFAS emitted from a fluoropolymer manufacturing site in the Netherlands. CTMs, such as CMAQ and WRF-Chem, are the most complex and computationally expensive modelling techniques. They incorporate detailed chemical reaction schemes and deposition calculations, allowing for more accurate representation of the dynamic behaviour of PFAS in the atmosphere. The US EPA has developed a specialised version of the CMAQ model (CMAQ-PFAS) specifically for supporting PFAS emission to air impact assessments.

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1 Introduction

1.1 Purpose of this report

Logika Group has been contracted by Concawe to investigate, and characterise, the use and resultant potential emissions to air of PFAS from the refining sector. The study is an initial, desk-based review of existing literature to understand the potential types of PFAS used in the sector, and the resultant potential releases to the environment through the emissions to air pathway. This will allow the nature and extent of PFAS use in the sector, and potentially emitted to the atmosphere, to be better defined.

In addition to identifying potential use and potential emission sources, the report also reviews available measurement techniques that can be used to establish the concentration and mass of PFAS emitted from point source (stack) emissions. Finally, the review also extends to dispersion modelling techniques that can support assessments to quantify the impacts of PFAS emissions to air by predicting ambient air concentrations and deposition rates.

PFAS use cases in other sectors as well as emissions to other environmental compartments are not in the scope of the current study.

1.2 Background context

As a family of emerging contaminants, PFAS compounds have been subject to attention and study in recent years, and a deeper understanding of the fate and transport of PFAS has developed, particularly in groundwater and soil compartments. With respect to the fate and pathway of PFAS in the air, dispersion of PFAS via air has been studied in the context of particulates. However, since PFAS compounds are not characterised by volatility due to their inherent properties, comparatively less attention has been paid to the study of emissions of PFAS to air. This report aims to focus on summarising the scientific evidence around PFAS use and potential emissions to air in the refining sector. Additionally, the assessment presented here seeks to gauge the extent to which these emissions can be expected to be significant.

In particular, this study, therefore, has three key aims:

- To investigate the potential use and potential associated aerial emission sources of PFAS in the refining sector;
- To review the available measurement techniques to establish and quantify point source (stack) emissions of PFAS. These techniques can be used to support potential future compliance assessment requirements and/or to fill any gaps in data identified during this study; and
- To review available modelling techniques to support robust impact assessment of PFAS emissions to air to establish suitable modelling technique(s) which account for the complex behaviour of PFAS in the atmosphere.

1.3 Report structure

The remainder of this report is set out as follows:

- **Section 2** provides a general overview of PFAS to provide the context for concepts and terminology introduced in other report sections.
- **Section 3** provides the literature review to identify and characterise PFAS use in the refining sector and associated potential emissions to air.

- **Section 4** reviews currently available and emerging techniques for monitoring PFAS emissions to air from point source (stack) releases.
- **Section 5** provides an overview of the fate and behaviour of PFAS in the atmosphere, and reviews available dispersion modelling techniques, including identification of the advantages and limitations of these techniques, for PFAS emissions to air impact assessments.
- **Section 6** contains conclusions from the study.

2 An overview of PFAS

Key messages

PFAS are a very large family of synthetic organic compounds containing fluorine. Although more than 10,000 unique substances form the PFAS family, they can be divided into two main classes: non-polymers and polymers.

As a result of the carbon-fluorine bond, PFAS possess unique physicochemical properties that make them ideal substances to support a range of functions. For some PFAS, these properties include oil, water, stain and soil repellence, thermal and chemical stability, low flammability, and low co-efficient of friction.

Applications are diverse, with use in industry supporting operations in the energy, aerospace, semiconductor, medical, transport, construction, electronics and aviation sectors amongst many others. Whilst a large number of PFAS are thought to exist, industrial use is limited to a smaller number of fluoropolymers and functional non-polymeric PFAS.

Human exposure to PFAS occurs through multiple pathways. Historically, most focus has concerned exposure through consumer products and industrial discharges to water and ground. The emissions to air pathway is, however, poorly understood. Whilst still an emerging and active area of research, this pathway may become a potential component of the overall PFAS risk assessment framework.

2.1 Introduction

This section of the report provides a high level of overview of PFAS, including the different types and typical applications of PFAS compounds, as well as a summary of impact pathways for human exposure. The purpose of this section of the report is to introduce concepts and terminology that are used in other sections of the report.

2.2 What are PFAS?

PFAS is a generic term used to describe a very large family of synthetic organic compounds containing fluorine. There is no universally accepted definition as to what constitutes a PFAS compound, but perhaps the most widely quoted definition internationally, and that which forms current regulatory approaches in Europe, is that put forward by the OECD¹:

"Fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (-CF₃) or a perfluorinated methylene group (-CF₂-) is a PFAS."

The OECD definition is used as the basis for identifying PFAS of relevance in this report.

The OECD estimates there are 4,730 unique PFAS compounds with Chemical Abstracts Service (CAS) Registry Numbers² that could be on the global market but it is estimated by the European Chemicals Agency (ECHA)

¹ OECD (2021). 'Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance. No. 61'.

[https://one.oecd.org/document/ENV/CBC/MONO\(2021\)25/En/pdf](https://one.oecd.org/document/ENV/CBC/MONO(2021)25/En/pdf)

² OECD (2018). 'Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFASs).' [https://one.oecd.org/document/ENV/JM/MONO\(2018\)7/en/pdf](https://one.oecd.org/document/ENV/JM/MONO(2018)7/en/pdf)

that the PFAS family could contain more than 10,000 individual compounds³, whilst the US EPA have documented that the PFAS family may include (at the time of publishing) more than 16,000 unique substances^{4,5} although not all of these are documented to be used by industry. For example, it is estimated only 256 of the PFAS compounds with CAS numbers are commercially relevant globally⁶. Whilst there are a large number of individual PFAS compounds, one aspect they all share in common is a carbon-fluorine bond, and it is this bond that provides PFAS with their unique properties.

As the most electronegative element, when fluorine forms a covalent bond with carbon, it pulls electrons in that bond towards it providing partial ionic character to the bond. The fluorine atom adopts a partial negative charge and the carbon atom a partial positive charge. As a result, the carbon-fluorine bond is the strongest bond in organic chemistry⁷. The strength of the bond is further increased as more fluorine atoms are added to the same carbon atom and when there are multiple carbon-fluorine bonds on the same alkyl chain.

PFAS are, therefore, typically characterised as having carbon atoms linked to each other and bonded to fluorine atoms, and the degree of fluorination imparts properties to the molecule. The carbons may be partially fluorinated (polyfluorinated) or fully fluorinated (perfluorinated). Other characteristics, such as addition of a functional group e.g., a carboxylic acid, alcohol group etc., and other substitutions, for example, chlorine, all affect the physicochemical properties of an individual PFAS compound.

The PFAS family can be divided into two major classes: non-polymers and polymers. Non-polymers can be further categorised to two sub-classes: perfluoroalkyl substances (i.e., where every carbon-hydrogen bond on the alkyl chain has been replaced by a carbon-fluorine bond) and polyfluoroalkyl substances (i.e., where some carbon atoms on the alkyl chain are bonded to an atom other than fluorine e.g., hydrogen or chlorine). The polymers class can be further categorised to three sub-classes: fluoropolymers, polymeric perfluoropolyethers (PFPE) and side-chain fluorinated polymers.

Figure 2-1 presents a high level diagram which maps out the different classes, sub-classes and groups forming the PFAS family and identifies those groups which are typically associated with the potential for human health or environmental effects.

Certain groups of PFAS possess several unique physical and chemical properties that make them ideal substances to support a range of functions. These groups exert significant oil, water, stain and soil repellence, they are both extremely thermally and chemically stable and low in flammability, and they also have a very low co-efficient of friction.

Some PFAS compounds, such as perfluoroalkyl acids (PFAAs) have an amphiphilic structure where the main fluorinated alkyl chain is hydrophobic, but also containing a hydrophilic functional group head such as a carboxylic acid. This particular property makes these compounds excellent surfactants.

Consequently, since the first scientific discovery in the 1930s, and wide scale commercialisation in the 1950s, many products commonly used by consumers and industry have been manufactured with or from PFAS. Applications are diverse, with use in industry supporting operations in the energy, aerospace, semiconductor,

³ ECHA (2025). 'Background Document to the Opinion on the Annex XV Dossier Proposing Restrictions on Per- and Polyfluoroalkyl Substances (PFASs)'

https://echa.europa.eu/documents/10162/17233/rest_pfas_bd_draft_240625_en.pdf/86488ab5-30c9-f7b9-547d-84db15535d9a?t=1755590462498

⁴ USEPA (2022). 'PFAS Structure Lists (Version 5).' <https://comptox.epa.gov/dashboard/chemical-lists/PFASSTRUCT>

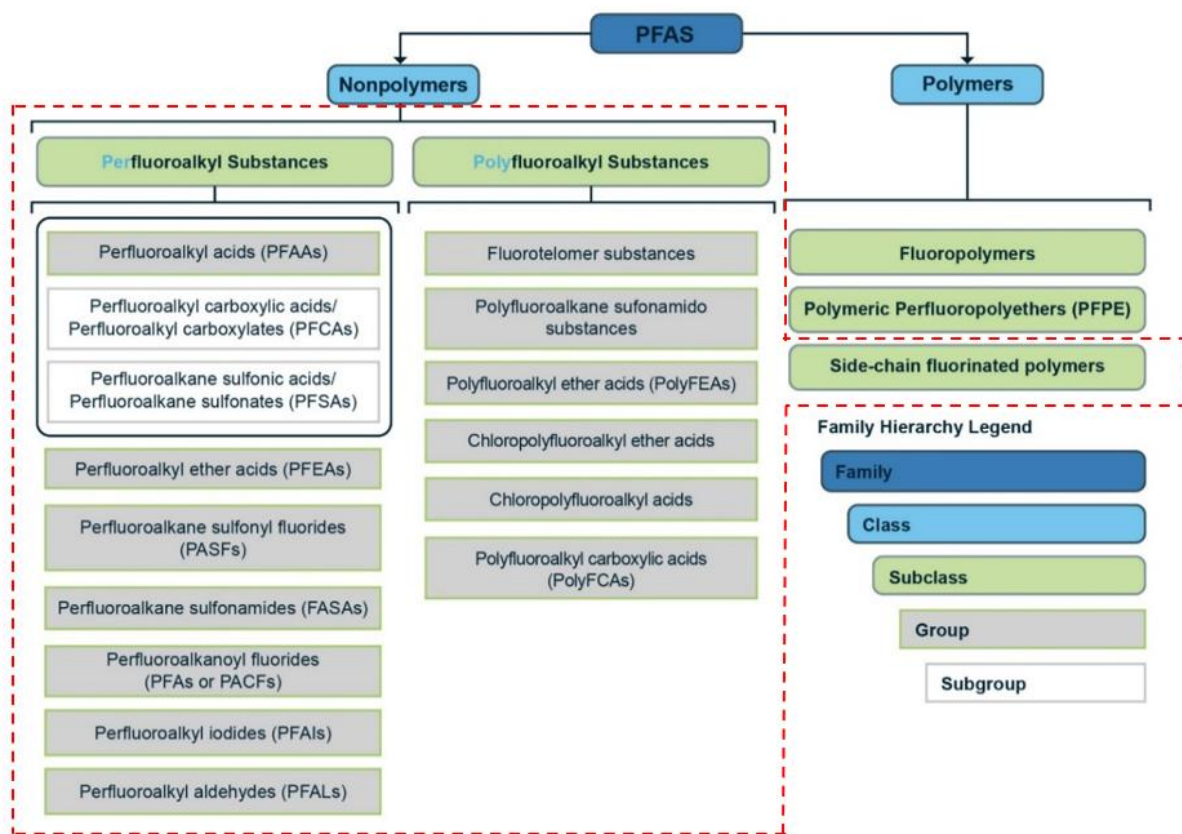
⁵ USEPA (2024). 'PFAS chemicals without explicit structures' <https://comptox.epa.gov/dashboard/chemical-lists/PFASDEV>

⁶ Buck, R., Korzeniowski, S., Laganis, E., Adamsky, F., 2021. Identification and classification of commercially relevant per- and poly-fluoroalkyl substances (PFAS). Integrated Environmental Assessment and Management 17, 1045-1055

⁷ O'Hagan, D (2008). 'Understanding organofluorine chemistry. An introduction to the C-F bond.' Chemical Society Reviews, 37, 308-319.

medical, transport, construction, electronics and aviation sectors amongst many others. Use in consumer products includes items such as carpets, clothing, furniture, food packaging, cooking appliances etc. PFAS can also be found in firefighting foams⁸.

Figure 2-1: The PFAS family



Source: Logika, adapted from Figure 2-4 in ITRC⁹ as valid at the date of publishing this report.

Groups and sub-classes in the red dashed line are those which are typically associated with greater concern in the context of environmental and health risks.

Different subclasses may further be split into different groups. For example, the fluoropolymers subclass contains both fluoroplastics and fluoroelastomers.

2.3 Human exposure to PFAS

The strength of the carbon-fluorine bond means that most PFAS do not degrade easily in the environment which can lead to their persistence. Some PFAS, particularly the shorter chain length compounds, can be highly mobile and easily transported in groundwater, surface water and soil. Some PFAS (although not all) have potential negative health impacts and can be bioaccumulative, with longer chain compounds exhibiting greater bioaccumulative properties than the shorter chain compounds⁹. However, due to the number of individual compounds which comprise the PFAS family, many substances haven't been analysed and tested in detail.

⁸ Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A., van Leeuwen, S.P.J. (2011) 'Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins.' *Integrated Environmental Assessment and Management*, 7, 513-541

⁹ ITRC (2023) 'PFAS Technical and Regulatory Guidance Document' <https://pfas-1.itrcweb.org/>

Understanding of the risks posed by PFAS is continually evolving and improving, but gaps in knowledge still remain.

Alongside how it is used, the type of PFAS determines the relative environmental significance. Non-polymeric PFAS (both perfluoroalkyl substances and polyfluoroalkyl substances) and some side-chain fluorinated polymers are considered to pose greater risks when released to the environment than fluoropolymer substances as they are typically more bioavailable¹⁰. Fluoropolymers are often termed polymers of low concern because they are stable, have large molecular weights, are insoluble in water and not bioavailable¹⁰. The Interstate Technology Regulatory Council's (ITRC) PFAS Technical and Regulatory Guidance Document⁹ provides more extensive information on the properties and behaviour of different groups of PFAS in the environment.

Human exposure to PFAS may occur through a wide variety of pathways including inhalation, ingestion and dermal absorption, although not all exposure routes will be applicable for different compounds. For example, exposure through dermal absorption is unlikely to occur for fluoropolymers. To date, most focus has concerned exposure through consumer products and industrial discharges to water and ground, including associated ingestion of contaminated water and foodstuffs grown on land, or via food packaging where PFAS has been intentionally used to impart beneficial properties to the packaging e.g., oil/grease repellence. As referenced in Section 1.2, until recently, little attention has been given to emissions to air and/or potential environmental exposure through the inhalation pathway but this is now starting to be recognised as a potential exposure route of consideration.

¹⁰ Henry, B.J., Carlin, J.P., Hammerschmidt, J.A., Buck, R.C., Buxton, L.W., Fiedler, H., Seed, J., Hernandez O. (2018) 'A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers.' *Integrated Environmental Assessment and Management*, 14(3), 316-334

3 Literature review on potential PFAS use and emission sources associated with the refining sector

Key messages

The findings of the literature review point to a number of potential different uses of PFAS within the refining sector, the bulk of which are fluoropolymers in applications such as cables, piping, coatings, and other process components.

In addition, there is limited evidence of use of non-polymeric PFAS in hydrocarbon processing, although the literature, in general, is not specific on the exact functions and applications of these substances. Examples have been cited, however, linking non-polymeric PFAS use to enhancing the efficiency of the alkylation process and use in firefighting foams.

Information on the volumes of use is limited, and generally aggregated in nature, typically representing broader use beyond just the refining sector, or representing groupings of PFAS substances. The available information on emissions to air associated with uses is very limited and not specific to the refining sector, representing a significant evidence gap.

However, based on the limited available evidence, PFAS use and potential emissions in the sector is expected to be very small compared to use and emissions from other sectors.

3.1 Introduction

This section of the report presents the outcome of a literature review to identify the types of PFAS that may be associated with operations in the refining sector. This involved a desk-based review to confirm which PFAS substances are being used in refineries, compiling available information on volumes of use, market information, and any available information on emissions to air.

The literature review does not present a detailed, comprehensive assessment of PFAS use and emissions to air in the sector. It represents a rapid, limited review of available evidence within the public domain conducted over a period of one month. Due to the time constraints of the study, we did not carry out any engagement or surveys with operators in the refining sector, nor interview experts to confirm the outputs of the review and complete any data gaps. Nonetheless, the quasi-systematic approach aims to ensure rigour, relevance and reproducibility by focussing on key evidence only, thereby providing more efficient project completion than a full, systematic review whilst remaining sufficiently detailed and reproducible.

3.2 Approach

The starting point for this review was ECHA's universal PFAS (U-PFAS) restriction proposal dossier¹¹. The proposal was originally submitted in 2023 but was revised in August 2025. The literature review was initiated prior to the release of the updated 2025 restriction dossier, which was retroactively integrated into the review upon its publication. Alongside this, relevant documents submitted as a response to the 2023 consultation were extracted. This included responses from the International Association of Oil and Gas Producers (IOGP), the European Sealing Association (ESA), Plastics Europe Fluoropolymer Products Group (FGP), the American Petroleum Institute (API) and certain refinery operators. We also reviewed several documents internally produced by Concawe, and reports produced by the Norwegian Environment Agency on PFAS use in the petroleum and mining sector.

Following this initial review, a broader search on Google Scholar using search strings and snowballing was conducted. The search strings were designed to capture as many relevant sources as possible. Approximately 50 citations were reviewed for each string, and either included or excluded based on the relevance of the title and abstract. Inclusion criteria were reports that addressed the downstream operations in the oil and gas sector (i.e. excluding oil and gas exploration and extraction, and those outside of the oil and gas sector), written in English, with information on PFAS. The search strings used included, for example:

- PFAS OR fluorosurfactants OR fluorochemicals + downstream uses + mineral oil refining OR gas refining
- PFAS OR fluorosurfactants OR fluorochemicals + market + mineral oil refining OR gas refining
- PFAS OR fluorosurfactants OR fluorochemicals + uses + mineral oil refining OR gas refining
- PFAS market + mineral oil refining OR gas refining
- PFAS OR fluorosurfactants OR fluorochemicals + downstream uses + petroleum
- PFAS OR fluorosurfactants OR fluorochemicals + market + petroleum
- PFAS OR fluorosurfactants OR fluorochemicals + uses + petroleum
- PFAS market + petroleum
- PFAS + contamination + mineral oil refining OR gas refining

We then conducted snowballing from sources with the most relevant information (using the reference lists of the sources to identify further relevant material), to ensure that data saturation was obtained (i.e. no new information was being identified in additional sources). Additionally, a targeted search for grey literature, including relevant non-academic reports and articles was conducted. For example, we reviewed technical literature data from e.g. conferences, trade associations, and industry actors. In total, 157 relevant sources were retrieved to be reviewed in more detail, including those from the search strings.

Identified sources were systematically reviewed and any relevant information was extracted into a tabular register (Microsoft Excel) to log details on PFAS substances, use cases, quantitative data, information on air emissions, and additional context.

3.3 Synthesis of information

The review highlighted a number of different specific uses. For the purpose of the synthesis of information, these were consolidated into the following broader use categories.

- Seals and joints
- Piping and tubing
- Coatings and lubricants
- Firefighting foams
- Electrical cabling and equipment
- Process equipment
- Membranes and filtration
- Hydrocarbon processing

- Safety and safety equipment
- Other uses.

The following sections provide a more granular mapping of specific PFAS compounds and utilisation within these categories. Section 3.4 presents the identified information on volumes of use, while Section 3.5 sets out findings with respect to emissions of PFAS to air.

3.3.1 Seals and joints

PFAS compounds, predominantly present as fluoropolymers, including fluoroplastics and fluoroelastomers, are widely used in the refining sector as coating materials for seals and joints used in components in a wide range of equipment¹¹. One of the most common uses identified in the literature is their application in O-ring seals^{12,13,14,15,16,17}. Here, as with other seals listed, the components can either be made using fluoropolymers (e.g. PTFE, FKM) or coated in fluoropolymers (e.g. PTFE on a rubber core¹⁸). These seals are used in e.g. pipe connections, pumps, and valves, to prevent unwanted releases of chemicals and fluids¹⁵. Other types of seals that use PFAS include custom geometry seals (to fit specific shapes), lip seals (used in e.g. centrifugal pumps¹⁵ and cryogenic valves to transport LNG at low temperatures¹⁴), mechanical seals¹⁷ used to seal rotating shafts as they enter the housing of pumps, centrifugal compressors, and agitators¹⁴ (including gaskets^{14,15,17,12,19,20,21}, which provide static seals between stationary components¹⁴, and dry gas and abradable seals both used for rotating equipment¹⁵), and pump seals in engines¹⁷. PFAS are also used as sealing in flexible pipes and cables¹⁵, and PTFE thread tape or paste for gas cylinder and tank assemblies¹¹.

Several components containing PFAS are also used alongside seals. For example, PFAS are often used in packing material to create tight seals^{12,17} and prevent fugitive emissions¹⁵. Compression packing yarns¹⁴, spiral wound gasket filler (a specific type of gasket that uses a PTFE filler)¹⁵, v-ring packers¹⁷, and valve packing¹⁵ all contain various PFAS substances as listed in Table 3-1.

Other uses of PFAS relating to seals and joints in machinery include the sealing, coating, and lining of: expansion joints^{14,17}, bellows²², flanges¹⁵, valve seats^{15,17}, bearings, corrosion barrier rings¹⁵, valves^{12,13,22,23} (e.g. pipeline, ball, check¹⁷, butterfly, safety, blow-out preventor¹³) and anti-abrasion rings in three-piece ball valves¹⁷. In this sector, valves and washers may also be made entirely of PFAS¹⁵.

The literature review identified several instances where the evidence noted the specific substance(s) used in seals and joints. Where this has been identified it is set out in Table 3-1. Some sources do not distinguish between the specific PFAS compounds used, while other use cases are associated with particular substances (including PTFE, PCTFE, and PFA). The specific substances identified for seals and joints are predominantly fluoropolymers.

¹¹ https://echa.europa.eu/documents/10162/17233/rest_pfas_bd_draft_annex_a_240625_en.pdf/5478d66b-1f5c-6b33-8689-e206df8a131f?t=1755590519703

¹² <https://www.miljodirektoratet.no/sharepoint/downloaditem?id=01FM3LD2R3K5XU7HZ275GJ7NKF3DGGZ576>

¹³ https://www.concawe.eu/wp-content/uploads/Rpt_24-12.pdf

¹⁴ <https://www.eurosealing.com/wp-content/uploads/2022/03/ESA-Position-Statement-on-proposed-PFAS-regulation-March-2022.pdf>

¹⁵ ExxonMobilPetroleum & Chemical BV (EMPC) Comments on Annex XV restriction report on PFAS – fluoropolymer use in upstream, refining, and petrochemical manufacturing (2023)

¹⁶ <https://iogpeurope.org/wp-content/uploads/2024/02/PFAS-restriction-proposal-paper.pdf>

¹⁷ Letter from the American Petroleum Institute to ECHA for the CfE for the U-PFAS restriction and reports from Arcadis (2023)

¹⁸ <https://www.canyoncomponents.com/post/ptfe-coated-o-rings-benefits-applications-and-maintenance>

¹⁹ https://www.concawe.eu/wp-content/uploads/Rpt_24-8.pdf

²⁰ PFAS Study in Refinery & Fuel Distribution Equipment (Concawe, 2023)

²¹ <https://www.rsc.org/policy-and-campaigning/policy-library/risk-based-regulation-for-pfas>

²² <https://pubs.rsc.org/en/content/articlehtml/2020/em/d0em00291g> (Supplementary information)

²³ <https://fluoropolymers.eu/wp-content/uploads/2023/09/FPG-Uses-and-Analysis-of-Alternatives-fluoropolymers-EU-PFAS-restriction-proposal-for-publication-Sept-2023.pdf>

Table 3-1: PFAS compounds identified in use in seals and joints

Substance	Polymer/Non-polymer	Uses
FKM/FFKM	Polymer	O-rings ^{12,13,15,17,21} , mechanical seals (including gaskets ^{12,15,16,17,22}), sealing in flexible pipes and cables, packers/packing elements, v-ring packers, valve seats, valves (e.g. pipeline, ball) ¹⁷ , expansion joints ¹⁷ /bellows ²²
PTFE	Polymer	O-rings ^{15,17,21} , lip seals ¹⁵ , mechanical seals (including gaskets ^{14,15,16} and dry gas and abradable seals ¹⁵), valve packing, spiral wound gasket filler, bearings, corrosion barrier rings, washers ¹⁵ , compression packing yarns ¹⁴ , expansion joints ¹⁴ /bellows ²² , valves (e.g. check) ¹⁷ , valve seats ¹⁵ , thread tape, sealing paste ¹¹
PCTFE	Polymer	Gaskets (especially for LNG), seals, anti-abrasion rings in three-piece ball valves ¹⁷
PFA	Polymer	Lip seals ^{14,17} , mechanical seals (including gaskets) ¹⁴ , compression packing yarns ¹⁴ , expansion joints ¹⁴ /bellows ²²
Fluorotelomers	Non-polymer	Gaskets ¹⁵
PFPEs	Polymer	Gaskets ¹⁵
ETFE/ECTFE	Polymer	Gaskets, expansion joints/bellows ²²
FEP	Polymer	Gaskets, expansion joints/bellows ²² , elastomer seals in valves ¹⁵ , valves ²⁴
MFA	Polymer	Gaskets, expansion joints/bellows ²²
TFE/P	Polymer	Gaskets, expansion joints/bellows ²² , seals ¹⁵
PVDF	Polymer	Seals ¹⁵ , valves ²⁴
FPM/FFPM	Polymer	Elastomer seals in valves ¹⁵

3.3.2 Piping and tubing

PFAS are widely used in piping and tubing in the refining sector, predominantly as fluoropolymers, including in transportation and distribution of oil and gas to ensure their safe conveyance¹¹. This includes the lining of various pipes in oil and gas transport²², such as flexible pipe liner¹⁵ and linings specifically for oil pipes¹⁷, as corrosion-resistant lining is more cost-effective than manufacturing pipes from corrosion-resistant alloys. Flexible gaskets/seals composed of PFAS are still required between fittings of corrosion resistant alloy materials. Through the application of PFAS lining, pipe interiors can be made resistant to acidic corrosion from oil-based products. PFAS micro-powders are also used in the primers and overcoats of pipe lining²². Pipes and tubing can also be composed of PFAS themselves, including hoses^{13,20,23,19} (such as flexible hoses¹⁷), tubes (including multi-layer tubes^{13,17}), and non-metallic composite (flexible) pipes¹⁶. PFAS are used in pressure sheaths^{17,23} and in tapes to prevent releases from piping¹⁷.

An estimation of the use of PVDF in piping has been calculated by IOGP taking account of the 1,437 km of piping produced globally from 2012-2022 (note that PVDF has been used for piping for over 20 years in total)¹⁶. This represents an average annual tonnage of 1,050 – 1,500 tonnes of PVDF globally, and 140 – 190 tonnes per year in the European Economic Area (EEA); approximately 12% of global production. These figures are based on data collected by the Sureflex joint industry project (JIP), covering total PVDF supply from Baker Hughes, NOV,

²⁴ <https://link.springer.com/article/10.1186/s12302-023-00721-8#change-history>

and TechnicFMP (2012-2022), all of whom predominantly manufacture for the energy industry. Tonnage of PVDF is estimated based on pipe diameter and typical liner thickness. This data is specific to flexible pipes.

PFAS are also used as base materials or additives in tubing extrusion and injection moulding, as well as extrusion of thin-walled tubing¹³, for high-performance requirements. PFAS can also be found in fuelling nozzles¹⁷, spray nozzles (for cooling towers, desulphurisation, and chemical injection during processing)¹¹, and transportation flowlines¹³. This is because this equipment comes into direct contact with petroleum-based products so must withstand corrosion¹¹.

The literature review identified specific substances used in piping and tubing; these are set out in Table 3-2. The specific substances identified for piping and tubing are predominantly fluoropolymers, with the exception of the non-polymer 6:2 FTS.

Table 3-2: PFAS compounds identified in use in piping and tubing

Substance	Polymer/Non-polymer	Use
PFA	Polymer	Linings for oil pipes, multi-layer tubes ¹³ , hoses ¹⁵
PTFE	Polymer	Primers and overcoats of pipe lining ¹³ , hoses ¹⁵ , tape to prevent releases from piping ¹⁵ , linings for oil pipes ^{11, 13} , spray nozzles ¹¹
PE-RT	Polymer	Non-metallic composite (flexible) pipes – spoolable ²³
PEEK/PEEK-CF	Polymer	Non-metallic composite (flexible) pipes – not spoolable ²³
PPS/PPS-CF	Polymer	Non-metallic composite (flexible) pipes – not spoolable ²³
PVDF	Polymer	Flexible pipes ^{15, 23, 13} , pressure sheaths in flexible pipes ^{15, 23} , hoses ²⁰ , flowlines ¹³ , spray nozzles ¹¹
PVDF-CF	Polymer	Flexible pipes ²³
PVF	Polymer	Flexible pipes ²³
6:2 FTS	Non-polymer	Hoses ¹⁷
FKM	Polymer	Hoses and fuelling nozzles ¹⁷
FFKM	Polymer	Hoses ²⁰
FEP	Polymer	Hoses ^{17,20}
EFEP	Polymer	tubing extrusion and injection moulding, extrusion of thin-walled tubing ¹³

3.3.3 Coatings and lubricants

PFAS, present as fluoropolymers, are used in anti-corrosion paints, paint additives and emulsifiers¹⁹, antifoam additives in lubricants, grease^{20, 13}, lubricating oils^{19,25}, and lubricants^{20, 13,25,11}. These uses of PFAS are not limited in their application to refining activities. The benefits of these PFAS uses are in preventing degradation of assets and enhancing durability of equipment. They are also used to protect steel pipes from corrosion¹⁷. PFAS coatings^{20,26,21,23} are used to protect equipment¹⁹, stacks, ducts, stud bolts and threaded fasteners¹³ from corrosion, chemical attack, and/or abrasion¹¹. According to one estimate, the fluoropolymer coatings market

²⁵ <https://onlinelibrary.wiley.com/doi/full/10.1002/ajim.23362>

²⁶ https://books.google.co.uk/books?hl=en&lr=&id=ZZkiEAAAQBAJ&oi=fnd&pg=PR11&dq=fluorochemicals+%2B+uses+%2B+mineral+oil+refining+OR+gas+refining&ots=3vaX5sL9lo&sig=SGH-VOq4fqdLG9sXXZEPIaYEjTl&redir_esc=y#v=onepage&q&f=false

is expected to reach \$2bn by 2025, which would imply an annualised growth of 6% between 2019 and 2025²⁶. This estimate is for the overall market, inclusive of the PFAS used in coatings in the refining sector.

In several cases, the literature review identified specific substances used in coatings and lubricants. These are set out in Table 3-3. The specific substances identified for coatings and lubricants are predominantly fluoropolymers.

Table 3-3: PFAS compounds identified in use in coatings and lubricants

Substance	Polymer/Non-Polymer	Uses
Fluorosilicones or Fluorosiloxanes (FLSs)	Polymer	Antifoam additives in lubricants ²⁰
FEP	Polymer	Coatings ^{20, 13} , liners for valves ²⁰
PFA	Polymer	Coatings ²⁰ , corrosion protection on steel pipes ¹³ , liners for valves ²⁰
PVDF	Polymer	Coatings ²⁰ , liners for valves ²⁰
FKM/FFKM	Polymer	Coatings ¹³ , tank linings, stack and duct coatings ¹³ , lubricants ²⁰
PTFE	Polymer	Coatings ^{20, 13} , grease ²⁵ , lubricants ^{20,25} , liners for valves ¹⁹ , tank linings, coatings on stud bolts and threaded fasteners ¹³
ETFE/ECTFE	Polymer	Coatings ¹³ , liners for valves ²⁰
MFA	Polymer	Coatings ¹³
TFE/P	Polymer	Coatings ¹³
PFPEs	Polymer	Grease ^{13,25} , lubricants ^{25, 11}
PPFAE	Polymer	Grease, lubricants ²⁵
PCTFE	Polymer	Grease, lubricants ²⁵
THV	Polymer	Tank linings ¹³
PCTFE	Polymer	Lubricants ¹¹

3.3.4 Electrical cabling and equipment

Within this category, PFAS, present as fluoropolymers, have specific uses for electrical insulation, including for the electric grid and general cable and wiring insulation^{17,12,23}. PFAS are also used in cable and wiring equipment as well as power supply equipment²⁰. These use cases are not specific to the refining sector but are nonetheless required for its operation, with the use of PFAS in cables allowing for their downsizing. Specific to this sector, PFAS coatings on cabling is preferable due to resistance to high temperatures and harsh chemicals and is also used to insulate heating wires of heated pipelines¹¹.

In several cases, the literature review identified specific substances used in electrical cabling and equipment. These are set out in Table 3-4. The specific substances identified for electrical cabling and equipment are all fluoropolymers.

Table 3-4: PFAS compounds identified in use in electrical cabling and equipment

Substance	Polymer/Non-polymer	Uses
PTFE	Polymer	Electrical insulation ¹⁹ ; cable insulation ¹⁷
PVF	Polymer	Submersible cable systems ¹⁹
PVDF	Polymer	Submersible cable systems ¹⁹ , cable and wiring ²³
ECTFE	Polymer	Submersible cable systems ¹⁹
PFA	Polymer	Cable ^{17, 12} and wiring insulation ¹²
FFKM	Polymer	Cable and wiring insulation ²³
FEP	Polymer	Cable and wiring insulation ²³

3.3.5 Firefighting foams

There was considerably more information on firefighting foams in the literature than other uses, and this was the only use not dominated by fluoropolymers. EU Member States voted in favour of restricting PFAS in firefighting foams in April 2025²⁷, though currently PFAS-containing firefighting foams are still utilised at some refineries due to their efficacy against large-scale oil and gasoline fires²⁸, or Class B (flammable liquid) fires²⁹. This restriction was formalised on 23 October 2025 through Commission Regulation (EU) 2025/1988 which establishes that firefighting foams shall not be placed on the market or used from 23 October 2030 which contain PFAS at a concentration equal to or greater than 1 mg/l for the sum of all PFAS, with specific exceptions and transition periods for certain industries like offshore oil and gas installations, military and civilian ships, and establishments under the Seveso Directive, which have until October 2035. There is also a public consultation running for the UK REACH restriction of PFAS in firefighting foams³⁰.

The firefighting foams being addressed contain Aqueous Film Forming Foam (AFFF) or Alcohol-resistant AFFF (AR-AFFF), which contain several PFAS substances. According to the information in the ECHA Annex XV restriction report on PFAS in firefighting foams, the EU chemical/petrochemical sector uses approximately 10,620 tonnes of PFAS-containing firefighting foams per year, equating to consumption of approximately 283 – 330 tonnes of fluorosurfactants in the sector annually and emissions across all environmental media of 200 tonnes per year (from Seveso III installations in the oil and (petro-)chemical industry)³¹ based on 2020 estimates. Data specific to the refining sector are not reported. It is important to note that since 2020, under both Persistent Organic Pollutants Regulations and REACH Regulations, PFOA, PFHxA, PFHxS and the C9 – C21 PFCAs have been restricted in their use, meaning that at the time of reporting (2026) use of PFAS in AFFF will be significantly lower than those estimates.

AFFFs and AR-AFFFs are used at many industrial facilities, including refineries, to control Class B flammable liquid fires and for training purposes, with PFAS (fluorinated surfactants) being an active ingredient in many Class B firefighting foams.

When mixed with water and discharged, the foam forms an aqueous film that cuts off oxygen to the fire, cools it, extinguishes it, and prevents re-ignition. Due to the surfactant properties and low surface tension, inclusion of PFAS within AFFFs allows the foam to spread rapidly and form a thin, continuous film on top of the burning liquid. Although composition will vary by individual product, a typical composition of 3% AFFF will include ~60% water,

²⁷ <https://ec.europa.eu/transparency/comitology-register/screen/documents/107291/1/consult?lang=en>

²⁸ https://www.concawe.eu/wp-content/uploads/2016/06/Rpt_16-8.pdf

²⁹ <https://norden.diva-portal.org/smash/get/diva2:1295959/FULLTEXT01.pdf>

³⁰ <https://press.hse.gov.uk/2025/08/18/public-consultation-opens-on-restricting-pfas-in-firefighting-foams/>

³¹ <https://echa.europa.eu/documents/10162/4524f49c-ae14-b01b-71d2-ac3fa916c4e9>

~20% organic solvents, 15 – 18% surfactants with ~ 2 – 3% of these being fluorosurfactants, and other additives and modifiers⁹.

Historically, PFOA and/or PFOS were the fluorosurfactants of choice for AFFFs, but these have generally been replaced by short-chain (C6) fluorotelomer-based surfactants in more modern formulations. However, PFOA may still be found in these more modern AFFFs as an unintended impurity or byproduct of the manufacturing process but at much smaller quantities (parts per billion) than legacy foams⁹.

The available information indicates the following PFAS substances could be found in firefighting foams as an example. The specific formulation and types of PFAS present, which may include one or a combination of the below, will depend on the type, manufacturer and year of formulation.

- 8:2³² and 6:2 FTS^{32,20}
- 8:2 and 6:2 FTOH^{33,34}
- PFOS^{32, 20, 24}
- PFOA^{32, 20}
- PFBS²⁰
- PFBA²⁰
- PFHA²⁰
- PFNA²⁰

All of the identified PFAS substances for firefighting foams are non-polymers. The ECHA restriction report notes that the range of PFAS substances contained in firefighting foams is highly diverse, including both long- and short-chain PFAS and fluorotelomers³¹ and will depend on the type of foam, manufacturer and year of formulation. A list of 64 PFAS substances previously identified across a range of different firefighting-foams is provided in Annex B 1.1 of the ECHA restriction report³⁴.

3.3.6 Hydrocarbon processing

Hydrocarbon processing involves several potential PFAS uses, some of which are already described by other sectors of this report, as operations involve high temperatures and pressures, as well as aggressive chemicals, which equipment must withstand to avoid releases of harmful substances. PFAS are often the only material able to withstand these operating conditions¹¹.

The evidence suggests PFAS may be used in bonding agents¹⁹, downstream hydrocarbon processing¹⁷, and the manufacture of coke and refined petroleum products²².

Use or emission of TFA from the alkylation process has also been cited where it may be used to enhance the reaction efficiency^{35,36}. These studies have shown that adding TFA to sulphuric acid in the alkylation of isobutane

³² https://minds.wisconsin.edu/bitstream/handle/1793/84445/2018_LSNERR_PFAS-Analysis-of-2018RefineryFire.pdf?sequence=1&isAllowed=y

³³ Favreau, P.; Poncioni-Rothlisberger, C.; Place, B. J.; Bouchex- Bellomie, H.; Weber, A.; Tremp, J.; Field, J. A.; Kohler, M. Multianalyte Profiling of Per- and Polyfluoroalkyl Substances (PFASs) in Liquid Commercial Products. *Chemosphere* 2017, 171, 491–501

³⁴ <https://echa.europa.eu/documents/10162/d66bdab3-fdb3-93ba-ee81-1dba3977f36d>

³⁵ Lindley, A.A., 2023. 'An inventory of fluorospar production, industrial use, and emissions of trifluoroacetic acid in the period 1930 to 1999.' *Journal of Geoscience and Environment Protection*, 11, 1-16.

³⁶ Li, L., Zhang, J., Du, C., Luo, G., 2018. 'Intensification of the sulfuric acid alkylation process with trifluoroacetic acid.' *American Institute of Chemical Engineers AIChE J*, 65: 113–119

with 2-butene can increase the solubility of isobutane and decrease the viscosity of the acid system, leading to a more intensified reaction and improved alkylate quality. Whilst the literature identifies the potential use of TFA in the alkylation process, any resultant emissions to air from this use are uncertain. For example, one study³⁵ estimates 1.3 million tonnes of fluorspar was used between 1930 – 1999 in petroleum alkylation but the resultant emission of TFA was reported as “0 tonnes”. It is unclear whether this is due to rounding/resolution of the reported emissions (the minimum emission value quoted for any activity is 60 tonnes) or an indication that there is no potential whatsoever for TFA to be emitted from this use.

It has been estimated approximately 3.4-8.5 tonnes of PFAS per year (including the UK, based on a PFAS content of 2-5% and tonnages provided by national authorities and suppliers during ECHA’s most recent call for evidence) are used as anti-foaming agents used as part of either production or refining processes¹¹.

The literature review identified specific substances potentially used in hydrocarbon processing; these are set out in Table 3-5. Some sources do not distinguish between the specific PFAS compounds used. The specific substances identified for hydrocarbon processing are predominantly non-polymers, with the exception of the fluoropolymers FKM/FFKM and PCTFE.

Table 3-5: PFAS compounds identified that may be used in hydrocarbon processing

Substance	Polymer/Non-polymer	Uses
PFAS (unspecified)	N/A	PFAS in aqueous mixes to reduce evaporation losses in storage ^{22,25} , bonding agents ¹⁹ , downstream hydrocarbon processing ¹⁷
FKM/FFKM	Polymer	Downstream hydrocarbon processing ¹⁷
PCTFE	Polymer	Downstream hydrocarbon processing ¹⁷
1-propanesulfonic acid, 2-methyl-, 2-[[[1-oxo-3-[(γ-ω-perfluoro-C4-16-alkyl)thio]propyl]amino] derivs., sodium salts	Non-polymer	Manufacture of coke and refined petroleum products ²²
6:2 fluorotelomer sulfonamide betaine	Non-polymer	Manufacture of coke and refined petroleum products ²²
Thiols, C8-20, γ-ω-perfluoro, telomers with acrylamide	Non-polymer	Manufacture of coke and refined petroleum products ²²
Fluorinated alkylsiloxanes/polysiloxanes	Non-polymer	Anti-foaming agents ¹¹
TFA	Non-polymer	Enhancing the efficiency of the alkylation process ^{35,36}

3.3.7 Membranes and filtration

Diaphragms^{17, 13}, filters¹³, and membranes^{13,22} including fluoropolymer-coated membranes used for separation of non-aqueous liquid (e.g. for deep desulphurisation of gasoline and diesel, or H₂ recovery in refineries)¹⁷ are all equipment items that potentially contain PFAS.

In several cases the literature review identified specific substances used in membranes and filtration; these are set out in Table 3-6. Some sources do not distinguish between the specific PFAS compounds used. The specific substances identified for membranes and filtration are predominantly fluoropolymers, with the exception of the non-polymers PFOS and PFOA.

Table 3-6: PFAS compounds identified in use in membranes and filtration

Substance	Polymer/Non-polymer	Uses
Unspecified fluoropolymers	Polymer	Fluoropolymer-coated membranes used for separation of non-aqueous liquid ¹⁷ , membranes for filtration ²²
FKM	Polymer	Diaphragms ¹⁷
PTFE	Polymer	Diaphragms, filters, membranes ¹³
ETFE	Polymer	Filters ¹³
PFOS	Non-Polymer	Filters ¹³
PFOA	Non-Polymer	Filters ¹³
PVDF	Polymer	Filters ¹³

3.3.8 Process equipment

Process equipment which may contain PFAS (primarily fluoropolymers) includes absorption towers, agitators, compressors, conveyors, cooling towers, devices for process analysis and control, distillation towers, fans, fired heaters, gas purification units, heat exchangers, processing / auxiliary aids²⁰, inserts, stirrers, and liners in testing equipment¹⁵, and pumps^{20,17,13,21,23}. Fluoropolymers may also be used as materials for various pump parts, such as vanes, tubes, stators, and diaphragms¹¹.

Oil and gas refining relies on electrical equipment which may utilise fluoropolymer components in their drive systems, as with engines and gearboxes, for their resistance to the harsh operating conditions in refineries¹¹.

In cooling towers, PVDF can be used to reduce microbiological activity and to help with sunlight resistance. Heat exchangers may contain fluoropolymers in their oleophilic surface, and ETFE may be used for a wide range of corrosives and solvents in pumps²⁰.

The literature review identified several specific substances used in process equipment; these are set out in Table 3-7. Some sources do not distinguish between the specific PFAS compounds used. The specific substances identified for process equipment are predominantly fluoropolymers.

Table 3-7: PFAS compounds identified in use in process equipment

Substance	Polymer/Non-polymer	Uses
Fluoropolymers (specific substance not defined)	Polymer	Absorption towers, agitators, compressors, conveyors, cooling towers, devices for process analysis and control, distillation towers, fans, fired heaters, gas purification units, heat exchangers, processing / auxiliary aids ²⁰ , pump parts (e.g. vanes, tubes, stators, diaphragms) ¹¹
PTFE	Polymer	Inserts, stirrers, and liners in testing equipment ¹⁵ , pumps ^{20,13,21} , heat exchangers
FKM/FFKM	Polymer	Pumps ^{17,21,23}
ETFE/ECTFE	Polymer	Pumps ^{20,13,21}
FEP	Polymer	Pumps ^{20,21,23} , heat exchangers

Substance	Polymer/Non-polymer	Uses
PFA/MFA	Polymer	Pumps ^{20,21}
PVDF	Polymer	Pumps ^{20,23} , cooling towers, heat exchangers
TFE/P	Polymer	Pumps ²¹

3.3.9 Safety and safety equipment

PFAS may also be present in other safety equipment. For example, they are often used in oil and gas containment measures for spills on water as certain PFAS compounds introduce a chemical barrier which prevents the further spreading of oil or gasoline. This improves the concentration, collection and control of an oil spill and helps in maintaining an optimal oil slick thickness for skimming^{22,25}. Safety clothing such as PPE to protect workers while handling chemicals and fluids used in the sector (e.g. gloves, gowns)¹¹ may also contain PFAS^{20,13,17}. They may also be used in other plant safety equipment²⁰.

The literature review identified specific substances used in safety and safety equipment; these are set out in Table 3-8. However, some sources do not distinguish between the specific PFAS compounds used. The specific substances identified for safety and safety equipment are predominantly non-polymers, with the exception of the polymers FKM and PTFE.

Table 3-8: PFAS compounds identified in use in safety and safety equipment

Substance	Polymer/Non-polymer	Uses
Fluorinated surfactants	Non-polymer	Oil containment for spills on water ²²
Fluoropolymers (unspecified)	Polymer	Plant safety equipment, PPE ²⁰
Fluorotelomers	Non-polymer	Plant safety equipment
Perfluoroalkyl acids	Non-polymer	Plant safety equipment
Poly-fluorinated n-alkanes and alkenes (excl. F-Gases)	Non-polymer	PPE ²⁰
FKM	Polymer	Safety clothing and gloves
6:2 FTS	Non-polymer	Safety equipment
PFHA	Non-polymer	Safety equipment
PTFE	Polymer	Safety equipment

3.3.10 Other

Some specific uses of PFAS in the refining sector could not be categorised for the purpose of this report but nonetheless may be found on refinery sites. These include the use of PFAS in high-performance hydraulic fluids¹⁹ and refrigerants in industrial machinery^{20,13,25}.

The literature review identified specific substances whose uses have been categorised as other; these are set out in Table 3-9. Some sources do not distinguish between the specific PFAS compounds used, while other use

cases are associated with particular substances. The specific substances identified are predominantly non-polymers.

Table 3-9: PFAS compounds identified in other use cases

Substance	Polymer/Non-polymer	Uses
PFAS (unspecified)	N/A	Hydraulic fluids, refrigerants
Fluoropolymers	Polymer	Refrigeration equipment
HFCs, HFC/HFO Blends, and HFC blends ^A	Non-polymer	Refrigerants
Poly-fluorinated n-alkanes and alkenes (excl. F-Gases) ^B	Non-polymer	Refrigerants

^A Dependent on the specific definition used, these compounds can either be considered to be, or not considered to be, included within the PFAS family. These compounds are regulated under the Kyoto Protocol and EU F-gas regulation (Regulation (EU) 2024/573) due to their high global warming potential (GWP) rather than their risks to human health.

^B These compounds are considered to be PFAS by the OECD definition, as they contain multiple –CF₂– or –CF₃ groups (this is the definition used throughout this report), and by the EU REACH definition, if they meet the structural criteria of having a perfluorinated carbon chain. However, they are not considered to be PFAS according to some narrower definitions, which require polar functional groups and/or bioactivity.

3.4 Volumes of use

The literature review found limited information on the volumes of use for PFAS substances in the refining sector. Therefore, this section focusses on gathering the available, albeit limited, data on use volumes.

Note that we do not attempt to make estimates on volumes via assumptions but rather assess what available data exists. Where volumes or market values were available, they were often aggregated globally. Little information was found specific to refining activities. Any volume data provided for specific uses has been detailed in the respective sub-section above, in section 3.3. Less granular data is provided in Table 3-10 below.

Although data on volumes of use was limited, it is expected that use of PFAS in the refining sector is small in comparison to other sectors. For example, in the dossier supporting the updated U-PFAS restriction, estimated annual tonnages of use for PFAS for the petroleum and mining sector as a whole represented just 0.002% of the total estimated use across all sectors subject to the restriction proposal. There are two caveats to this estimate:

- The revised U-PFAS restriction has clarified that, in terms of use of PFAS in the petroleum sector, this only includes upstream processes and does not include use and emission estimates from refining operations (refer to Section A.3.16 within Annex A of the U-PFAS restriction proposal dossier)
- The estimate does not include polymeric PFAS

However, as the restriction focusses on sectors considered to be of greatest relevance, and as fluoropolymers are currently considered to be less of a concern than non-polymer PFAS, the volumes of use of non-polymeric PFAS in the refining sector would be expected to be an even smaller fraction of total non-polymeric PFAS use in Europe.

Table 3-10: Available data for volumes of PFAS use

Substance	Polymer/ Non-polymer	Volume Information
FKM/FFKM	Polymer	Global consumption of FKM/FFKM (not sector specific) was estimated at 24 kT in 2014 and 30.4 kT 2019 ²⁶ . FKM/FFKM accounted for the joint third largest share of fluoropolymers produced in the EU in 2020 at 8% ¹³ , approximately 3.2kt ³⁷ . No further specific data on use volumes was located in the literature, though some information was available on the FKM/FFKM market size, valued at US\$1.21bn in 2017 and projected to reach \$1.64bn by 2022 (6% CAGR) (not sector specific) ²⁶ . 29% of the fluoropolymer products produced in the EU in 2020 were by the chemicals sector (including energy) ³⁷ , so FKM/FFKM consumption could be estimated at 0.9kt for 2020 in the broader sector.
Fluoropolymers	Polymer	<p>There was approximately 49kt of fluoropolymers produced (and 40kt sold) in the EU in 2020. According to a market study conducted in 2022 on European Fluoropolymer use, application in the EU petroleum industry in 2020 was approximately 11.5 kt¹³. No information for specific activities or uses at a more granular level was provided.</p> <p>Different individual fluoropolymer components in equipment used in one particular refinery operators processes have been estimated at between 1 - 5 million components for six sites in the EEA in 2022¹⁵.</p> <p>According to a report written in 2021, one supplier estimated total sales of fluoropolymer in Europe for use in the petroleum and mining sector to be approximately 3,500 – 7,500 tonnes per year. This is approximately 5% of total fluoropolymer sales in Europe (i.e. sales to all sectors)¹².</p> <p>Another estimate, based on data from participating PlasticsEurope Fluoropolymer Products Group (FPG) members, places this sector-specific value at 2,500-10,000 tonnes in 2022²³.</p>
PTFE	Polymer	<p>PTFE accounts for the largest share of fluoropolymers produced in EU in 2020 (56%, approximately 22.4kt³⁷)¹³.</p> <p>No information was retrieved from the literature on use volumes in the refining sector. 29% of the fluoropolymer products produced in the EU in 2020 were by the chemicals sector (including energy)³⁷, so PTFE consumption could be estimated at 6.5kt for 2020 in the broader sector.</p>
FEP	Polymer	<p>FEP accounts for the joint third largest share of fluoropolymers produced in the EU in 2020 at 8%¹³, approximately 3.2kt³⁷.</p> <p>No information was retrieved from the literature on use volumes in the refining sector. 29% of the fluoropolymer products produced in the EU in 2020 were by the chemicals sector (including energy)³⁷, so FEP consumption could be estimated at 0.9kt for 2020 in the broader sector.</p>
PVDF	Polymer	PVDF accounts for the second largest share of fluoropolymers produced in EU in 2020 (12%, approximately 4.6kt ³⁷) ¹³ . Globally, has

³⁷ <https://fluoropolymers.eu/wp-content/uploads/2023/10/10.-Fluoropolymer-waste-in-Europe-2020-ProK.pdf>

Substance	Polymer/ Non-polymer	Volume Information
		<p>the second highest consumption volume among fluoropolymers at under 20% in 2015, and the fastest growing consumption volume of all fluoropolymers (not sector specific)²⁶.</p> <p>No information was retrieved from the literature on use volumes in the refining sector. 29% of the fluoropolymer products produced in the EU in 2020 were by the chemicals sector (including energy)³⁷, so PVDF consumption could be estimated at 1.3kt for 2020 in the broader sector.</p>

3.5 Emissions to air

3.5.1 Emission estimates

Very little information was available in the literature providing quantified estimates of PFAS emissions to air specifically from the refining sector. A report conducted for the Norwegian Environment Agency for the petroleum and mining sector as a whole provided air emission estimates for 2020 based on ECHA data¹² for FLS used in antifoaming agents, and two different fluoropolymer scenarios³⁸, shown in Table 3-11 below. However, most sources simply state detection of PFAS in air and dust (with little information on emissions or exposure pathways)²⁸ or mention air deposition in relation to AFFF and associated PFAS substances with no further information¹⁹.

Table 3-11: ECHA estimates of PFAS emissions to air

Substance	Polymer/Non-polymer	Air emissions in 2020 (kg)
FLS (Fluorosiloxane)	Polymer	85-635
Unspecified monomeric PFAS (low scenario)	Non-polymer	1-2
Unspecified monomeric PFAS (high scenario)	Non-polymer	270-850

Similar to estimates of use in the updated U-PFAS restriction dossier, estimated emissions (to all media) from the petroleum and mining sector as a whole represented a very small proportion (0.002%) of the total estimated emissions from all sectors covered by the restriction. The same caveats as applied to usage estimates in Section 3.4 also apply to this emission estimate. Consistent with the subsequent discussion in Section 3.4 around expected use in the refining sector, it would be expected that emissions to air of non-polymeric PFAS would also represent an even smaller fraction of total emissions.

Whilst information on PFAS emission sources specific to the refining sector was limited in the literature, there are several generic release mechanisms which, whilst of relevance across multiple sectors, are nonetheless also applicable to the refining sector. These include:

- Fugitive emissions from aerosolisation and volatilisation of firefighting foams.

³⁸ The 'high' scenario was informed by the ECHA (2014) Annex XV restriction report on PFOA to derive estimates for the proportion of total fluoropolymer used containing different concentrations of monomeric PFAS – 67% of the market uses a 0ppm PFAS concentration, 17% uses a concentration of 35 ppm, and 17% uses a concentration of 1500 ppm. The 'low' scenario makes the broad assumption of 1ppm concentration for PFAS (unspecified) in all fluoropolymers.

- Point and/or fugitive emissions from thermal degradation of fluoropolymers or abrasion/weathering of fluoropolymers.
- Fugitive emissions of F-gases from refrigeration systems.
- Fugitive emissions from wastewater treatment plants.

Further information is provided in the following sections.

3.5.2 Emissions from the use of firefighting foams

Section 3.3.5 has documented the presence of a number of non-polymeric PFAS in AFFF and other firefighting foams. Non-polymeric PFAS groups of most relevance in terms of potential human health and environmental factors are typically present in their ionic (non-volatile) forms in water and other aqueous media. However, these can transition to their non-ionic (volatile) forms when in contact with organic solvents and other organic matrices. To maintain equilibrium between ionic and non-ionic forms, the proportion of the more volatile, non-ionic forms increases in organic solvents compared to water^{39,40}. Solvents, including for example diethylene glycol monobutyl ether, propylene glycol and 2-butoxyethanol, can comprise up to 20% of AFFF⁴¹.

Hence, a scenario exists where non-polymeric PFAS could be lost to volatilisation shortly after AFFF is used in an actual firefighting application or in simulated tests, or is accidentally spilled. As water in the AFFF evaporates, the proportion of higher boiling point solvents within the AFFF increases. The equilibrium state of PFAS taken up into these solvents, or in contact with other organic materials including petroleum products, would then shift to its non-ionic, volatile form³⁹. Research has previously demonstrated that a range of PFAS found in AFFF, including PFOA and PFOS, would become volatile after application of AFFF to paved areas including airfield pavements as the residual water evaporates. In some cases, this volatilisation may be significant, comparable to that of semi-volatile hydrocarbons found in kerosene³⁹.

The replacement of legacy PFAS in modern AFFF formulations by neutral fluorosurfactants, which are more volatile, further increases the potential for fugitive PFAS emissions from volatilisation of AFFFs⁴².

Samples of the headspace of AFFF under typical environmental conditions with no heat applied have detected the presence of a range of PFAS, including fluorotelomer alcohols and fluorotelomer disulphides. The steady-state emission rate of one particular FTOH, 6:2 FTOH, under experimental headspace conditions has been estimated at 5 ng/min per ml of AFFF solution⁴². Once emitted to the atmosphere, FTOHs will undergo photochemical oxidation involving reactions with hydroxyl radicals, generating PFCAs as the terminal reaction product⁴³. For example, 8:2 FTOH will degrade to PFOA (see Section 5.2.2 for further information).

³⁹ Bastow, T., Douglas, G. and Davis, G., 2022. 'Volatilization Potential of Per- and Poly-fluoroalkyl Substances from Airfield Pavements and during Recycling of Asphalt.' *Environmental Toxicology*, 41, 2202 - 2208

⁴⁰ Kütt, A., Selberg, S., Kaljurand, I., Tshepelevitsh, S., Heering, A., Darnell, A., Kaupmees, K., Piirsalu, M., & Leito, I., 2018. 'pKa values in organic chemistry — Making maximum use of the available data'. *Tetrahedron Letters*, 59, 3738–3748.

⁴¹ Harding-Marjanovic, K. C., Houtz, E. F., Field, J. A., Sedlak, D. L., & Alvarez-Cohen, L., 2015. 'Aerobic biotransformation of fluorotelomer thioether amido'. *Environmental Science & Technology*, 49, 7666–7674

⁴² Mattila, J., Krug, J., Roberson, W., Burnette, R., McDonald, S., Virtaranta, L., Offenber, B. and Linak, W., 2024. 'Characterizing volatile emissions and combustion by-products from aqueous film-forming foams using online chemical ionization mass spectrometry.' *Environmental Science & Technology*, 58, 3942 – 3952.

⁴³ Ellis, D., Martin, J., De Silva, A., Mabury, S., Hurley, M., Andersen, M. and Wallington, T., 1998. 'Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids.' *Environmental Science & Technology*, 38, 3316-3321.

Other release mechanisms for PFAS to air during application of AFFFs include the generation of aerosols as the foam is applied under pressure, converting the PFAS-containing substances into fine droplets which are subsequently dispersed by the wind⁴⁴.

However, following the introduction of Commission Regulation (EU) 2025/1988 described in Section 3.3.5, emissions of PFAS from the use of firefighting foams may not be significant post 2035 due to the restrictions on the marketing and use of firefighting foams containing PFAS that would enter force during that year. Under both the Persistent Organic Pollutants Regulations and REACH Regulations, PFOA, PFHxA, PFHxS and C9 – C21 PFCAs have also been restricted in their use since 2020.

3.5.3 Emissions from the use of fluoropolymers

Section 3.3.8 has demonstrated that fluoropolymers may be used in certain process equipment at refineries which require the application of heat. Whilst thermal stability is a property inherent of fluoropolymers, studies have suggested that when fluoropolymers are heated to certain temperatures (this is dependent on the individual compound but thermolysis thresholds can range from between 200 - 500°C), the C-F bond begins to cleave, releasing fluorinated radicals. These radicals can then react in the presence of oxygen or moisture to form PFCAs⁴⁵. Research has suggested trace emissions of vapour phase PFOA have been detected well below commonly cited thermolysis thresholds for some fluoropolymers used in consumer products⁴⁶. Other research has demonstrated that thermolysis of fluoropolymers in industrial applications e.g., in ovens and stationary combustion engines, could potentially be a source of TFA in urban rain water, and an additional source of longer chain PFCAs⁴⁷.

However, there is also contradictory evidence on the potential formation of PFOA from thermolysis of fluoropolymers, with the same reference source which cites formation of PFCAs during thermolysis also citing evidence that PFOA can decompose rapidly under the same conditions where PTFE begins to degrade, and with further testing indicating no short- or long-chain PFAS were detected from various fluoropolymers exposed to temperatures ranging from 200 - 890°C⁴⁵. Rather, the main degradation products were identified as tetrafluoroethylene (TFE) and fluorobenzene.

Hence, whilst there is the potential for emissions of the relevant PFAS from process equipment containing fluoropolymers that requires the application of heat in excess of design temperatures, there is no research that quantifies any such emissions from specific refinery sources and the evidence on formation is uncertain. Appropriate selection of the most appropriate fluoropolymer for the specific process conditions will help to minimise any emissions that may occur via this pathway.

Fluoropolymers may also be released by abrasion or any physical stress even at typical environmental temperatures. Such discharges could include both point source and fugitive emissions but, unlike thermal degradation, these emissions could theoretically be in the form of small particles of the fluoropolymer⁴⁸.

⁴⁴ Nilsson, S., Smurthwaite, K., Aylward, L., Kay, M., Toms, L., King, L., Marrington, S., Barnes, C., Kirk, M., Mueller, J. and Braunig, J., 2022. 'Serum concentration trends and apparent half-lives of per- and polyfluoroalkyl substances (PFAS) in Australian firefighters.' *International Journal of Hygiene and Environmental Health*, 246, 114040.

⁴⁵ Dolatabad, A.A., Zhang, X., Mai, J., Kubatova, A., Cao, J. And Xiao, F, 2025. 'Thermal decomposition of fluoropolymers: stability, decomposition and possible PFAS release.' *Journal of Hazardous Materials*, 496, 139322

⁴⁶ Schlummer, M., Solch, C., Meisel, T., Still, M., Gruber, L. and Wolz, G., 2015. 'Emission of perfluoroalkyl carboxylic acids (PFCA) from heated surfaces made of polytetrafluoroethylene (PTFE) applied in food contact materials and consumer products.' *Chemosphere*, 129, 46-53.

⁴⁷ Ellis, D., Mabury, S., Martin, J. and Muir, D., 2001. 'Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment.' *Nature*, 412, 321-324.

⁴⁸ Lohmann, R., Cousins, I., DeWitt, J., Gluge, J., Goldenman, G., Herzke, D., Lindstrom, A., Miller, M, Ng, C., Patton, S., Scheringer, M., Trier, X. and Wang, Z, 2020. 'Are Fluoropolymers Really of Low Concern for Human

3.5.4 Emissions from the use of refrigerants

Some refrigerants using a HFC, or mixture of HFCs, can be classified as PFAS under the OECD definition as they contain multiple $-CF_3$ or $-CF_2-$ groups. Examples include pentafluoroethane (HFC-125) and 1,1,1,2-tetrafluoroethane (HFC-134a). Whilst typically used in closed-loop systems which limits emissions, leaks of refrigeration systems or inappropriate discharge can, therefore, contribute to fugitive emissions of PFAS.

However, whilst some HFCs or refrigerant blends can technically be classified as PFAS, they have different properties and the primary concern of HFCs from an environmental perspective is their high global warming potential and contribution to climate change.

Research has, however, demonstrated that TFA may be formed from the degradation of some HFCs, including HFC-134a, in the troposphere⁴⁹. This degradation pathway is initiated by reaction with a hydroxyl radical, forming CF_3COF , followed by in-cloud hydrolysis of CF_3COF to form TFA, which can then be deposited to the surface by washout or dry deposition. The initial rate of reaction with the hydroxyl radical is, however, slow with a half-life estimated at 14.4 years⁵⁰. Hence, degradation of HFCs to form TFA is a regional or global transport mechanism and areas local to a HFC source are unlikely to be materially impacted by exposure to TFA from degradation of HFCs associated with refrigerant leaks.

Regulation (EU) 2024/573 (the “F-gas regulations”) introduces requirements for the use of certified technicians to install, service or repair equipment containing F-gases, whilst operators and users of equipment containing F-gases are required to implement a regular, pro-active leak detection and repair system, thereby helping to control potential fugitive emissions from this source.

3.5.5 Emissions from wastewater treatment plants

Some studies have demonstrated the presence of PFAS in both incoming wastewater and treated effluent from industrial and municipal wastewater treatment plants (WwTP) attributed to their ubiquitous use and incomplete removal at the WwTP^{51,52}. Dependent on the industrial process, incoming effluent streams may contain PFCAs and PFSA, but could also include PFAA precursors which, dependent upon the treatment process, can be subsequently transformed into PFCAs and PFSA during biotic degradation in the WwTP. For example, FTOHs can be converted into PFCAs, including PFOA, whilst perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs) can be converted into PFSA, including PFOS, in WwTPs⁵³.

Although the processes at an individual industrial WwTP will differ, and share much in common with municipal wastewater treatment plants, they typically involve some variation of the following stages:

- **Primary treatment** – a physical treatment process to remove insoluble solids, where wastewater is directed to, and held in, settlement tanks allowing heavier solids to settle to the bottom of the tank as sludge and lighter components to form as a “scum” on the surface where they can be removed by a skimmer.

and Environmental Health and Separate from Other PFAS?’ *Environmental Science & Technology*, 54, 12820 – 12828.

⁴⁹ Franklin, J., 1993. ‘The atmospheric degradation and impact of 1,1,1,2-tetrafluoroethane (hydrofluorocarbon 134a).’ *Chemosphere*, 27, 1565-1601

⁵⁰ Kotamarthi, V., Rodriguez, J., Ko, M., Tromp, T. and Sze, N., 1998. ‘Trifluoroacetic acid from degradation of HCFCs and HFCs: a three dimensional modelling study.’ *Journal of Geophysical Research*, 103, 5747 – 5758.

⁵¹ Seay, B., Dasu, K., MacGregor, I., Austin, M., Rile, R., Frank, A., Fenton, G., Heiss, D., Williamson, R., Buehler, S., 2023. Per- and polyfluoroalkyl substances fate and transport at a wastewater treatment plant with a collocated sewage sludge incinerator. *Science of the Total Environment*, 874, 162357.

⁵² Winchell, L., Ross, J., Wells, M., Fonoll, X., Norton Jr, J., Bell, K., 2020. Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review. *Water Environment Research*, 93, 826-843

⁵³ Zhou, T., Li, X., Liu, H., Dong, S., Zhang, Z., Wang, Z., Li, J., Nghiem, L., Khan, S., Wang, Q., 2024. Occurrence, fate, and remediation for per-and polyfluoroalkyl substances (PFAS) in sewage sludge: A comprehensive review. *Journal of Hazardous Materials*, 466, 133637.

Flocculants may be added to support the sedimentation process or pressurised gas can be injected to support this separation, such as in dissolved gas flotation tanks. Alternatively, sand filtration may be used to remove insoluble solids.

- **Secondary treatment** – generally a biological treatment stage where aeration and/or biological action of bacteria and other microbes breakdown dissolved organic matter. This can involve the use of activated sludge plant/aeration lanes, trickle filters or biological contactors.
- **Tertiary treatment** – final filtration and chemical treatment using e.g., chlorine, activated carbon, or ozone to “polish” the effluent.
- **Sludge handling and processing** – settled sludge from the primary and secondary treatment stages is collected and further treated on-site e.g., dewatered and/or exported off-site for further treatment e.g., incineration, anaerobic digestion or, in some cases, applied to land as an agricultural soil improver.
- **Effluent discharge** – the final treated water/effluent is released into a local watercourse e.g., river through an outfall or pipe, or discharged to sewer.

PFAS emissions to air at WwTPs have been linked to aerosolisation and volatilisation during processes where the effluent is vigorously aerated or agitated, including in activated sludge plants and at outfalls^{54,55}. Many PFAS, including PFCAs, exhibit surfactant properties due to the hydrophobic alkyl chain and hydrophilic functional group head. These compounds will, therefore, naturally accumulate at air-water interfaces, and the additional surface turbulence induced by aeration/mixing enhances aerosol-mediated transport⁵⁶.

Studies have reported the presence of volatile, semi-volatile and non-volatile PFAS in the ambient air at, and around, WwTPs^{56,57,58}. These studies consistently found higher concentrations of PFAS (by several orders of magnitude in some cases) in the air adjacent to aeration lanes compared to more quiescent holding tanks such as primary settlement tanks.

Aerosolisation results in the generation of fine particles within which the PFAS compounds are dissolved and is the dominant phase under which semi- or non-volatile PFAS groups, including PFCAs and PFSAs, have been monitored at WwTPs. One study observed that the main PFCAs and PFSAs monitored adjacent to aeration tanks were PFOS, PFHxA, PFOA and PFDA with most of these compounds identified in the particle phase⁵⁶.

However, the additional turbulence during aeration also increases the volatilisation of more volatile groups including FTOHs and other fluorotelomer species including iodides (FTIs) acrylates (FTACs) and methacrylates (FTMACs)⁵⁵. One study⁵⁶ observed that average gas-phase concentrations of FTOHs (11,000 pg/m³ at the aeration lane and 590 pg/m³ at the secondary settlement tank) were one to three orders of magnitude higher than PFCAs and PFSAs (~ 70 pg/m³ at the aeration lane and 34 pg/m³ at the secondary treatment tank). Conversely, concentrations of PFCAs and PFSAs in the particle phase were 10 - 500 times higher than that of particle-phase FTOHs, with average particle-phase concentrations of PFOS (3,900 pg/m³) approaching the

⁵⁴ Kizhakkethil, J., Shi, Z., Bogush, A., Kourtchev, I., 2024. Aerosolisation of per- and polyfluoroalkyl substances (PFAS) during aeration of contaminated aqueous solutions. *Atmospheric Environment*, 334, 120716

⁵⁵ Chen, C., Wang, J., Li, L., Xu, W., Liu, J., 2020. Comparison of fluorotelomer alcohol emissions from wastewater treatment plants into atmospheric and aquatic environments. *Environment International*, 139, 105718

⁵⁶ Vierke, L., Ahrens, L., Shoeib, M., Reiner, E., Guo, R., Palm, W., Ebinghaus, R., Harner, T., 2011. Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. *Environmental Chemistry*, 8, 363 – 371

⁵⁷ Ahrens, L., Shoeib, M., Harner, T., Lee, S., Guo, R., Reiner, E., 2011. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environmental Science & Technology*, 45, 8098 – 8105

⁵⁸ Shoeib, M., Schuster, J., Rauert, C., Su, K., Smyth, S-A., Harner, T., 2016. Emission of poly and perfluoroalkyl substances, UV-filters and siloxanes to air from wastewater treatment plants. *Environmental Pollution*, 218, 595 – 604

average gas-phase concentration of 6:2 FTOH (5,700 pg/m³). However, with the exception of PFOS, the average concentration of most other PFCAs and PFSA was less than 100 pg/m³, suggesting that FTOHs and PFOS are the primary compounds of relevance for emissions from aeration tanks.

Another study identified that the alkyl chain length and pH influences the extent of PFAS aerosolisation, as does the type of functional group head, with PFSA demonstrating a greater potential for aerosolisation compared to PFCAs⁵⁴.

Whilst many studies have measured ambient concentrations of PFAS in the air at, or around, WwTP, there are fewer studies that have attempted to calculate the emission rate to air. One study that attempted to do used two-film resistance theory to estimate emission rates of 6:2 FTOH and 8:2 FTOH from monitored ambient concentrations⁵⁵. Emission rates were estimated at 0.15 – 1.49 g/day for 6:2 FTOH and 0.29 – 2.73 g/day for 8:2 FTOH with some seasonal variation in the emission levels. This was linked to seasonal variation in wind speed, with higher wind speeds promoting more rapid mass transfer of FTOHs from water to air.

Other studies have estimated much lower total PFAS emissions from WwTPs at 0.02 g/day using a simple inverse Gaussian modelling approach, but the study authors advise that this estimate should be treated with caution as it was derived from a single measurement from one sampling location⁵⁹. Similar Gaussian modelling approaches have also been made in another study that estimated annual emissions of PFAS from a WwTP containing eight aeration tanks at 2,560 g/yr (or 320 g/yr/tank) with these emissions dominated by 6:2 FTOH, 8:2 FTOH, PFOS and PFBA⁵⁷. Other studies estimated PFAS aeration tank emission rates using a Gaussian approach at 10 – 110 g/yr/tank⁵⁸.

Although aerosolisation and volatilisation of incoming and treated liquid effluent is expected to represent the primary emission to air pathway at a WwTP, several studies have identified the presence of PFAS, including PFCAs and PFSA, in sewage sludge⁵³. Indeed, studies have identified that, because most WwTPs do not incorporate specific PFAS treatment/removal processes, sewage sludge becomes a major sink for PFAS with other research indicating PFAS concentrations in sewage sludge can range between tens to thousands of ng/g dry weight⁶⁰. The handling and treatment of this sludge therefore presents an additional potential release pathway to air through fugitive emission (dust or volatilisation associated with agitation during handling)⁵³.

Whilst none of the above literature specifically addresses WwTPs at refineries, other case studies have demonstrated the presence of PFAS in refinery effluents primarily linked to the historic use of firefighting foams and subsequent runoff from contaminated areas⁶¹. There is, therefore, the potential for processes at refinery WwTPs, particularly those incorporating biological treatment stages involving aeration and where PFAS containing firefighting foams have been previously used, to cause fugitive emissions to air of PFCAs and PFSA due to aerosolisation of the liquid effluent.

As aerosolisation is an identified release mechanism to air for PFAS compounds contained within aqueous media, there is also the potential for cooling towers to act as a source of PFAS emissions to air as cooling tower 'drift' is a well-known phenomenon from certain types of cooling towers. However, no specific literature could be found that quantified emissions to air of PFAS from cooling towers, with most studies either demonstrating aerosolisation mechanisms in analogous systems (e.g., sea spray, WwTPs) or characterising cooling tower drift without PFAS-specific chemical analysis.

⁵⁹ Lin, H., Lao, J-Y., Wang, Q., Ruan, Y., He, Y., Lee, P., Leung, K., Lam, P., 2022. Per- and polyfluoroalkyl substances in the atmosphere of waste management infrastructures: Uncovering secondary fluorotelomer alcohols, particle size distribution, and human inhalation exposure. *Environment International*, 167, 107434

⁶⁰ Moodie, D., Coggan, T., Berry, K., Kolobaric, A., Fernandes, M., Lee, E., Reichman, S., Nugegoda, D., Clarke, B.O., 2021. Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in Australian biosolids. *Chemosphere*, 270, 129143

⁶¹ https://assets.publishing.service.gov.uk/media/66ebe9a6c8398625c331e778/Annex_C_PFAS_WP4_Phase_4_-_Report_Rev0_REDACTED.pdf

3.5.6 Ambient air monitoring near to refineries

Some studies have monitored concentrations of PFAS in air and soils around refineries. For example, one study identified 34 PFAS compounds in samples taken from a refinery in southwestern China with TFA and HFPO-DA being the dominant PFAS compounds detected. However, given the ubiquitous nature of these compounds and their persistence, with the potential for long-range transport of TFA (as summarised in 3.5.4), the study makes no assessment as to whether the presence of these compounds is directly related to refinery activities or represents general “background” contributions⁶².

In Europe, the Flemish Government commissioned a study to monitor concentrations of PFAS in ambient air and deposition in the Flanders region between July 2022 and August 2023⁶³. Measurement campaigns were conducted at various types of locations across Flanders, including rural and urban background locations, coastal locations, and locations near to industrial activities in the Port of Antwerp where a PFAS manufacturing plant operates and two refineries and/or petrochemical complexes operate.

At the four monitoring locations within the port complex, the majority of PFAS measured in ambient air and in deposition samples were PFCAs, ranging between 52% to 80% of total PFAS detected. The PFCAs primarily comprised PFPrA, PFBA, PFOA and PFOS. Fluorotelomers and PFASs were the next most significant groups, with these groups contributing up to 35% and 17%, respectively, of total PFAS in ambient air.

The average ambient concentration of PFAS in the Port of Antwerp was comparable to other monitoring locations, with the exception of the monitoring locations near to one PFAS manufacturing site which were elevated by several orders of magnitude compared to other locations due to the well-known historic contamination at this site. The monitoring report, therefore, identified that distance from this site was the primary factor influencing monitored PFAS concentrations at other locations. As such, it is not possible to draw any conclusions from this study in terms of potential contributions from refining and/or petrochemical complex activities in the Port of Antwerp beyond observing that the contribution to air from refinery emission sources would not be materially different than other industries within the port area that may also use PFAS, and that potential emissions from refineries are considerably less than PFAS manufacturing industries.

3.6 Summary

The findings of the literature review point to several different uses of PFAS within the refining sector, the bulk of which are fluoropolymers in applications such as cables, piping, coatings, and other process components. In addition, there is limited evidence pointing to use of non-polymeric PFAS in hydrocarbon processing, although the literature, in general, is not specific on the exact functions and applications of these substances. The main use of non-polymeric PFAS would appear to be related to enhancing the efficiency of the alkylation process and use in firefighting foams.

Information on the volumes of use is limited, and generally aggregated in nature, typically representing broader use beyond just the refining sector, or representing groupings of PFAS substances. The available information on emissions to air associated with uses is even more limited and not specific to the refining sector, representing a significant data gap. However, based on estimates from the dossiers supporting the U-PFAS restriction for the broader petroleum and mining sector, use and potential air emissions from the refining sector are expected to be very small compared to other sectors considered by the restriction proposals.

⁶² Maosen Zhao, Yiming Yao, Xiaoyu Dong, Mujtaba Baqar, Bo Fang, Hao Chen, and Hongwen Sun, 2023. 'Nontarget Identification of Novel Per- and Polyfluoroalkyl Substances (PFAS) in Soils from an Oil Refinery in Southwestern China: A Combined Approach with TOP Assay.' *Environmental Science & Technology*, 57, 20194-20205

⁶³ VITO, 2024. 'Exploratory research into PFAS in ambient air and deposition in Flanders.' VITO reference 2023/HEALTH/R/3098

4 Emissions to air measurement techniques

Key messages

Although there is no international, multi-laboratory validated and standardised measurement method for stationary source emissions of PFAS to air, measurement of PFAS emissions to air has been performed in some industries using non-standardised methods for nearly 20 years. It is only within the last five years that documented methods have been introduced in the form of OTM-45 and OTM-50, from which domestic standards have recently been developed and published in some European countries.

OTM-45 and OTM-50 are both examples of periodic, extractive measurement techniques which require samples to be extracted from a stack, temporarily stored and then transported for subsequent analysis in a laboratory. Due to the ubiquitous nature of many PFAS in the environment and industrial/consumer products, including those that can be found in emissions measurement and laboratory analytical equipment, potential sample contamination is a significant issue, requiring use of different kinds of sample blanks and specialised sampling equipment.

Due to the recent nature of publication of OTM-45 and OTM-50, the number of laboratories accredited for sampling and analysis to these standards remains low. However, it is expected that the number of accredited laboratories will increase in the future driven by the recent emphasis beginning to be placed on the importance of PFAS emissions to air in the overall PFAS risk assessment framework.

Emerging techniques, including the use of instrumental techniques for PFAS emissions to air such as SIFT-MS, may extend the scope of coverage of PFAS emissions to air monitoring, and allow real-time, continuous measurement of these emissions.

4.1 Introduction

This section reviews techniques that have been developed for measuring point source (stack) emissions to air of PFAS. The purpose of this review is to provide information on key aspects of the techniques, including sampling requirements, accuracy and limits of detection, and any limitations/constraints of the methods to help operators select an appropriate measurement technique.

Measurement of emissions in this way can also help to provide key data to close some of the gaps identified in the previous section of the report.

4.2 Overview

As of November 2025, there is no internationally accepted or harmonised method for measuring emissions to air of this family of compounds. The current absence of standardised methods to measure PFAS emissions, and the limited availability of data on the performance of methods to measure PFAS, introduces considerable uncertainty in understanding the release of PFAS into the air from industrial sources.

However, despite the absence of a standardised method, measurement of PFAS emissions to air has been performed using unaccredited methods for the last 20 years at some industrial facilities. For example, personnel from Logika managed the bi-annual emissions to air measurement surveys at a European fluoropolymer manufacturer between 2007 – 2019 by sampling portions of the gas stream isokinetically into an impinger train containing dimethyl sulfoxide and deionised water, with subsequent analysis by Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS). Stationary source emissions tests of PFAS have also been performed in

North Carolina and New Hampshire from industrial facilities that synthesise PFAS, or use PFAS in the manufacturing process⁶⁴.

The first “official” measurement method for PFAS was released by the US EPA in 2021 in the form of Other Test Method (OTM) 45⁶⁵. As an OTM, the method is not regulatory approved, nor endorsed by the US EPA, but the technical documentation supporting its development has been reviewed by the US EPA’s Emission Measurement Center (EMC) and has been determined as potentially useful for the wider measurement community⁶⁶. OTM-45 has since been used as the basis for developing domestic methods in some European countries. For example, LUC/VI/003⁶⁷ in Flanders and XP X 43-126⁶⁸ in France are both derived from OTM-45 and use the same sampling train, whilst OTM-45 is currently listed as the preferred monitoring method for PFAS emissions to air in the UK⁶⁹.

OTM-45 is only suitable for polar, semi-volatile or non-volatile PFAS. Consequently, the US EPA has been developing other methods to address other compounds, including those that are non-polar and volatile. In early 2025, OTM-50 was released to provide a method for sampling volatile compounds⁷⁰.

OTM-45 and OTM-50 both fall into the category of periodic/extractive measurement techniques and do not allow real-time/continuous measurements of PFAS emissions to air. Whilst there are no certified test methods for continuous measurements of PFAS, certain instrumental techniques, including Selected Ion Flow Tube-Mass Spectrometry (SIFT-MS), have been cited as an emerging technique for both stationary source and ambient monitoring of PFAS in air⁷¹ and has previously been used on a trial basis to measure real-time emissions of certain non-polar, volatile PFAS from a European industrial site.

An overview is provided of OTM-45, OTM-50, and emerging techniques, such as SIFT-MS, in this section, including details on the measurement principle, sampling requirements, accuracy and limits of detection, and any limitations/constraints of the method.

The number of laboratories with OTM-45 and OTM-50 within their schedule of accreditation is currently low, largely because of the recent introduction of these methods. For example, in France, as of 27 November 2025, there are only three stack testing laboratories that are accredited to OTM-45 (and four which are accredited to the domestic standard derived from OTM-45) and none to OTM-50, whilst, in the UK, as of 25 February 2026, only one stack testing laboratory is accredited to OTM-45 and OTM-50, although it is understood from personal communication with this accredited laboratory that several others are in the process of gaining this

⁶⁴ <https://www.deq.nc.gov/news/key-issues/genx-investigation/air-quality-sampling>

⁶⁵ US EPA, 2021. ‘Other Test Method 45 (OTM-45) Measurement of Per- and Polyfluorinated Alkyl Substances from Stationary Sources’ https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

⁶⁶ US EPA, 2025. ‘EMC Other Test Methods.’ <https://www.epa.gov/emc/emc-other-test-methods>

⁶⁷ VITO, 2024. ‘Determination of the concentration of per- and polyfluoroalkyl compounds (PFAS) in a guided gas stream.’ https://reflabos.vito.be/2025/LUC_VI_003_eng_.pdf

⁶⁸ AFNOR, 2024. ‘Stationary Source Emissions - Sampling and Analysis of Polar Semi-Volatile Per- and Polyfluoroalkylated Compounds (PFAS).’ <https://norminfo.afnor.org/norme/xp-x43-126/emissions-de-sources-fixes-prelevement-et-analyse-de-composes-per-et-polyfluoroalkylees-pfas-semi-volatils-polaires/206279>

⁶⁹ Environment Agency, 2025. ‘Guidance: Monitoring stack emissions: techniques and standards for periodic monitoring.’ <https://www.gov.uk/government/publications/monitoring-stack-emissions-techniques-and-standards-for-periodic-monitoring/monitoring-stack-emissions-techniques-and-standards-for-periodic-monitoring#per-and-polyfluorinated-alkyl-substances-pfas>

⁷⁰ US EPA, 2025. ‘Other Test Method 50 (OTM-50) Sampling and Analysis of Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters.’ <https://www.epa.gov/system/files/documents/2025-01/otm-50-release-1-r1.pdf>

⁷¹ Swift, S.J., Gnioua, M.O., Dryahina, K., Spanel, P., 2025. ‘A SIFT Study of Reactions of Positive and Negative Ions With Polyfluoroalkyl (PFAS) Molecules in Dry and Humid Nitrogen at 393 K.’ *Rapid Communications in Mass Spectrometry*, 39:e9975

accreditation. However, it is expected that the number of accredited laboratories will grow in time, reflecting the increasing importance and regulatory scrutiny being placed on PFAS emissions in general

4.3 OTM-45

4.3.1 Measurement principle

OTM-45 is a performance-based method applicable to the collection and quantitative analysis of specific semi-volatile (boiling point > 100°C) and particulate-bound PFAS in air emissions from stationary sources.

Gaseous and particulate bound target PFAS are extracted isokinetically from the gas stream using a heated probe and sample line. Particle-bound PFAS are collected on a heated glass wool or quartz filter (120 °C or at least 10 °C above stack gas temperature) following which gaseous PFAS are captured via a primary adsorbent cartridge (XAD-2), a condensation bottle, a series of impingers with absorption reagent (ultrapure water) and then a secondary adsorbent (XAD-2) cartridge to identify breakthrough. The target compounds are extracted from the individual collection media, resulting in four separate extract fractions for analysis.

The extracted samples are analysed by LC-MS/MS in multiple reaction monitoring (MRM) mode with quantification of each analyte using an isotope dilution technique. The method is not intended to differentiate between target compounds in particle or vapour fractions and uses isotopically labelled standards to improve method accuracy and precision.

The target analytes of OTM-45 are provided in Table 4-1.

Table 4-1: OTM-45 target analytes

PFAS Group	Target analytes
Perfluoroalkylcarboxylic acids (PFCAs)	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFTrDA, PFTeDA, PFHxDA, PFODA
Perfluorinated sulfonic acids (PFSAs)	PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS
Perfluorinated sulfonamides (FOSAs)	FOSA, MeFOSA, EtFOSA
Perfluorinated sulfonamide ethanols (FOSEs)	N-MeFOSE, N-EtFOSE
Perfluorinated sulfonamidoacetic acids (FOSAAs)	MeFOSAA, EtFOSAA
Fluorotelomer sulfonates (FTS)	4:2 FTS, 6:2 FTS, 8:2 FTS, 10:2 FTS
Fluorinated Replacement Chemicals	ADONA, HFPO-DA, 9Cl-PF3ONS, 11Cl-PF3OUdS
Additional targets	NFDHA, PFESA, PFDoS, PFMBA, PFMPA, PFecHS, 8:2 FTUCA, 10:2 FDEA, 8:2 FTA, 6:2 FHUEA, 6:2 FTCA, 3:3 FTCA, 5:3 FTCA, 7:3 FTCA

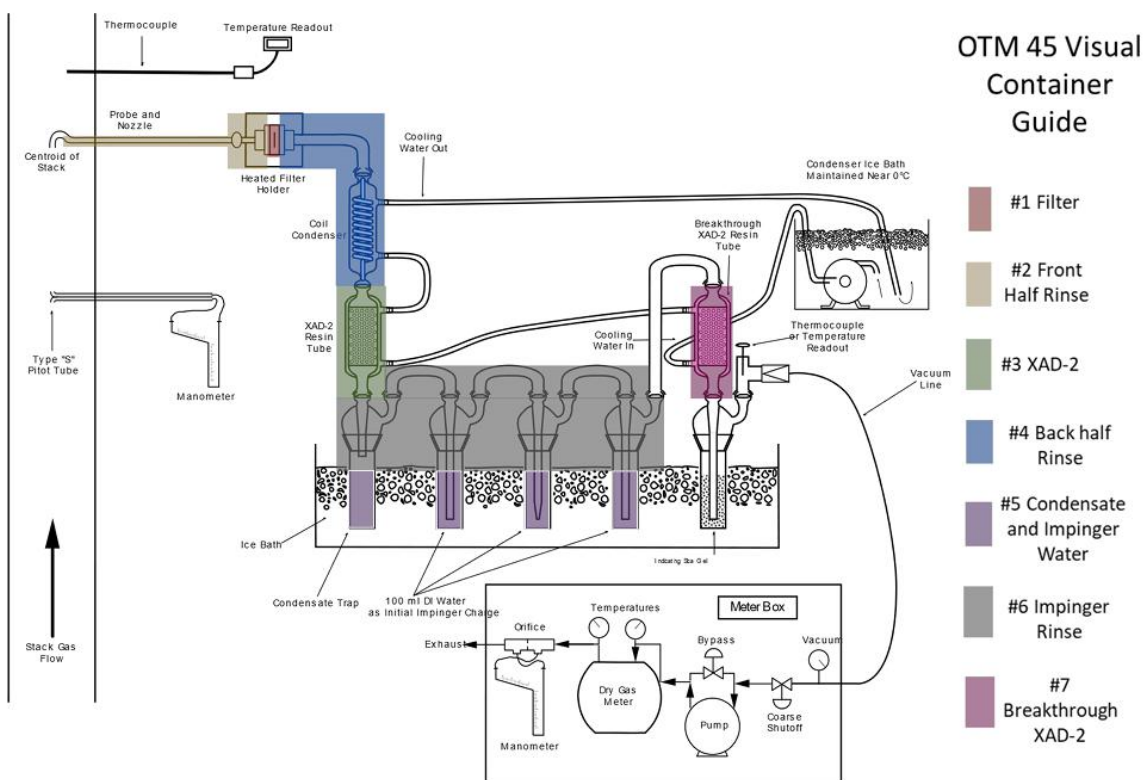
4.3.2 Sampling requirements

The OTM-45 sampling system is largely derived from the US EPA Method 5 sampling train used for the determination of particulate matter emissions from stationary sources. The specific OTM 45 adaptations include:

- the use of condenser and XAD-2 adsorbent module, which are used for the primary capture of PFAS compounds that pass through the glass or quartz-fibre filter in the gas phase;
- a series of impingers for additional capture of PFAS compounds that pass through the primary XAD-2 adsorbent module; and
- a secondary XAD-2 adsorbent module which is to determine the breakthrough of PFAS compounds not captured by the primary XAD-2 adsorbent module and impingers.

Figure 4-1 provides a schematic of the OTM-45 sampling train.

Figure 4-1: OTM-45 sampling train



Source: US EPA (2021)⁶⁵

The sampling train must consist of borosilicate or quartz glass (probe, filter holder, condenser, condenser bottle, impingers, etc.). Although Teflon (PTFE) should be avoided as much as possible due to the risk of contamination, the method does allow it to be used for example in connections, including O-rings and/or coatings, subject to verification that it does not lead to contamination. Polypropylene or polyethylene products are suitable materials. Different blanks are provided to check absence of contamination linked to the media and reagents, the sampling train used, or the on-site measurement implementation.

General specifications for the different parts of the sampling train include:

- The quartz filter must have an efficiency of at least 99.95%.
- Tubing, condenser, and XAD-2 cartridges should be oriented vertically in the sampling train to facilitate maximal flow and avoid moisture buildup inside the train compartments.

- Adsorbent cartridges should consist of water-jacketed glass cartridges containing 20-40 g of solid adsorbent (XAD-2).
- The temperature of the incoming gas flow at the XAD-2 cartridges must be kept below 20°C. This (incoming) temperature is measured at the primary XAD-2 cartridge. An ice bath can be used to circulate pump-cooled water to the condenser and adsorbent cartridges. If the ambient temperature is > 20°C, the XAD-2 cartridges are required to be cooled.
- During sampling, the XAD-2 cartridges should be wrapped with aluminium foil to protect the adsorbent from radiant heat and sunlight.
- The impingers should be filled with approximately 100 ml of ultrapure water.
- Samples must be transported in such a way as to protect them from light and temperatures. All field samples, with the exception of the filter, should be stored temporarily on ice at ~4°C and in the dark prior to transport to the laboratory. The adsorbent (XAD-2) must be stored and transported in glass cartridges or clean wide mouth HDPE jars.
- At the laboratory, samples must be stored in the dark at a temperature not exceeding 6°C and extracted within 28 days of collection.

4.3.3 Accuracy and limits of detection

Data to support OTM-45 method performance to date is limited. The method has been developed based on a combination of empirical knowledge and data, as well as incorporation of procedures and concepts adapted from other methods and measurement practices. The collection of blanks, in replicate and representing multiple forms (e.g., field sample media blank, sample train proof blank, sample train field blank), is particularly important to data interpretation and validation due to the ubiquitous nature of PFAS in the environment which can cause sample contamination. Managing PFAS sample contamination from a variety of sources, particularly XAD-2, has been a critical and acknowledged factor to collecting emissions data of known and acceptable quality.

Based on field evaluation trials, an average pre-sampling standard recovery of 100.3% was observed for PFOA, whilst the equivalent result for PFOS was 73.0%.

Maintenance of the sampling train components is required to ensure they are in suitable condition for stack sampling e.g., checking their integrity, undamaged etc. Components of the sampling train will need to undergo periodic calibration prior to being used on site e.g., the metering device (usually a dry gas meter) to ensure it can achieve isokinetic measurements, the thermocouples used to record the sampling train temperatures, and the barometer to record auxiliary measurements for atmospheric pressure. Any probe nozzle diameters will also need to be calibrated before being used on site.

There are several quality control aspects that must be taken into account when monitoring to OTM-45, the specifications and requirements of each is described below:

- **Blanks:** Due to the contamination risk, strict quality control procedures are required. This includes the requirements for several blank samples to be taken including a media and reagents blank (to determine whether spent media, reagents or other interferences are introduced into the sample through transportation, and storage), a field blank (of the whole sampling train system, to determine whether contamination is introduced due to the sampling train or the on-site measurement implementation or field environment), and a post field blank (to check whether all PFAS have been adequately captured when rinsing sampling train after recovery of media). The different sampling blanks are collected during each campaign or measurement.
- **Pre-sampling standards:** For each stack measurement, isotope-labelled sampling standards (SS) are added to the primary XAD-2 adsorbent to control for the entire sampling and analysis process. The first version of

OTM-45 released in 2021 required the addition of two standards for C8 compounds (PFOA and PFOS) in the resin. The most recent version provides for three additional standards for C4 compounds (PFBA and PFBS) and C12 compounds (PFDoA). The recoveries of these standards, after correction for the recovery of the internal standards (IS), must demonstrate per stack measurement that recovery of the labelled standards meets a required range of 70 - 130%. The method considers that recoveries between 50 - 70% are still acceptable, but recoveries must be flagged and reported and that, below 50% standard recovery, the reason must be investigated and a new measurement might be required. The percentage recovery should be evaluated on the entire sampling train (sum of analysis fraction recoveries), as migration of the recovery standards throughout the train compartments cannot be excluded.

- **Pre-extraction and pre-analysis standards:** As for sampling, standards are added at the sample analysis stage in the laboratory, before extraction and analysis of samples. OTM-45 method sets recovery targets of 20-130% and 50-150% respectively.
- **Sampling train leak test:** Before and after each measurement, a leak test shall be performed.
- **Relative breakthrough:** The relative breakthrough (BT; %) of PFAS through the sampling train is evaluated per compound based on the mass ratio between the secondary (breakthrough) XAD-2 cartridge and the sum of all fractions) in the sampling train. If the relative breakthrough is greater than 10%, OTM-45 provides for the quantified mass for each PFAS compound from secondary XAD-2 cartridge to be added to the other fractions to calculate the total PFAS emission concentrations. The BT value must be less than 30%. Failure to meet this requirement may invalidate the results and require repeat sampling.

The limit of quantification of a measurement is derived from the analytical limit of quantification for each sample fraction, the total gaseous stack sample volume collected, and the sample preparation steps in this method. Increasing the sampling time and the volume sampled will lower the measurement quantification limit. Depending on practices and standards considered, the sensitivity of the method is sometimes expressed as a limit of detection (LoD) or a limit of quantification (LoQ), with sometimes different definitions for these quantities. The comparison of these performance characteristics given in the various standards must, therefore, be treated with caution.

In OTM-45, the method detection limit (MDL) and quantitative reporting level (QRL) are presented for a nominal sample volume of 3 m³. The MDL is defined as the minimum qualitatively recognisable signal in laboratory analyses above background for a target compound with 99% confidence, whilst the QRL is defined as the minimum quantitative level that can be reported.

Quoted MDLs and QRLs are analyte specific, but range between 0.14 – 2.77 ng/m³ in terms of the MDL, and 0.50 – 5.53 ng/m³ in terms of the QRL. The Method suggests that, by extending the sampling duration, detection limits in orders of magnitude of pg/m³ might be possible.

4.3.4 Limitations and constraints

OTM-45 is only suitable for the measurement of specified polar, semi-volatile and particulate-bound PFAS. Whilst a list of 49 targeted compounds are provided in the method, in principle the method could be extended to other semi-volatile PFAS assuming appropriate standards are available to allow calibration of the LC-MS/MS analyser. However, the method cannot be used for measuring volatile and/or non-polar compounds.

The method identifies several interferences which may affect the accuracy of the result. For example, high concentrations of other organic compounds in the matrix may interfere with the analysis. OTM-45 provides examples of extraction and cleanup procedures to reduce, but not necessarily eliminate, matrix effects due to high concentrations of organic compounds.

Furthermore, target compound contaminants or related organics in solvents, reagents, glassware, isotopically labelled spiking standards, and other sample processing hardware are potential method interferences. PTFE

products including PTFE cap liners can be a source of PFAS contamination. The use of PTFE in this method must be avoided or the product must be tested and shown to be contaminant free before use.

Other limitations/constraints of the method include:

- As OTM-45 uses a sampling train largely derived from US EPA Method 5, the same constraints inherent to Method 5 equipment are also associated with this method. Sample ports must be of sufficient diameter to allow access to the sampling probe and filter. Typically, this requires a 4" BSP sample socket, which may make the method unviable for very narrow diameter stacks.
- The requirement for a heated sample system (primarily the filter and probe components) can present potential safety concerns in some locations with hazardous area classifications.
- As an extractive technique, results are delayed due to the requirement for subsequent laboratory analysis. The method also returns an average emission concentration over the spot sample duration and it is not possible to monitoring the evolution of the emissions in real time or over a long-term, continuous period.
- The transport and storage requirements for the samples are rigorous e.g. all collected field samples are to be stored and transported in the dark (shielded from UV light) and on ice (~4°C), with the exception of filters. To avoid contamination of the media and field samples, special attention should be paid to hygiene during transport, field handling, sampling, recovery and laboratory analysis, as well as during the preparation of the XAD-2 cartridges.

With these limitations in mind, overall OTM-45 is considered to be potentially applicable to refinery emission sources, particularly those emission sources where particulate matter monitoring is already performed. It is less likely to be applicable for smaller diameter vents e.g., on storage tanks due to the requirement to sample isokinetically requiring a minimum 4" sample port. However, it is unknown whether this method has already been applied to refineries.

4.4 OTM-50

4.4.1 Measurement principle

OTM-50 is a performance-based method applicable to the collection and quantitative analysis of specific volatile fluorinated compounds (referred to as VFCs in the method) rather than PFAS specifically. The target list is derived from known industrial products and products of incomplete thermal destruction (Table 4-2). Several of the compounds on the list are not PFAS even though they contain fluorine (e.g., HCFC-22, CFC-13 and CFC-11) whilst others are F-gases which, whilst considered PFAS under OECD definitions, are not associated with direct toxicity effects.

Table 4-2: OTM-50 target list

Targeted compounds		
Carbon tetrafluoride	Hexafluoroethane (HFC-116)	Tetrafluoroethene
Trifluoromethane (FC-23)	Octafluoropropane	Difluoromethane (HFC-32)
Fluoromethane (HFC-41)	Pentafluoroethane (HFC-125)	Hexafluoropropene
Hexafluoropropene oxide	Decafluorobutane	Dodecafluoropentane
Tetradecafluorohexane	1H-Perfluoropentane	Hexadecafluoroheptane
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	1H-Perfluorohexane	1H-Perfluoroheptane

Targeted compounds		
2H-Perfluoro-5-methyl-3,6-dioxanonane	1H-Perfluorooctane	Octadecafluorooctane
1H-Nonafluorobutane	1H-Heptafluoropropane	1,1,1,2-Tetrafluoroethane (HFC-134a)
1,1,1-Trifluoroethane (HFC-143a)	Chlorodifluoromethane (HCFC-22)	Chlorotrifluoromethane (CFC-13)
Octafluorocyclobutane (FC-C318)	Octafluorocyclopentene (FC-C1418)	Trichloromonofluoromethane (CFC-11)

The method involves collection of VFCs in evacuated six litre passivated silicon ceramic lined stainless-steel canisters, or equivalent. Gas samples are collected from a sampling manifold using evacuated canisters equipped with a critical orifice for sample flow control. Samples are collected directly from the manifold with or without a water and acid gas management system.

VFCs are identified and quantified in gas samples from the canisters by Gas Chromatograph Mass Spectrometry (GC/MS).

OTM-50 incorporates some of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and sample preparation) from other methods that are essential to conduct OTM-50, including US EPA Methods 1, 2, 3 and 4. It is applicable to for undiluted VFC samples ranging from the detection limit to approximately 1 mg/m³. Above this concentration, samples may be diluted with dry, ultra-high purity nitrogen or air.

4.4.2 Sampling requirements

Two sampling train configurations are defined by the method:

- Direct VFC sampling system; and
- VFC canister system with water/acid gas conditioning system

For stacks where the moisture content is less than 3% v/v and acid gases are not present, the Direct VFC sampling system can be used.

The Direct VFC Sampling System is configured by connecting a heated transfer probe, a heated filter, a heated transfer line, and the heated critical orifice and connecting fittings to a bypass pump. The bypass vacuum pump is used to extract and deliver a representative gaseous sample from the source through the critical orifice tee, which directs a portion of the sample gas through the critical orifice to a cleaned and evacuated canister. Excess sample gas can be vented from the bypass pump back to the stack, or vent, or treated to remove any VOCs and vented to the atmosphere.

For stacks where the moisture content is greater than 3% v/v or acid gas levels (including CO₂) are a concern e.g., for any stack involving emissions from combustion/incineration processes), an additional sampling conditioning system must be used due to moisture and CO₂ interfering with the subsequent analysis.

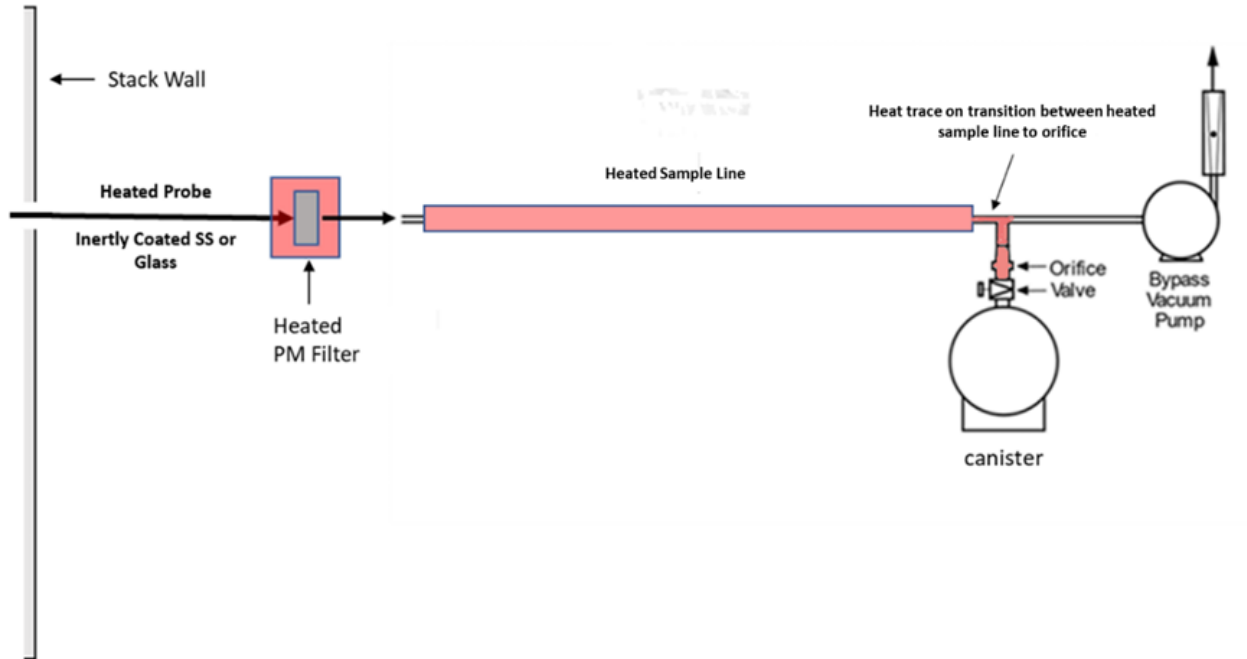
In the VFC Sampling System with Water/Acid Gas Management, a representative portion of stack gas is extracted through a heated transfer probe, a heated filter, an impinger conditioning system, an unheated transfer line and the unheated critical orifice and connecting fittings to a bypass pump. The outlet of the critical orifice directs a portion of the sample gas to a passivated canister. Excess source gas is vented from the bypass pump back to the stack or vent or treated to remove VOC and vented to the atmosphere

In both sampling systems, the heated sample probe and filter must be controllable to at least 150°C. The sample probe should include a silanised stainless steel or borosilicate glass liner, whilst the heated filter should consist of

a borosilicate glass housing and glass fibre or quartz fibre filters. In the Direct VFC Sampling System, a heated PFA sample line (controllable to $\geq 150^{\circ}\text{C}$) is used to connect the filter exit to the critical orifice tee.

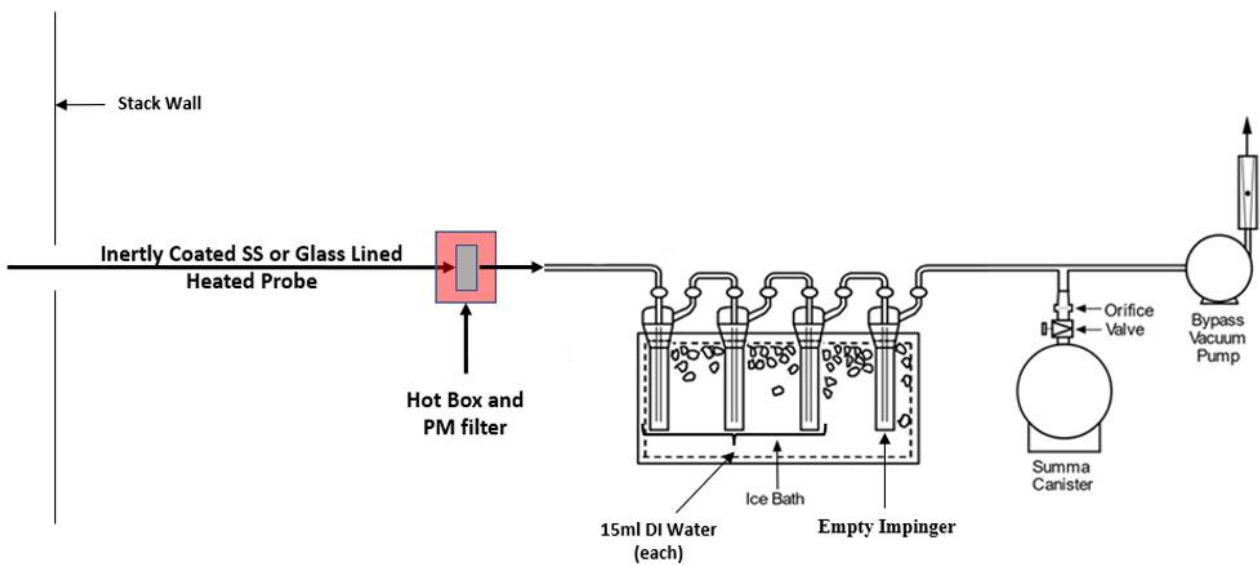
The canisters should be constructed of passivated silicon ceramic lined stainless steel or equivalent. They should be stored for no longer than 30 days before analysis.

Figure 4-2: OTM-50 direct sampling system



Source: US EPA (2025)⁷⁰

Figure 4-3: OTM-50 sampling system with water/acid gas conditioning system



Source: US EPA (2025)⁷⁰

4.4.3 Accuracy and limits of detection

Like OTM-45, data to support the method performance of OTM-50 are limited. However, research by the US EPA, including field evaluation testing⁷², has produced data to support specific performance criteria including MDLs and QRLs, calibration bias, analytical precision and standard stability. For example, the relative percent difference (RPD) for duplicate analysis of sample standards returned RPD values ranging between -6.1% to 18.2% for different compounds.

MDLs for individual compounds ranged between 0.027 and 0.271 µg/m³, whilst QRLs ranged between 0.081 and 0.813 µg/m³.

4.4.4 Limitations and constraints

OTM-50 is only suitable for the measurement of 30 specific non-polar, volatile PFAS and cannot be used for measuring polar compounds, or PFAS adsorbed to particulate matter. However, whilst a list of targeted compounds are provided in the method, OTM-50 provides some flexibility for analysis of other compounds. The laboratory may select GC columns, GC conditions, and mass spectrometry conditions different from those used to develop the method. Other VFCs may be determined by this method after completion of verification studies that include qualitative identification and subsequent validation.

Gas samples containing significant quantities of CO₂ and condensed water or water vapour can interfere with the analytical results. Water in the sample gas was found to coelute with analytes on certain chromatography columns used to evaluate the method and affected the response of those analytes. Poor or inconsistent water management during preconcentration can cause peak broadening and retention time shifts.

Acid gases and water condensed in canisters can result in corrosion of the interior surface of the canisters, resulting in reactive surfaces that compromise target compounds. CO₂ in the collected sample may coelute and/or interfere with the quantitation of target compounds in this method.

Interferences can include target analytes as well as other VOCs that coelute and may have similar mass spectra as the target analytes. If coeluting compounds have common ions, the common ions should not be used as the target's quantifying or qualifying ions.

Contamination in the sampling system and canisters may interfere if sampling equipment is not properly cleaned before use.

Other limitations/constraints of the method include:

- The requirement for a heated sample system (primarily the filter and probe components and, in the case of the direct sampling method, a heated sample line) can present potential safety concerns in some locations with hazardous area classifications.
- As an extractive technique, results are delayed due to the requirement for subsequent laboratory analysis. The method also returns an average emission concentration over the spot sample duration and it is not possible to monitoring the evolution of the emissions in real time or over a long-term, continuous period.

⁷² The specific nature and sector of this field testing is not quoted.

4.5 Emerging techniques

4.5.1 SIFT-MS

As previously described, SIFT-MS has been identified as a potential emerging technique that would allow continuous measurement of PFAS emissions to air and overcome some of the limitations associated with the extractive measurement techniques of OTM-45 and OTM-50.

SIFT-MS is a direct-analysis technique that uses soft chemical ionisation to quantify volatile PFAS or PFAS that can partition from a condensed phase to vapour in real time. Reagent ions (e.g., H_3O^+ , NO^+ , $\text{O}_2^{+\bullet}$, OH^- , $\text{O}^{-\bullet}$, $\text{O}_2^{-\bullet}$, NO_2^- , and NO_3^-) are generated from humidified or dry air using a microwave discharge. Ion lenses and a quadrupole mass filter are subsequently used to select the reagent ions according to the target compound. This provides both broad spectrum and high-specificity real-time analysis due to multiple ionisation mechanisms which can be rapidly switched.

The selected reagent ion then reacts with the target analyte in a flow tube under soft chemical ionisation conditions. Carrier gases, including helium or hydrogen, are used to cool reagent ions prior to introduction of the sample and to carry the reagent and product ions along the flow tube. A certified gas standard containing several VOCs at low ppm concentration in air or nitrogen is used to align mass-to-charge ratios (m/z) and account for the different transmission of ions through the flow tube.

The products of the reaction are then detected and quantified by a second quadrupole mass spectrometer and an electron multiplier which are used to separate ions by their m/z ratio and measure the count rates of ions in the relevant m/z range allowing real-time analysis.

SIFT-MS has been used to measure concentrations in air matrices of a range of different PFAS groups, including semi-volatile PFCAs, and volatile HFCs such as 1,1,1,2-tetrafluoroethane (HFC-134a)⁷³. Logika has had previous involvement in a study to monitor volatile PFAS in stack emissions from an industrial installation using SIFT-MS. The benefits of real-time monitoring were evident in these data which indicated a batch/cyclical nature to the emissions which otherwise would not have been identified using periodic extractive techniques. Based on these field trials, LOQs have been observed in the low ppb range, whilst information provided by the supplier indicates LODs can be in the ng/m^3 range for some compounds.

To protect damage to the analyser, gas samples need to be conditioned to remove water droplets and particulate matter. This is achieved by sampling through a heated filter and heated sample line to keep the sample gas above its dew point. This can limit SIFT-MS to volatile PFAS, or some semi-volatile PFAS that easily partition between the condensed and vapour phases. The technique is unlikely to be suitable for continuous measurements of PFAS which are adsorbed to the surfaces of particles, due to the requirement to filter particles from the gas stream presented to the analyser. Therefore, whilst suitable for obtaining measurements from industrial sources, the technique is likely limited to certain types of PFAS only.

4.5.2 OTM-55

The US EPA is currently developing and evaluating another method (OTM-55) that would address the coverage gaps of OTM-45 and OTM-50. Specifically, OTM-55 is being developed to allow the measurement of non-polar, semi-volatile and non-volatile PFAS, including FTOHs and products of incomplete combustion⁷⁴. This is expected to be based on whole canister sampling and analysis, but little has been published about this method or its performance at present.

⁷³ SYFT (undated). 'Real-time measurement of PFAS in complex matrices using negative reagent ions'
https://syft.com/public/assets/Knowledge-Centre/Syft-Technologies_PFAS-in-ambient-air.pdf

⁷⁴ US EPA, 2024. 'Using EPA's Stationary Source Measurement Methods for PFAS Air Emissions.' Northeast Waste Management Officials Association Webinar, September 25, 2024 <https://www.newmoa.org/wp-content/uploads/2024/08/JacksonAnalyticalSept2024.pdf>

4.6 Summary

Table 4-3 provides a summary of some of the key aspects of OTM-45, OTM-50 and SIFT-MS as measurement methods for PFAS emissions to air.

Table 4-3: Summary comparison of PFAS emissions to air monitoring techniques

	OTM-45	OTM-50	SIFT-MS
Measurement type	Periodic/extractive	Periodic/extractive	Continuous/real-time
Standardised method?	No (Other Technical Method)	No (Other Technical Method)	No
Scope of coverage	Polar, semi-volatile PFAS	Non-polar, volatile PFAS	Volatile PFAS i.e., similar scope as OTM-50, or semi-volatile PFAS that can easily partition to the gas phase from the condensed phase
Measurement principle	<p>Sample of stack gas is extracted isokinetically through a heated sample probe, filter and sample line. Particle-bound PFAS are collected on a heated glass wool or quartz filter following which gaseous PFAS are captured via a primary adsorbent cartridge (XAD-2), a condensation bottle, a series of impingers with absorption reagent (ultrapure water) and then a secondary adsorbent (XAD-2) cartridge to identify breakthrough. The target compounds are extracted from the individual collection media and analysed by LC-MS/MS.</p>	<p>Sample of stack gas is extracted through a heated probe and filter into a six litre passivated silicon ceramic lined stainless-steel canister(s). If the stack emission contain moisture greater than 3% v/v and or acid gases, a conditioning system comprising an ice bath and impinger train is used prior to the canister.</p> <p>The contents of the canister are then analysed in a laboratory using GC/MS.</p>	<p>Uses soft chemical ionisation to react the PFAS sample analyte with a selective reagent ion generated from humidified or dry air using a microwave discharge. Ion lenses and a quadrupole mass filter are used to select the reagent ions according to the target compound.</p> <p>The products of the reaction are then detected and quantified by a second quadrupole mass spectrometer and an electron multiplier which are used to separate ions by their m/z ratio and measure the count rates of ions in the relevant m/z range allowing real-time analysis.</p>
Typical limits of detection	Low ng/m ³ levels	Low µg/m ³ levels	Low ng/m ³ levels
Relative cost (Low = < €2k per stack; Medium = €2-4k per stack; High = > €4k per stack)	Medium	Medium	High

	OTM-45	OTM-50	SIFT-MS
Limitations/constraints	<ul style="list-style-type: none"> • Provides results for an individual spot sample. Does not support longer-term monitoring or identification of short-term trends in emissions. • Potential for sample contamination if sample handling procedures are not followed correctly. • High concentrations of other organic compounds can interfere with the analysis. • The requirement for a heated sample system (primarily the filter and probe components) can present potential safety concerns in some locations with hazardous area classifications. • Method may not be viable for very narrow diameter stacks due to the requirement for a 4" sampling socket to allow access for the sample probe and filter. • Limited number of laboratories with OTM-45 within their Schedule of Accreditation at present. 	<ul style="list-style-type: none"> • Provides results for an individual spot sample. Does not support longer-term monitoring or identification of short-term trends in emissions. • High concentrations of moisture or acid gases can interfere with the results without appropriate sample conditioning. • The requirement for a heated sample system (primarily the filter and probe components) can present potential safety concerns in some locations with hazardous area classifications. • Limited number of laboratories with OTM-50 within their Schedule of Accreditation at present. 	<ul style="list-style-type: none"> • Still considered an emerging technique with no documented monitoring standard at present, although has been used successfully to monitor stack emissions of certain PFAS compounds. • Limited number of suppliers of the instrument. • High capital costs to purchase and maintain the instrument. • Cannot be used to measure PFAS that are adsorbed to the surfaces of particles. • The requirement for a heated sample system (primarily the filter and probe components) can present potential safety concerns in some locations with hazardous area classifications.

5 Emissions to air impact assessment techniques

Key messages

PFAS exhibit complex behaviour in the atmosphere determined by the physicochemical properties of the individual compounds. This complexity, and significant variation in the properties between different groups of PFAS, complicates attempts to quantify the impact of their emissions to air.

Gaussian plume, Lagrangian models and Chemical Transport Models have all previously been used to model the transport and fate of PFAS in the atmosphere. However, the different assumptions inherent to each of these modelling approaches must be understood before deciding which model/modelling approach is best suited for the specific scope of the study.

Partitioning and chemical transformation should be considered in order to provide the most accurate representation of dispersion of PFAS emissions in air, particularly for long-range transport and/or where deposition is the primary interest. These factors can only be considered with the use of a Lagrangian model or Chemical Transport Model.

However, Gaussian plume models can be suitable for an initial screening assessment of peak PFAS concentrations in air near to an emission source where the inhalation pathway is a key factor of the assessment.

Due to the significant variation in behaviour between different PFAS compounds, any assessment of PFAS emissions to air should be at the individual compound level, rather than group level, as is often practiced for other groups of organic compounds e.g., PAHs. Whilst providing the most robust assessment, compound specific assessments are likely to increase burden and costs compared to a group-level approach.

Whilst the level of knowledge concerning the behaviour and fate of PFAS in the atmosphere is improving, application of dispersion models to this family of compounds is more limited, with many of the examples in literature focussing on emissions from fluoropolymer production, where the nature of the release and PFAS of relevance may be materially different to potential refinery emission sources.

5.1 Introduction

This section of the report provides an overview of the behaviour and fate of PFAS emitted to the atmosphere, and summarises the various factors which increase the complexity of PFAS emissions to air impact assessments compared to other common air pollutants.

Three different classes of dispersion models are reviewed to assess their suitability and applicability for supporting robust impact assessments of PFAS emissions to air accounting for this complexity. Such assessments may be required in the future to establish site-specific emission limits, or form a permit compliance assessment as a result of new guidance, such as in response to the new BAT guidance for PFAS emissions to air in Flanders⁷⁵. The three classes of dispersion models reviewed are:

- Gaussian plume models;
- Lagrangian models; and
- Chemical transport models.

⁷⁵ <https://emis.vito.be/en/article/final-report-bat-study-limiting-pfas-air-emissions-published>

5.2 Behaviour and fate of PFAS emissions to air

There are many factors that determine the fate of aerial emissions of PFAS. Furthermore, as some PFAS (although by no means all) can be persistent, mobile and/or bioaccumulate, impact pathways other than inhalation can be important considerations in the overall risk assessment framework. Factors that affect PFAS fate and transport in the atmosphere, and the wider environment after deposition of a PFAS compound from the air to soil and surface water, can be divided into two broad categories:

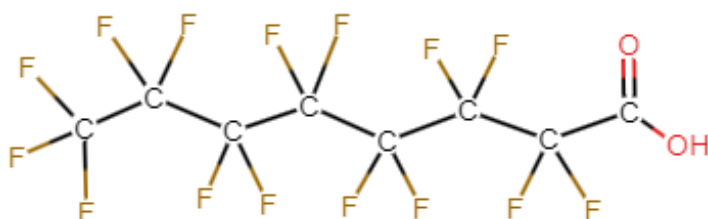
- **Individual PFAS characteristics.** Factors such as the alkyl chain length, ionic state of the compound, the type of functional group and the extent of fluorination are all important characteristics that influence the physicochemical properties of an individual PFAS compound. These properties influence the degree of partitioning between different environmental media and transformation. For example, PFAAs typically favour partitioning to particle or aqueous phases, whereas FTOHs and F-gases are generally found as vapours under environmental conditions.
- **Site characteristics.** These include factors which determine the nature of the release (e.g., where/how the emission occurs and whether the PFAS is emitted as a vapour, particle or multi-phase) and how a PFAS compound interacts with the environment. Relevant factors include release characteristics (e.g., temperature of release), prevailing atmospheric conditions, precipitation rates, soil type and depth, redox conditions, surface water flow rates etc.

Whilst the relevant impact pathways for PFAS are similar to other organic pollutants, the fate and transport of PFAS can be quite different. Furthermore, the fate and transport of compounds within the PFAS family itself exhibits significant differences due to the large number of compounds and their significant variation in physicochemical properties. The environmental fate and effects of PFAS have previously been considered in other Concawe publications²⁸. Some of the main factors that influence the fate and transport of PFAS emissions to air, and which should be considered as part of any robust assessment of the impacts of such emissions, are described below.

5.2.1 Partitioning and deposition to land

Many PFAS found in the environment typically have a non-polar “tail” comprising the main fluoroalkyl chain, and a non-fluorinated “head” consisting of a polar functional group. For example, in the case of PFOA, the tail consists entirely of a perfluoroalkyl chain containing carbon-fluorine bonds, with the head comprising a carboxylic acid functional group (Figure 5-1).

Figure 5-1: Chemical structure of PFOA



The tail is typically hydrophobic (i.e., repellent to water), whilst the head is typically hydrophilic (i.e., attracted to water)¹. As a result of these properties, many PFAS exhibit surfactant behaviour and will naturally accumulate at air-water interfaces, with the hydrophobic tail oriented toward the air and the hydrophilic functional group head

dissolved in the water⁷⁶. This behaviour has a significant influence on aerosol-based transport and, in particular, deposition due to PFAS dynamically partitioning between the vapour and aerosol phases⁷⁷.

Important factors which determine the degree of partitioning between the vapour and aerosol phase include the compound specific vapour pressure, solubility and Henry's law constant (a factor that links the solubility of a gas in a particular solvent e.g., water with the partial pressure of the gas in equilibrium with the solvent). Additionally, volatilisation from water to air of acidic PFAS, such as PFAAs, appears to be pH-dependent⁷⁸. For some PFAAs, such as PFOA, which are acidic at environmentally relevant pH, the vapour pressure is low and solubility in water high, which limits volatilisation from aerosols to air. However, other PFAS, such as fluorotelomer alcohols (FTOHs), have functional groups that tend to increase volatility. Consequently, it is more likely that compounds such as PFAAs will be present in the atmosphere as an aerosol or adsorbed to the surface of particles, whereas compounds such as FTOHs are more likely to be found in the vapour phase^{79,80}. In general, results from ambient monitoring surveys also suggest that partitioning from the vapour phase to aerosol/particle phase is more favourable with increasing alkyl chain length and decreasing temperature⁸¹.

Dependent on the release conditions and physicochemical properties of the individual compounds, PFAS may be emitted to the atmosphere from an industrial process in different phases:

- Vapour
- Aerosol (dissolved within water droplets)
- Solid particles (adsorbed to the surface as particulate matter)

It is also possible for the release to be multi-phase, with compounds emitted simultaneously in all three phases, particularly where processes involve the application of heat. Once emitted to the atmosphere, the compounds may then further dynamically partition between the different phases.

This dynamic partitioning can have a significant influence on the atmospheric concentration of a PFAS compound, as well as its deposition to the surface. Deposition of PFAS can occur by either dry deposition or wet deposition and acts as a sink from the atmosphere⁸². Dry deposition occurs when PFAS compounds in the atmosphere are brought to the surface by gravitational settling, turbulence and diffusion, whilst wet deposition occurs due to rainout scavenging (within clouds) and washout scavenging (below clouds) of atmospheric PFAS.

Wet and dry deposition are the major mechanisms of removal of PFAS from the atmosphere and can occur from the scavenging of particle-bound PFAS or partitioning of gaseous PFAS to water droplets (aerosols). Dry deposition naturally favours PFAS typically associated with liquid or particle phases in air (aerosols) since the greater mass of the aerosol particle compared to vapour phase PFAS introduces an additional gravitational

⁷⁶ Kraft, M.P. and Riess, J.G. (2015). 'Selected physicochemical aspects of poly- and perfluoroalkylated substances relevant to performance, environment and sustainability — Part one' *Chemosphere*, 129, 4-19.

⁷⁷ Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H. (2006). 'Sources, fate and transport of perfluorocarboxylates.' *Environmental Science & Technology*, 40, 32-44

⁷⁸ Kaiser, M.A., Dawson, B., Barton, C., Botelho, M. (2010). 'Understanding Potential Exposure Sources of Perfluorinated Carboxylic Acids in the Workplace.' *The Annals of Occupational Hygiene* 54, 915-22

⁷⁹ Dreyer, A., Weinberg, I., Temme, C., Ebinghuas., R. (2009). 'Polyfluorinated compounds in the atmosphere of the atlantic and southern oceans: evidence for a global distribution' *Environmental Science & Technology*, 43, 6507-6514

⁸⁰ Dreyer, A., Kirchgeorg, T., Weinberg, I., Matthias, V. (2015). 'Particle-size distribution of airborne poly- and perfluorinated alkyl substances.' *Chemosphere*, 129, 142-149

⁸¹ Bossi, R. and Ellermann, T. (2003). 'Per- and polyfluoroalkyl substances (PFAS) in atmosphere and deposition.' DCE - Danish Centre for Environment and Energy - Scientific briefing No. 2023 | 20

⁸² Barton, C.A., Kaiser, A.M., Russell, M.H. (2007). 'Partitioning and removal of perfluorooctanoate during rain events: the importance of physical-chemical properties.' *Journal of Environmental Monitoring*, 9, 839-846

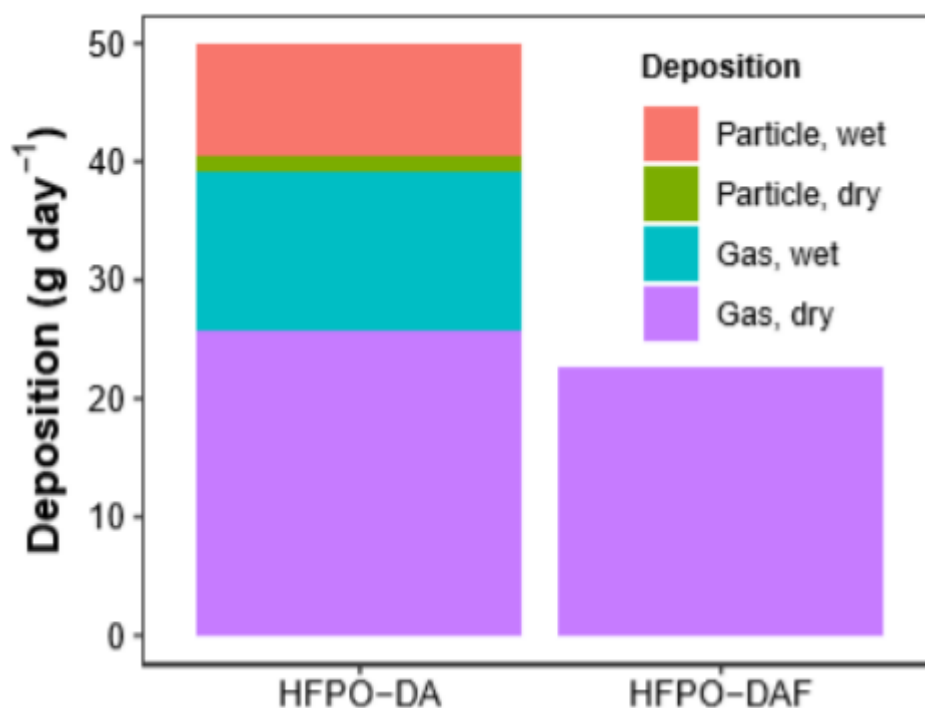
settling component which is not present for vapours. Additionally, scavenging is more effective at removing compounds already present in an aerosol or particle phase than vapour.

For example, Figure 5-2 presents the modelled deposition rates of two structurally similar PFAS, hexafluoropropylene oxide dimer acid (HFPO-DA) and hexafluoropropylene oxide dimer acid fluoride (HFPO-DAF), but which exhibit significantly different behaviour in the atmosphere and which, consequently, affects their associated deposition.

HFPO-DA is semi-volatile with a (comparably) low vapour pressure, so it preferentially favours partitioning to the aerosol phase. HFPO-DAF is volatile with a (comparably) high vapour pressure, so preferentially favours partitioning to the vapour phase. The predicted deposition rate of HFPO-DA (for the same mass release) is significantly increased compared to HFPO-DAF due to a combination of enhanced dry deposition, but also from the additional contribution from wet deposition that is not evident for HFPO-DAF in the vapour phase.

Consequently, as a PFAS compound undergoes dynamic partitioning in the atmosphere from its initial release phase, the rate of deposition and, therefore, the deposition footprint will change. As a result, deposition will be more affected by PFAS that exhibit appreciable partitioning behaviour under typical environmental conditions than those PFAS groups that do not.

Figure 5-2: Predicted deposition rates of two structurally similar PFAS but which are preferentially found in the atmosphere as a vapour (HFPO-DAF) and as an aerosol/particle (HFPO-DA)



Source: D'Ambro et al. (2020)

https://www.cmascenter.org/conference/2020/slides/D_AmbroMurphy_CMAQPFAS_CMAS2020.pdf

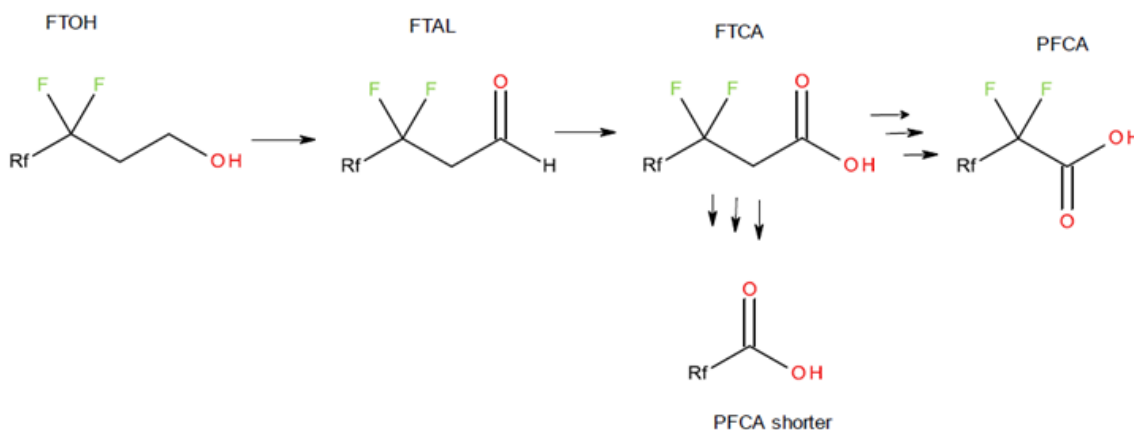
5.2.2 Transformation

Although chemical stability is inherent to most PFAS groups, especially the perfluorinated compounds, other PFAS, including polyfluorinated substances, are more susceptible to atmospheric transformation. This is a consequence of the other types of bond present on the alkyl chain of these compounds e.g., a carbon-hydrogen bond, which can allow transformation through abiotic and biotic processes.

Transformation of polyfluorinated substances through biotic and abiotic degradation has been demonstrated under laboratory conditions, but a number of recent field studies have also demonstrated the importance of these transformation pathways⁸³. Polyfluorinated substances that transform are often referred to as precursors and will typically transform to more chemically stable PFAAs.

For example, FTOHs will typically transform to their associated perfluorocarboxylic acid (PFCA) e.g., 8:2 FTOH is a precursor to PFOA, with transformation taking place in a series of steps, initially to a fluorotelomer aldehyde (FTAL), then a fluorotelomer carboxylic acid (FTCA), and finally to a PFCA. Figure 5-3 presents a generalised transformation pathway for a FTOH.

Figure 5-3: Generalised transformation pathway for a FTOH to a PFCA



Potential transformation mechanisms for certain PFAS groups, such as FTOHs, in the atmosphere include:

- Photolysis;
- Hydrolysis; and
- Oxidation by hydroxyl and chlorine radicals.

Although direct photolysis of PFAS has not been observed, indirect photolysis of some precursors has been cited as a significant contributor to deposition of PFCAs⁸⁴.

Acyl fluorides have been shown to undergo hydrolysis in the atmosphere to carboxylic acids⁸⁵ which can dramatically affect their solubility. As evidenced in Section 5.2.1, in the case of the hydrolysis of HPFO-DA to HPFO-DAF, this can have important implications for subsequent deposition of this group of compounds⁸⁶.

⁸³ Dassuncao, C., Hu, C.X., Zhang, X., Bossi, R., Dam, M., Mikkelsen., B., Sunderland, E.M. (2017). 'Temporal shifts in poly- and perfluoroalkyl substances (PFASs) in North Atlantic pilot whales indicate large contribution of atmospheric precursors.' *Environmental Science & Technology*, 51, 4512-4521

⁸⁴ Armitage, J.M., MacLeod, M., Cousins, I.T. (2009). 'Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model.' *Environmental Science & Technology* 43 (4):1134-1140

⁸⁵ Bunton, C.A., Fendler, J.H. (1966). 'The Hydrolysis of Acetyl Fluoride.' *The Journal of Organic Chemistry*, 31, 2307-2312

⁸⁶ D'Ambro, E.L., Pye, H.O.T., Bash, J.O., Bowyer, J., Allen, C., Efstathiou., C., Gilliam, R.C., Reynolds, L., Talgo, K. and Murphy, B.N., 2021. 'Characterizing the Air Emissions, Transport, and Deposition of Per- and Polyfluoroalkyl Substances from a Fluoropolymer Manufacturing Facility.' *Environmental Science and Technology* 55, 862-870

Hydroxyl and chlorine radicals have been shown to degrade 8:2 FTOH to PFOA in the atmosphere, with similar reactions for 6:2 FTOH and 4:2 FTOH⁸⁷, and for perfluoroalkyl sulfonamides, which may degrade to PFCAs and perfluorosulfonic acids (PFSA)s⁸⁸. Other semi-volatile precursors may also undergo atmospheric transformation to PFCAs⁸⁹.

As demonstrated by Figure 5-3, atmospheric transformation of PFCa precursors takes place in different steps. The ultimate yield of PFCAs is determined by several factors, one of which is the ratio of oxides of nitrogen (NO_x) and peroxy radicals (HO₂ and RO₂)⁸⁹ which affects the availability of hydroxyl radicals. High concentrations of NO_x results in lower production of long chain PFCAs, meaning transformation is typically enhanced in more rural areas. Theoretical yields for the formation of PFOA from 8:2 FTOH have been predicted to range between less than 1% to 40% dependent on local conditions⁹⁰.

In some industrial processes, it is common to find PFCa and PFSA precursors emitted alongside PFCAs and PFSA. In these scenarios, when determining the overall fate and impacts of a PFCa or PFSA, it is also necessary to give due consideration to the subsequent transformation of the precursor.

5.2.3 Transportation

The atmosphere serves as an important transport mechanism for PFAS, allowing PFAS to disperse with the prevailing wind conditions. Short range atmospheric transport and deposition can result in PFAS being observed in soils and surface water in the vicinity of significant emission sources of PFAS as a result of deposition⁹¹. These compounds may then migrate downwards from the surface soil layer into groundwater via leaching.

However, due to the unique physicochemical properties of PFAS, including, for many compounds, low reactivity, potential exposure to PFAS is not just limited to just short-range transport, with long-range transport also playing an important role. For example, researchers from the US EPA predicted that less than 5% of the total mass of PFAS emitted from a fluoropolymer manufacturing site in North Carolina was deposited within 150 km of the facility, with the majority of the mass emitted being transported beyond 150 km⁸⁶.

The long-range transportation potential for PFAS is further evidenced by the detection of PFAS in surface snow, ice cores and seawater in far remote regions such as the Arctic and Antarctic. Atmospheric transport has been estimated to account for between 34 – 59% of PFOA measured in the polar mixed layer of the Arctic Ocean⁹².

The atmosphere itself does not provide local, long-term accumulation of PFAS. However, it acts as a medium for long-range transport and accumulation through other environmental media e.g., soils and water bodies as a result of deposition from the atmosphere. However, exposure through direct inhalation remains a relevant pathway.

⁸⁷ Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Andersen, M.P.S., Wallington, T.J. (2004) 'Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids.' *Environmental Science & Technology*, 38, 3316-3321

⁸⁸ Martin, J.W., Ellis, D.A., Mabury, S.A., Hurley, M.D., Wallington, T.J. (2006). 'Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of n-ethyl perfluorobutanesulfonamide' *Environmental Science & Technology*, 40, 864-872

⁸⁹ Young, C.J. and Mabury, S.A. (2010). 'Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts.' *Reviews of Environmental Contamination and Toxicology*, 208, 1-109

⁹⁰ Thackray, C. and Selin, N. (2017). 'Uncertainty and variability in atmospheric formation of PFCAs from fluorotelomer precursors.' *Atmospheric Chemistry and Physics*, 17, 4585-4597

⁹¹ Davis, K.L., Aucoin, M.D., Larsen, B.S., Kaiser, M.A., Hartten, A.S. (2007). 'Transport of ammonium perfluorooctanoate in environmental media near a fluoropolymer manufacturing facility.' *Chemosphere*, 67, 2011-2019

⁹² Yeung, L.W.Y., Dassuncao, C., Mabury, S., Sunderland, E.M., Zhang, X., Lohmann, R. (2017). 'Vertical profiles, sources, and transport of PFASs in the Arctic Ocean.' *Environmental Science & Technology*, 51, 6735-6744

5.2.4 Uptake into plants and other biota

Once released to the atmosphere, PFAS will deposit to the surface of soils, vegetation and surface water through dry and wet deposition. Subsequent uptake into plants, and consumption of drinking water exposed to PFAS deposition from the air, may transfer PFAS to other fauna that consume those plants, and in the additional case of humans, from consumption of meat products derived from animals consuming plant matter containing PFAS. As some PFAS have the potential to bioaccumulate, this can result in accumulation of PFAS further up the food chain.

As some PFAS contain a hydrophilic functional group, plants can be expected to take some of these compounds up through their root systems, after which they would be transported through the internal plant structure to stems, shoots, leaves, and fruits.

PFAS uptake by plants is influenced by the physicochemical properties of the individual compound (e.g., alkyl chain length, head group functionality, water solubility, and volatility), plant physiology (e.g., transpiration rate, lipid and protein content), and abiotic factors (e.g., soil organic matter, pH, salinity, and temperature). Compounds with higher solubility in water with lower soil/air-water interface retention affinity are often observed to have greater uptake potential⁹³.

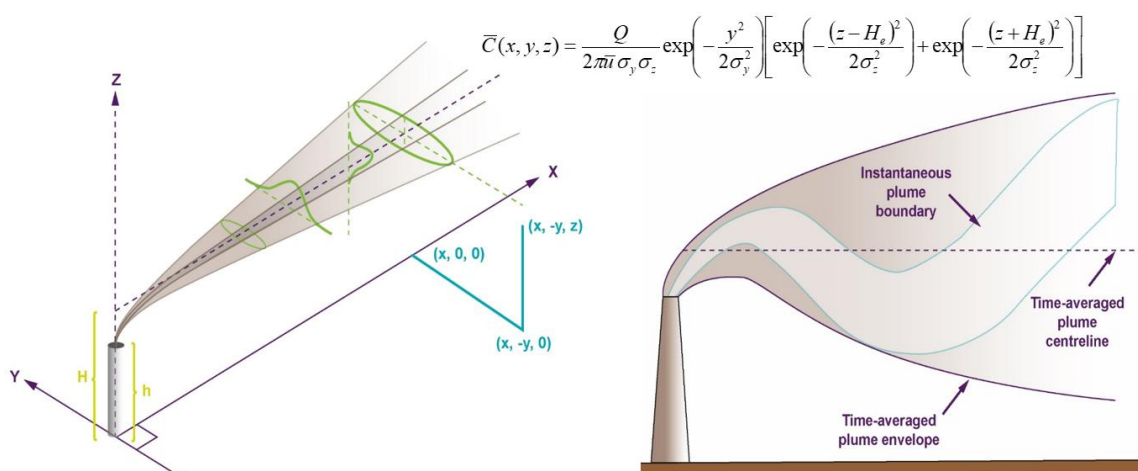
5.3 Review of dispersion model types for PFAS impact assessments

5.3.1 Gaussian plume models

The use of a Gaussian distribution for modelling the dispersion of atmospheric pollutants has been advocated as early as the mid-1940's and was subsequently advanced and refined through field studies in the 1960s. More recent examples of regulatory approved models for assessing the impacts of industrial emissions to air include ADMS and AERMOD.

The Gaussian approach assumes that the dispersion of pollutants in the horizontal and vertical directions accords to a normal distribution, and dictates that the maximum concentration occurs along the plume centreline and decreases with increasing distance from the plume centreline. The Gaussian, or normal distribution, is described in Figure 5-4 in terms of its application to atmospheric dispersion.

Figure 5-4: Gaussian distribution applied to atmospheric dispersion



Source: Logika

⁹³ Wang, W., Rhodes, G., Ge, J., Yu, X., Li, H. (2020). 'Uptake and accumulation of per- and polyfluoroalkyl substances in plants.' Chemosphere 261, 127584

In order to model atmospheric dispersion using standard Gaussian methods, the following assumptions and limitations have to be made:

- **Conservation of mass** – the entire mass of emitted pollutant remains in the atmosphere and no allowance is made for loss due to chemical reactions or deposition processes (although the standard Gaussian model can be modified to include such processes). Portions of the plume reaching the ground are assumed to be dispersed back away from the ground by turbulent eddies (eddy reflection).
- **Steady state emissions** – emission rates are assumed to be constant and continuous over the time averaging period of interest. This is unlikely to be the case for the majority of industrial sources where volume flows, and hence mass emission rates, can vary over short time periods.
- **Steady state meteorology** – no variation in wind speed, direction or turbulent profiles occur during transport from the source to the receptor. This assumption is reasonable within a few kilometres of a source but may not be valid for receptor distances in the order of tens of kilometres. For example, for a receptor 50 km from a source and with a wind speed of 5 m/s, it will take nearly three hours for the plume to travel this distance during which time many different processes may change (e.g., the sun may rise or set and clouds may form or dissipate affecting the turbulent profiles). For this reason, Gaussian models are practically limited to predicting concentrations within ~ 20 km of a source.

The assumptions of conservation of mass and steady state meteorology do limit the applicability of Gaussian plume models for robust assessments of PFAS emissions to air. Whilst basic chemistry schemes have been incorporated into models such as ADMS and AERMOD to account for photochemical reactions involving oxides of nitrogen and ozone, and, in the case of ADMS, for reactions involving amines, such reaction schemes are basic and unlikely to be able to account for the complex nature of PFAS transformation.

The models do not allow for dynamic partitioning and, as a result, any deposition output when applied to PFAS emissions to air modelling would be associated with increased uncertainty compared to other compounds. Attempts could be made to overcome this limitation by running two separate versions of the model and forcing all PFAS into the vapour phase in one, and forcing all PFAS into the particle phase in another. The results could then be compared and the maximum deposition rate from either model run taken forward for further assessment. This approach would allow a “worst-case” assessment of deposition rates at any location in the model domain to be made, but will not be appropriate for identifying the “true” location of peak areas of deposition, or a more realistic deposition estimate at a specific receptor location.

Furthermore, as these models are generally limited to predictions within 20 km of an emission source, they would not be suitable for accounting for the long-range transport potential of PFAS. As identified in Section 5.2.3, previous research has suggested that most of the mass of PFAS released from an emission source would be expected to be transported beyond 150 km.

However, that is not to say that Gaussian plume models do not have a role to play in PFAS emissions to air impact assessments. These types of models are computationally efficient, and allow consideration of multiple years of meteorological data with run times in the orders of hours.

Their main use is likely to be found as a screening model where the key areas of interest are peak concentrations/deposition in the vicinity of an emission source and where the inhalation pathway is the primary concern. Whilst most of the PFAS mass released would be expected to be transported beyond 150 km, the same research that identified this finding also demonstrated that peak ambient concentrations and deposition rates would be expected to occur within the first few kilometres.

Gaussian plume models have previously been used to predict fence-line concentrations of PFOA at an industrial facility in North America and these modelled concentrations were compared to monitored ambient

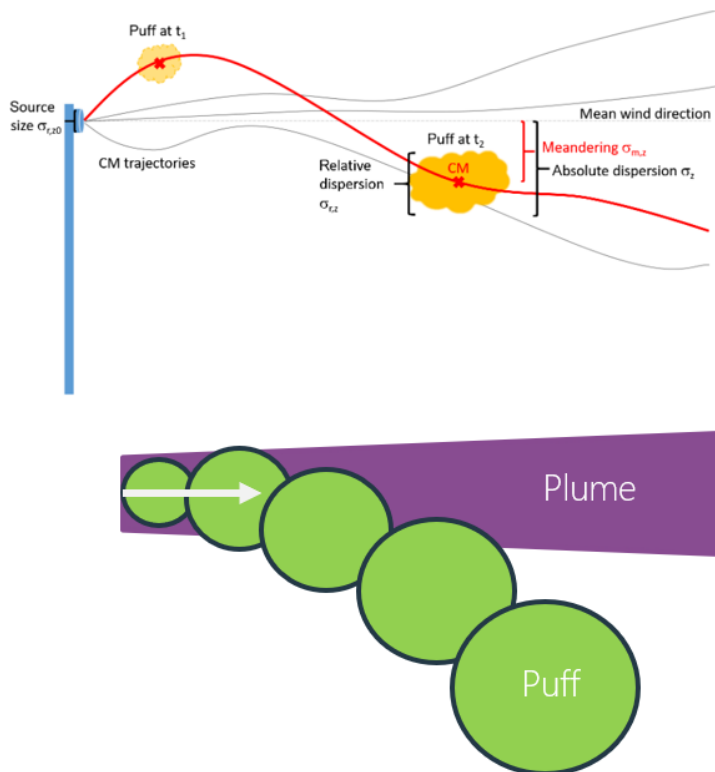
concentrations to validate the model⁹⁴. At the six monitoring locations where PFOA was above the detection limit of the monitoring method, the model was found to systematically overpredict monitored concentration by a factor ranging between 1.5 and 23.9. This demonstrates that such models may be suitable for initial screening assessments where a conservative estimate of peak concentrations in air is required.

5.3.2 Lagrangian models

Lagrangian models mathematically follow the pollution plume ‘parcels’ (also referred to as particles) as the parcels move in the atmosphere by adopting a random walk process. The model then calculates the dispersion of pollutants by computing the statistics of a large number of pollution plume parcels. This approach uses a moving frame of reference as the parcels move from their initial position. By following these parcels, these type of models can capture complex atmospheric transport processes, including meandering plumes and diffusion, providing detailed information on concentration fields, especially in the near-field of a source but also at large distances from a source (up to hundreds of kilometres). These types of models are also known as puff models, and include examples such as CALPUFF, SCIPUFF, AUSTAL and FLEXPART.

Unlike Gaussian plume models which assume steady state meteorological conditions, Lagrangian models are non-steady state and allow consideration of varying meteorological conditions between an emission source and a receptor both spatially and temporally. These models also retain “memory” of the plume parcels in time, rather than considering individual meteorological hours as discrete packages of information. Figure 5-5 provides a schematic of the Lagrangian principles applied to dispersion modelling, and its key difference between a Gaussian plume model.

Figure 5-5: Lagrangian dispersion model principles and illustrative comparison to Gaussian plume model



⁹⁴ Barton, C.A., Butler, C.E., Zarzecki, C.J., Flaherty, J., Kaiser, M., 2012. ‘Characterizing Perfluorooctanoate in Ambient Air near the Fence Line of a Manufacturing Facility: Comparing Modeled and Monitored Values.’ Journal of the Air & Waste Management Association, 56, 48-55

Some Lagrangian models do allow for basic chemical transformation. FLEXPART, for instance, includes a chemistry module that allows linear reactions with hydroxyl radicals but cannot account for non-linear reactions. At this time, there does not appear to be the capability for accounting for PFAS transformations specifically, although some studies applying Lagrangian dispersion models for PFAS emissions have allowed for consideration of partitioning.

For example, Lagrangian dispersion models have recently been applied in assessments which aimed to understand the regional transport of PFAS emitted from a fluoropolymer production plant in the Netherlands⁹⁵. The study considered the occurrence of HFPO-DA and other PFAS in airborne PM₁₀ and included a combination of ambient monitoring and predictive modelling using FLEXPART. Lagrangian dispersion modelling using FLEXPART revealed good agreement between measured and modelled HFPO-DA concentrations (Pearson's $r = 0.83$, $p \leq 0.05$, Wilmott's $d = 0.71$, mean absolute error = 3.66 pg m^{-3}) and also suggested that HFPO-DA could undergo long-range atmospheric transport with detectable HFPO-DA air concentrations predicted up to several thousand kilometres away including London, Hamburg and Reykjavik.

The model was found to slightly underestimate peak concentrations at the monitoring site, which the study authors concluded was a result of using simplified emission estimates and assuming constant emission rates throughout the sampling period.

Lagrangian dispersion models are most likely to be suitable for assessing the long-range impacts of PFAS that do not readily partition after release and which undergo limited transformation in the atmosphere. They are a more complex technique than Gaussian plume models, with resulting additional computational costs. They are, however, less complex and more computationally efficient than Chemical Transport Models (CTM) which are reviewed in the next section.

5.3.3 Chemical transport models

CTMs typically adopt an Eulerian-based modelling approach. Like the Lagrangian approach, these models follow a large number of parcels but, unlike the Lagrangian approach, the Eulerian approach adopts a fixed, rather than moving, frame of reference. These models aim to numerically solve the fundamental 3-dimensional mass conservation equation described in summary form overleaf and include highly detailed chemical reaction schemes and deposition calculations. CTMs include models such as CMAQ, CAMx, EMEP and WRF-Chem.

$$\frac{\partial C}{\partial t} = -\underline{u}\nabla C + K\nabla^2 C + R + E - D$$

Change of concentration with time	Advection	Turbulence	Chemical reactions	Emission and deposition
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CTMs use spatially and temporally varying meteorological outputs from a Numerical Weather Prediction (NWP) model to predict the dispersion from emission sources at local, regional and global scales. The detailed chemical mechanisms in CTM models contain hundreds of species and thousands of reactions, describing how pollutants transform in the atmosphere to form ozone, particulate matter, and other substances as they are transported from an emission source. The chemistry schemes address gas-phase chemistry, aerosol chemistry and multi-phase processes.

⁹⁵ Dalmijn, J., Shafer, J.J., Benskin, J.P., Salter, M.E., Johansson, J.H., Cousins, I.T., 2025. 'HFPO-DA and Other PFAS in Air Downwind of a Fluoropolymer Production Plant in the Netherlands: Measurements and Modeling.' *Environmental Science & Technology*, 59, 8662-8672

This level of detail does, however, come at a cost. CTMs are the most complex model type in terms of input requirements and are also the most computationally expensive. Unless run on high performance computers, run times in the orders of magnitudes of days or weeks are not uncommon.

Researchers at the US EPA have developed a branched version of the CMAQ model specifically for PFAS emissions to air impact assessments. This model, CMAQ-PFAS, contains a database of 26 PFAS species⁹⁶ and their associated physico-chemical properties, and an updated deposition module to account for the dynamic partitioning of these compounds. Model users can also enter user-defined PFAS if the associated physico-chemical properties are known, or use the model's lumped "PFAS other" category.

CMAQ-PFAS has been used to simulate the release and fate of PFAS emissions to air from a fluoropolymer manufacturer in North Carolina⁸⁶ to make predictions for ambient concentrations in air and deposition rates over an approximately 300 km x 300 km spatial domain at a resolution of 1 x 1 km. Emissions and dispersion over a full calendar year were considered. Deposition predictions were compared to monitored deposition rates with good agreement between the two datasets. Total PFAS concentrations in air and deposition rates at detectable levels were predicted at all locations across the model domain, with peak concentrations and deposition rates occurring in the near vicinity of the site

As previously described, inclusion of chemistry and dynamic partitioning is vital for capturing the correct atmospheric behaviour of PFAS. Modelled PFAS-specific physico-chemical properties are utilised by CMAQ-PFAS to simulate the dynamic partitioning of species to surfaces, particulate matter, and cloud droplets. To date, oxidative chemistry has not been included in the model capability, but will be developed as part of a future update.

5.3.4 Summary

Gaussian plume, Lagrangian models and CTMs have all previously been used to model the transport and fate of PFAS in the atmosphere but the number of studies is limited at the present time reflecting that the potential relevance of the aerial emissions pathway as a component of the overall risk assessment framework is still an emerging issue. The different assumptions inherent to each of these modelling approaches must be understood before deciding which model/modelling approach is best suited for the specific scope of the study.

Partitioning and chemical transformation should be considered in order to provide the most accurate representation of dispersion of PFAS emissions in air, particularly for long-range transport and/or where deposition is the primary interest.

Gaussian plume models benefit from fast run times and relative simplicity. Whilst they can, and have, been used for modelling PFAS emissions to air, the most appropriate use would be as an initial screening tool to determine the potential peak short range concentration of PFAS near to an emission source when the inhalation pathway is the primary focus. They are not typically complex enough to sufficiently represent the dynamic partitioning and transformation behaviour of most PFAS, so would have a greater associated uncertainty in making deposition rate predictions at specific receptors. They cannot be used to make predictions of long range transport and are generally limited to predictions within 20 km of an emission source.

At the other end of the complexity scale, CTMs are the most complex and computationally expensive modelling technique but are sufficiently resolved to account for the unique behaviour of PFAS in the atmosphere. The US EPA has released a CTM specifically to support PFAS emissions to air impact assessments which accounts for dynamic partitioning and which will also be subject to further updates to account for oxidative transformation. CTMs are/will consequently be a useful tool for assessment of PFAAs where the PFAA in question is emitted along with a precursor compound, such as an FTOH.

⁹⁶ These are linked to the specific types of PFAS emitted from the fluoropolymer manufacturing site which was considered in the development of the method, rather than the 26 specific PFAS compounds included in the US EPA's Drinking Water Treatability Database.

In between Gaussian plume models and CTMs in terms of complexity, Lagrangian dispersion models allow for consideration of long-range transport and their basic chemistry schemes may allow better simulation of dynamic partitioning and transformation than a Gaussian plume model, therefore making them more suitable for deposition predictions. They are likely to be the preferred method of choice for long-range transport where consideration of precursor transformation is not a key component of the assessment requirements.

As previously described earlier in this report, due to the variability in physical, chemical and toxicological properties of individual PFAS compounds, impact assessments of PFAS emissions to air should be completed on a substance-specific basis rather than as a single group using a proxy compound.

Table 5-1 summarises the key properties, benefits and limitations of the three modelling approaches reviewed. As a general note, whilst the level of knowledge of the behaviour and fate of PFAS in the atmosphere is improving, application of dispersion models to this family of compounds is more limited, with many of the examples in literature focussing on emissions from fluoropolymer production, where the nature of the release and PFAS of relevance may be materially different to potential refinery emission sources.

Table 5-1: Summary comparison of PFAS emissions impact assessment techniques

	Gaussian plume model	Lagrangian model	CTM
Model example	ADMS, AERMOD	CALPUFF, AUSTAL, FLEXPART	CMAQ-PFAS, CAMx, EMEP, WRF-Chem
Range of applicability from an emission source	< 20 km	Local, regional or global scale	Local, regional or global scale
Accounts for dynamic partitioning	No	Some basic functionality	Yes
Allows for chemical transformation	No	Some basic functionality	Yes
Complexity of input requirements	Low	Medium	High
Relative computational cost	Low	Medium	High
Benefits	<ul style="list-style-type: none"> • Computationally efficient • Allows consideration of multiple emission scenarios in a matter of hours/days • Most widely used modelling approach and generally accepted by regulators 	<ul style="list-style-type: none"> • Can account for long-range transport • Less complex and computationally expensive than CTMs 	<ul style="list-style-type: none"> • Most robust modelling tool for parameterising dynamic partitioning and transformation • Branched versions of CTMs are available that specifically account for PFAS emissions
Limitations	<ul style="list-style-type: none"> • Only suitable for short-range transport • No consideration of dynamic partitioning or transformation restricts their application for deposition predictions 	<ul style="list-style-type: none"> • Dynamic partitioning and chemical transformation treatment likely to be less complex than CTMs 	<ul style="list-style-type: none"> • Most complex and computationally expensive method with long run times

6 Conclusions

This report presents the outcomes of a literature review of PFAS use and potential associated emissions to air in the refining sector. Consistent with other research, the literature review suggests PFAS compounds are used in a variety of materials which may support refining processes. The available evidence suggests these are mainly fluoropolymers, which are typically considered to be of low concern from an environmental and human health perspective, but some examples of non-polymeric use are referenced. However, the limited amount of information available on non-polymer use restricts the robustness of this analysis.

The available research suggests non-polymeric PFAS may be used in a smaller number of use cases, including as additives or raw materials within the refining process itself e.g., in the alkylation process. However, broad usage categories are often referred to in the literature e.g., “used in the manufacture of coke and refined products” and there remains uncertainty as to exactly where and how non-polymeric PFAS are used in these processes.

Whilst several categories of use have been identified, information on usage quantities is more limited and, where estimates are provided, these are typically global in nature and/or generally not specific to the refining sector. Information on resultant emissions to air is even more limited and not sufficient to understand the scale and importance of this pathway for the sector. Potential release mechanisms have, however, been identified which, although applicable across multiple sectors, are nonetheless also of potential relevance to the refining sector. These include, for example, point source emissions resulting from thermolysis of fluoropolymers used in high temperature process equipment, and fugitive emissions from the use of firefighting foams and aerosolisation in wastewater treatment plants.

Whilst such mechanisms are considered plausible, there is currently no data to either confirm or discount these emissions in a specific refining context and this remains a significant data gap. However, based on information supplied, and sectors covered, as part of the European Chemicals Agency’s proposed “universal” PFAS restriction and, in particular, based on data in the background document, it is anticipated that use and emissions of non-polymeric PFAS from the refining sector would be insignificant in comparison to other sectors. An initial monitoring campaign of emissions sources at a proxy or representative number of refineries may be one method to conclusively determine whether PFAS are/are not being emitted to air from refinery activities.

The study has reviewed the available measurement and modelling techniques to support PFAS emissions to air impact assessments. Whilst there is no harmonised international standard for PFAS stack emissions monitoring, other test methods have been introduced in the last five years such as OTM-45 and OTM-50 and unvalidated methods have been used in some sectors for more than 20 years. Emerging techniques are also available to allow real-time/continuous measurement of PFAS emissions from stacks.

Gaussian plume, Lagrangian models and chemical transport models have all previously been used to model the transport and fate of PFAS in the atmosphere, but most of these studies have been applied to emission sources relevant to fluoropolymer manufacturing and not refinery emission sources. The different assumptions inherent to each of these modelling approaches must be understood before deciding which model/modelling approach is best suited for the specific scope of a study. Gaussian plume models are only likely to be suitable as an initial screening tool for establishing conservative estimates of peak PFAS concentrations in air. Chemical transport models provide the most representative parameterisation of dynamic partitioning and chemical transformation of PFAS in the atmosphere, but are complex and computationally expensive. However, a specific chemical transport model has been developed to support PFAS emissions to air impact assessments (CMAQ-PFAS).



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