Air Quality Consultants | Part of Logika Group

The complexities of modelling PFAS emissions to air and the potential role of CTMs

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Overview

- What are PFAS?
- Why are they considered an environmental risk?
- Complexity of assessing the impacts of PFAS emissions to air
- Case study – results of an initial screening assessment
- The role of Chemical Transformation Models in PFAS impact assessments

What are PFAS?

What are PFAS?

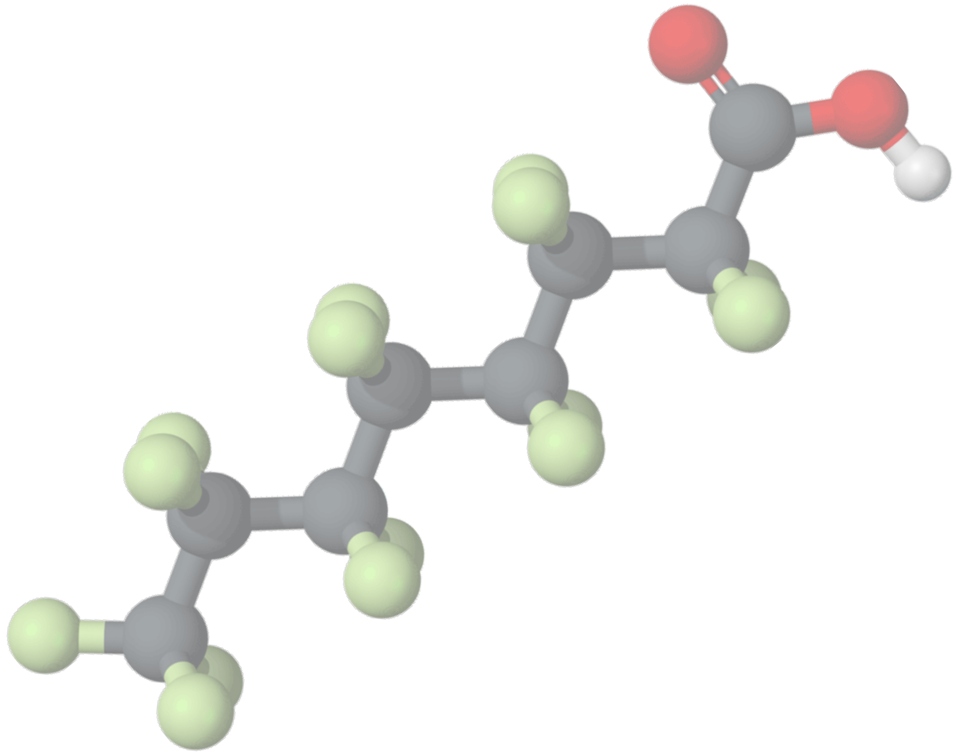
- Generic term used to represent a large family of synthetic organic compounds containing fluorine

- OECD definition:

"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 ($–CF_3$) or a perfluorinated methylene group ($–CF_2–$) is a PFAS"

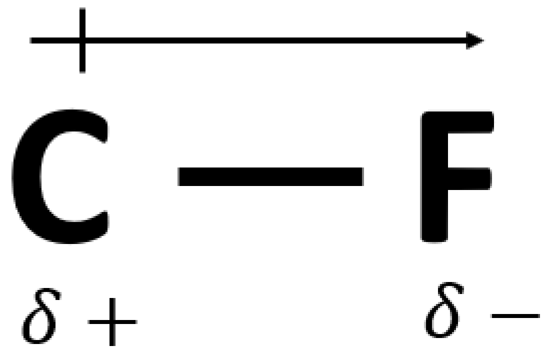
- UK definition (from HSE RMOA):

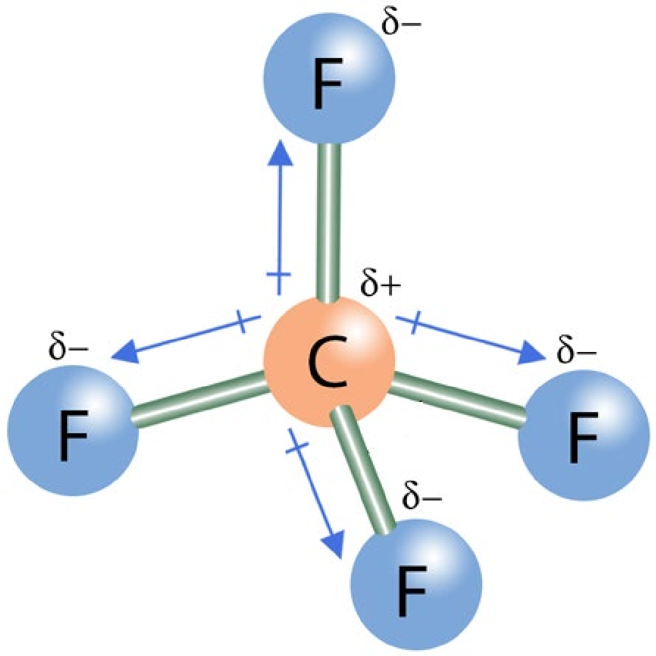
"…fluorinated substances that contain at least one fully fluorinated methyl carbon atom (without any hydrogen, chlorine, bromine or iodine atom attached to it), or two or more contiguous perfluorinated methylene groups ($–CF_2–$)."



The carbon-fluorine bond

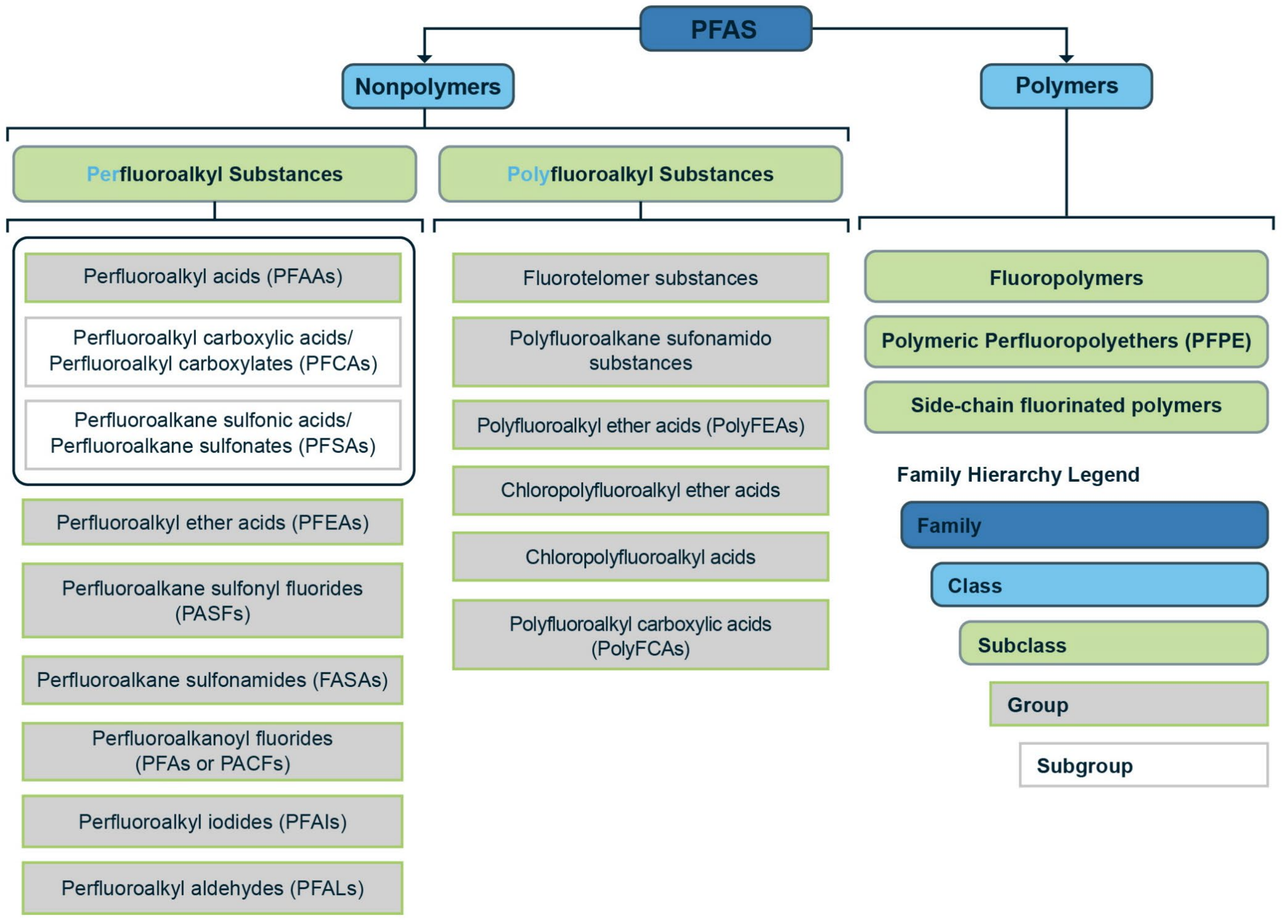
- Fluorine is the most electronegative element.
- When forming a covalent bond with carbon, significant polarity is formed providing partial ionic character.
- As a result, the carbon-fluorine bond is the strongest bond in organic chemistry, and one of the strongest single bonds in chemistry overall.
- The strength of the bond increases as more fluorine atoms are added to the same carbon atom and when there are multiple carbon-fluorine bonds on the same skeletal carbon-carbon structure.
- Carbon-fluorine bonds also strengthen the carbon-carbon bond itself.





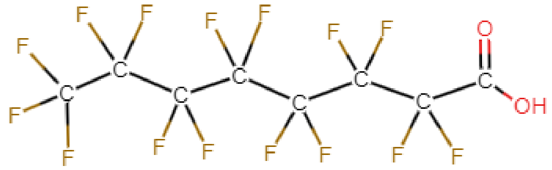
The PFAS family

- Potentially over 10,000 unique compounds are part of the PFAS family (~4,700 with CAS registry numbers)
- Two classes:
  - Polymers
  - Non-polymers
- Non-polymers cover two sub-classes:
  - **Per**fluoroalkyl substances
  - **Poly**fluoroalkyl substances
- Long and short-chain compounds

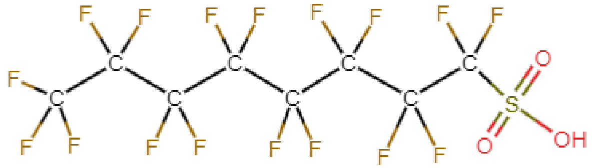


Some examples

Perfluoroalkyl substances

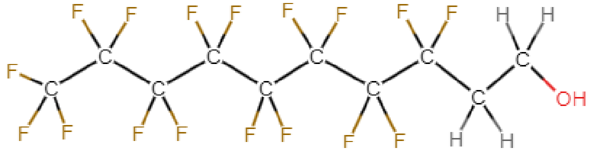


Perfluorooctanoic acid (PFOA)

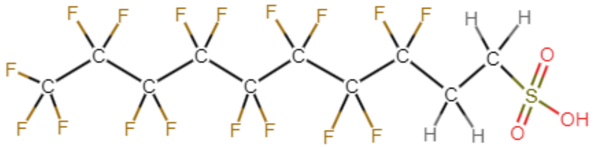


Perfluorooctanesulfonic acid (PFOS)

Polyfluoroalkyl substances

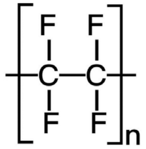


8:2 fluorotelomer alcohol (8:2 FTOH)

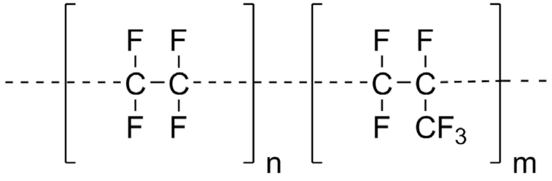


8:2 fluorotelomer sulfonic acid (8:2 FTSA)

Polymers



Polytetrafluoroethylene (PTFE)

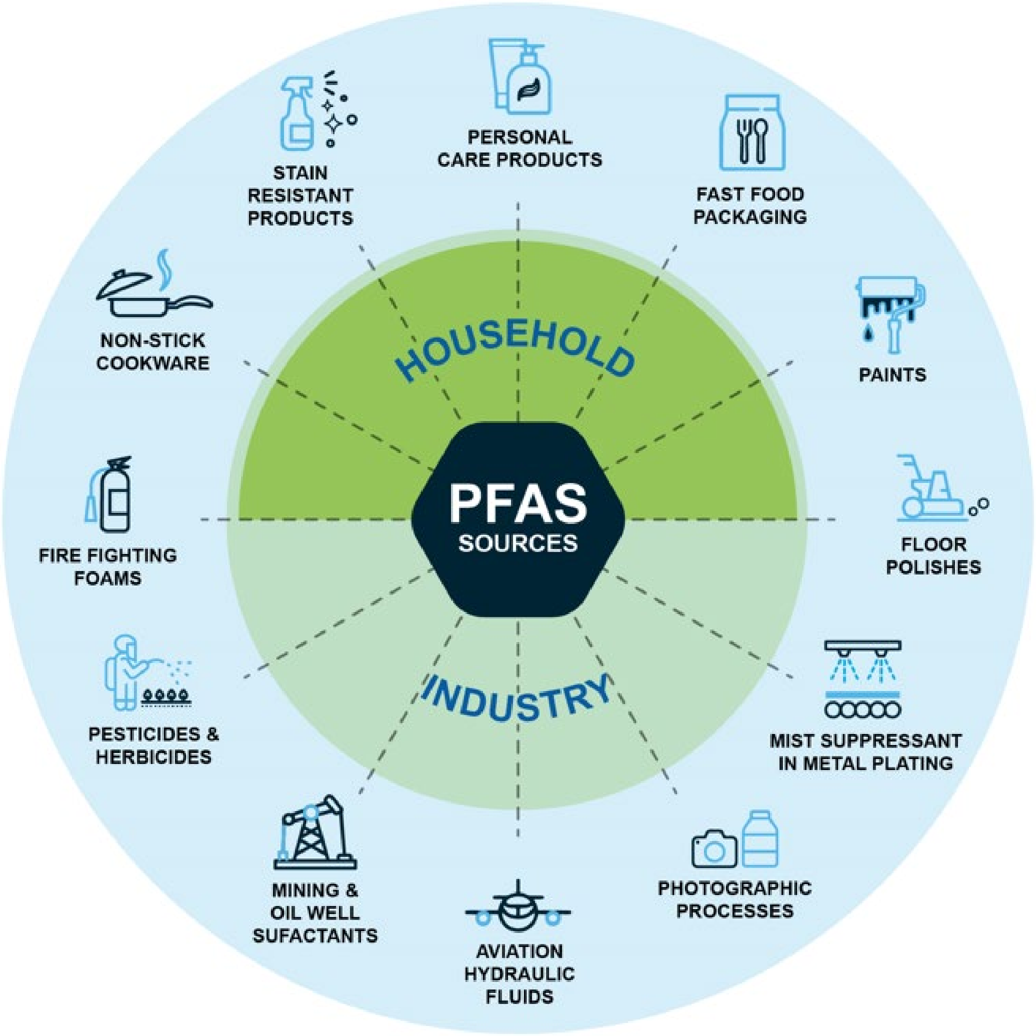


Fluorinated ethylene propylene (FEP)

Properties of PFAS

- PFAS retain unique physical and chemical properties which make them valuable compounds for use in a wide range of applications:
  - Oil, water, stain and soil repellence
  - Thermal stability
  - Low chemical reactivity
  - Low flammability
  - Low co-efficient of friction

- Some PFAS compounds, such as PFAAs, have an amphiphilic structure (hydrophobic “tail” with a hydrophilic “head”). This makes them excellent surfactants.



Where are PFAS found?

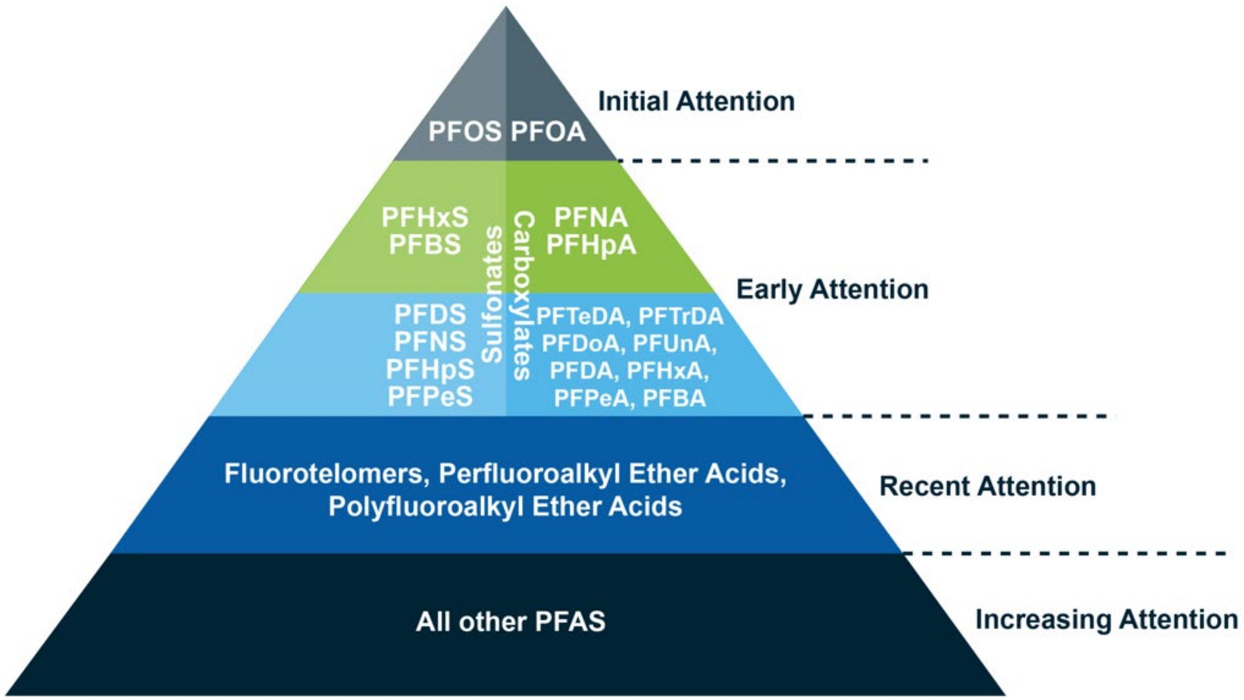




Why are they a growing environmental concern?

Emerging environmental concerns

- The specific properties of PFAS which make them an important component of modern day life also present certain risks:
  - The strength of the carbon-fluorine bond means that they do not degrade easily in the environment which can lead to their persistence
  - Some PFAS are mobile (particularly shorter-chain) and easily transported in groundwater, surface water and soil
  - Some PFAS have potential negative health impacts and can be bioaccumulative. Longer chain (C8+) PFAS exhibit greater bioaccumulative properties than shorter
- Awareness of potential health impact dates back to the 1970s but initial focussed attention not until the early 2000s due to improvement in analytical methods detecting PFOA and PFOS widely in environmental samples.
- Health implications plus further improvements in understanding and analytical methods has recently expanded the focus to all other PFAS.



Recent regulatory movements

Logika GROUP

HSE

Analysis of the most appropriate regulatory management options (RMOA)

Substance Name:	Poly- and perfluoroalkyl substances (PFAS)
EC Number:	N/A
CAS Number:	N/A
Date:	March 2023

Environment Agency

Environmental risk evaluation report: Hexafluoropropene [HFP]

(CAS no. 116-15-4)

Chief Scientist's Group report

April 2023

ECHA EUROPEAN CHEMICALS AGENCY

ANNEX XV RESTRICTION REPORT

PROPOSAL FOR A RESTRICTION

SUBSTANCE NAME(S): Per- and polyfluoroalkyl substances (PFASs)

IUPAC NAME(S): n.a.

EC NUMBER(S): n.a.

CAS NUMBER(S): n.a.

CONTACT DETAILS OF THE DOSSIER SUBMITTERS:

BAuA
Federal Institute for Occupational Safety and Health
Division 5 - Federal Office for Chemicals
Friedrich-Henkel-Weg 1-25
D-44149 Dortmund, Germany

Bureau REACH, National Institute for Public Health and the Environment (RIVM)
Antonie van Leeuwenhoeklaan 9
3721 MA Bilthoven, The Netherlands

Swedish Chemicals Agency (KEMI)
PO Box 2,
SE-172 13 Sundbyberg, Sweden

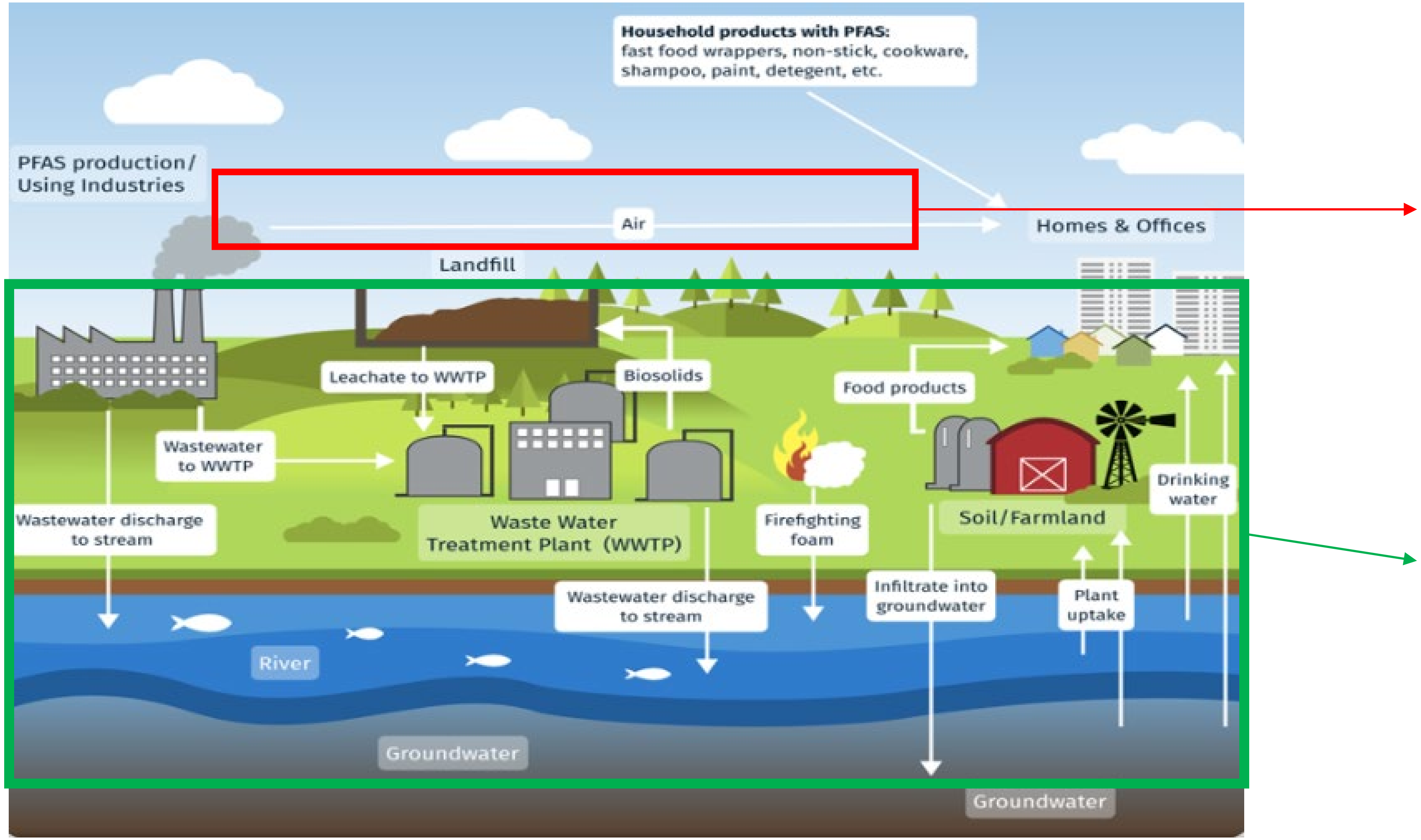
Norwegian Environment Agency
P.O. Box 5672 Torgarden
N-7485 Trondheim, Norway

The Danish Environmental Protection Agency
Tolderlundsvej 5
5000 Odense C, Denmark

VERSION NUMBER: 2

DATE: 22.03.2023

PFAS exposure

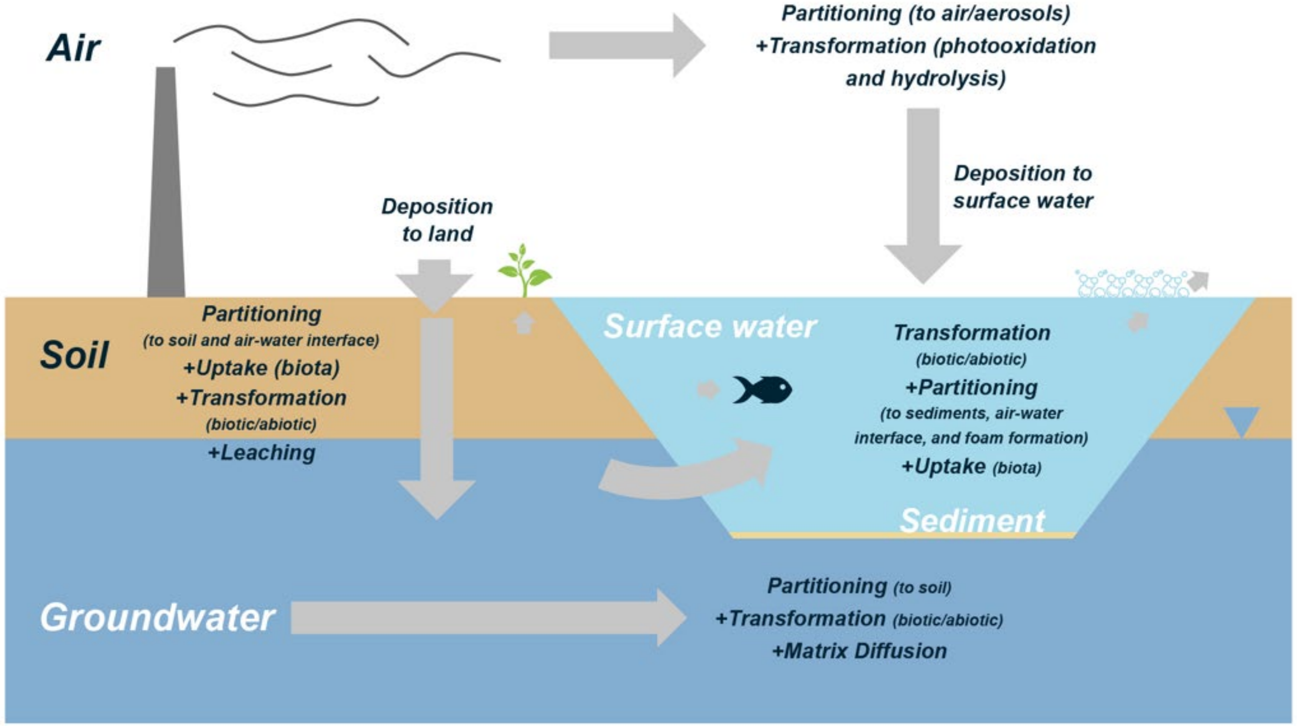


Until recently, little attention has been given to this exposure route

Most focus to date has been on these exposure routes

Complexity of assessing PFAS emissions to air

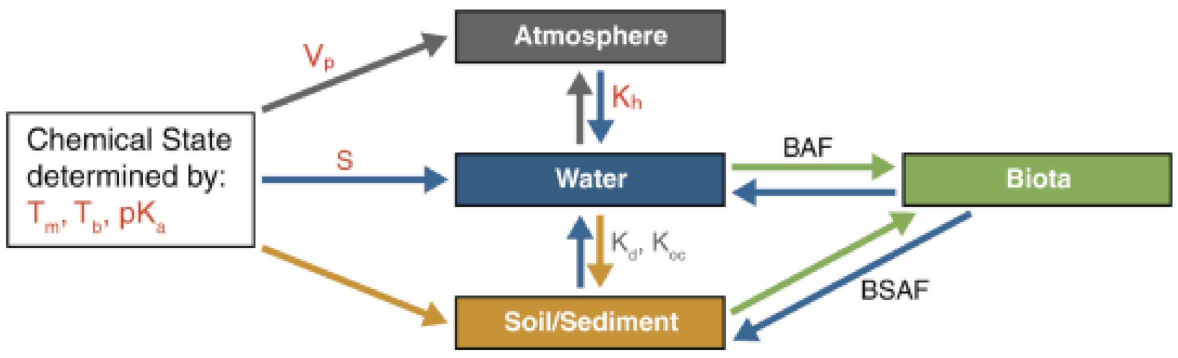
PFAS impact-pathways (air)



- Due to persistence, mobility and bioaccumulative properties, impact-pathways other than inhalation are important for PFAS emissions to air.
- Factors that affect PFAS fate and transport can be divided into two categories.
- PFAS characteristics:
    - Alkyl chain length, ionic state of the compound, the type of functional group, extent of fluorination (per- compared to polyfluorinated compounds) etc.
    - These determine the extent of PFAS partitioning and environmental transformation.
- Site characteristics:
    - Soil type, depth to groundwater, REDOX conditions, precipitation/infiltration rates, surface water flow rates, atmospheric conditions etc.
    - These all affect PFAS-media interactions.

PFAS partitioning

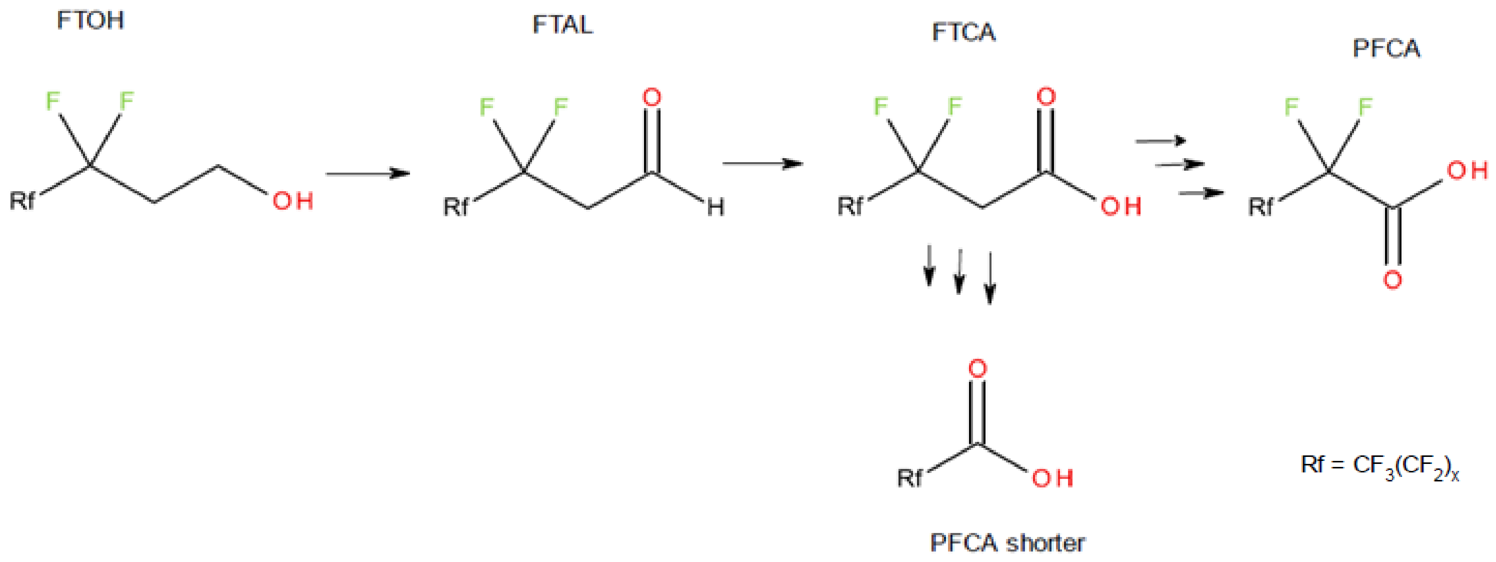
- Wide variety of PFAS compounds and associated chemical and physical properties means they are often emitted to air in different phases (possible for multi-phase releases):
  - Vapour
  - Aerosol
  - Solid
- Once emitted to the atmosphere, PFAS can further partition between these phases.
- Due to the surfactant properties of many PFAS, they naturally occur at air-water interfaces (hydrophobic C-F tail oriented towards the air and hydrophilic functional group dissolved in water droplet).
- The compound-specific vapour pressure and Henry's law constant are important parameters influencing partitioning between vapour and aerosols in the atmosphere.



T_m = melting point; T_b = boiling point; pK_a = acid dissociation constant; V_p = vapor pressure; S = solubility; K_h = dimensionless Henry's law constant; K_d = soil and sediment partitioning coefficient; K_{oc} = organic carbon partitioning coefficient; BAF = bioaccumulation factor; and BSAF = biota-sediment accumulation factor.

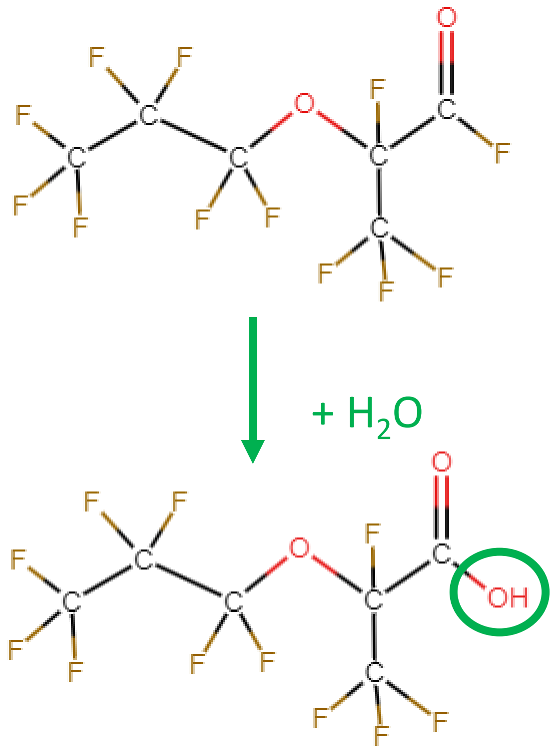
PFAS chemical transformation

- Certain PFAS, including the polyfluorinated alkyl substances are less stable / more subject to transformation than others.
- The other types of bond (e.g., C – H) on the main alkyl chain can allow transformation through abiotic degradation (hydrolysis, photo-oxidation, OH oxidation) and biotic degradation.
- Generally results in transformation to more stable PFAAs.
- Fluorotelomer alcohols can degrade to their associated PFCA e.g., 8:2 FTOH can degrade to PFOA.
- Possible for these PFAA precursors to be emitted with their equivalent PFAA itself.



PFAS chemical transformation

- Acyl fluorides can undergo rapid hydrolysis to carboxylic acids.

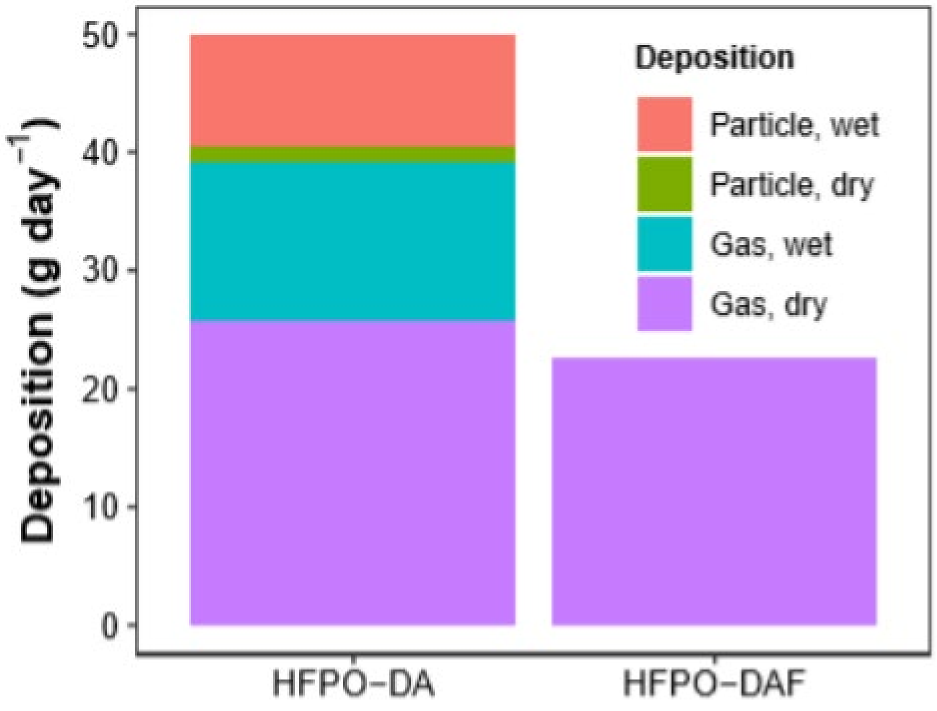


HFPO-DAF

Volatile:
H^{eff} = 0.05 M atm^{-1}
C*= 3.1 x 10^9 µg m^{-3}
Most likely present as a gas

HFPO-DA

Semi-volatile:
H^{eff} = 4.2 x 10^6 M atm^{-1}
C*= 9.8 x 10^5 µg m^{-3}
Most likely present as aerosol/particulate



Source: D'Ambro et al. (2020) https://www.cmascenter.org/conference/2020/slides/D_AmbroMurphy_CMAQPFAS_CMAS2020.pdf

Case study – screening assessment for inhalation

Case study

- UK manufacturing site emitting two PFAS compounds:
  - PFAS-1 (< 100 kg y^{-1} emitted)
  - PFAS-2 (> 10,000 kg y^{-1} emitted)
- Initial rapid screening assessment to assess risks through the inhalation pathway.
- Compounds emitted to air from vents (point sources) as well as fugitive releases during e.g., maintenance.
- Uses a Gaussian plume model (ADMS) to predict short-range process contributions in air.
- Force all PFAS into the vapour phase (worst-case for concentrations in air **N.B., not for deposition or other impact-pathways**).
- No chemical transformation considered. Although both compounds have groups which could potentially be susceptible to chemical attack, reactivity is very low and not important for short-range assessment (half-life in air ~10^{41} and ~10^{5} hours respectively).

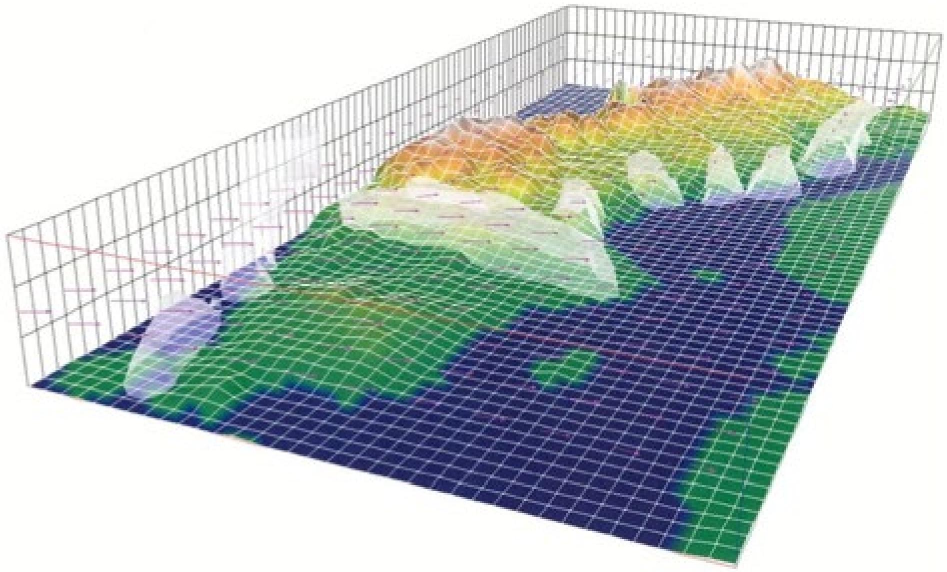
Case study

- Like many PFAS, no Environmental Assessment Levels (EALs) existed for the two compounds.
- Substance-specific EALs developed from toxicological studies establishing no observed adverse effect levels (NOAELs) using the EA's latest methodology for deriving EALs.
- No acute effects associated with either compound so only LT EALs developed:
    - PFAS-1: $NOAEL_{ing\text{-}rat\text{-}90d}$ = 10 mg kg.bw^{-1} day^{-1}; **EAL_{LT} = 87 µg/m^3**
    - PFAS-2: $NOAEL_{ing\text{-}rat\text{-}29d}$ > 1,000 mg kg.bw^{-1} day$^{-1;}$ **EAL_{LT} = 2,900 µg/m^3**
- Maximum process contributions of PFAS-1 and PFAS-2 were both less than 1% of the derived EAL and assessed as insignificant.
- Low risk of health impacts through the inhalation pathway.

The potential role of CTMs

Chemical transformation model

- Examples include CMAQ, CAMx, WRF-Chem, EMEP etc.
- Generally, Eulerian-based models with a fixed frame of reference.
- Aim to numerically solve the fundamental 3-D mass conservation equation.
- Can be applied to dispersion over significant distances (regional, country and continental scales) making them ideal for modelling the long-range transport of persistent pollutants.
- Allow detailed treatment of chemical reactions and transformations.
- **<u>However:</u>**
  - Most computationally expensive type of model so a limit to grid resolution
  - Chemical transformation requires detailed information on physical and chemical properties of the pollutant in question and reaction kinetics
  - Can be difficult to track individual sources, although some do have source apportionment modules

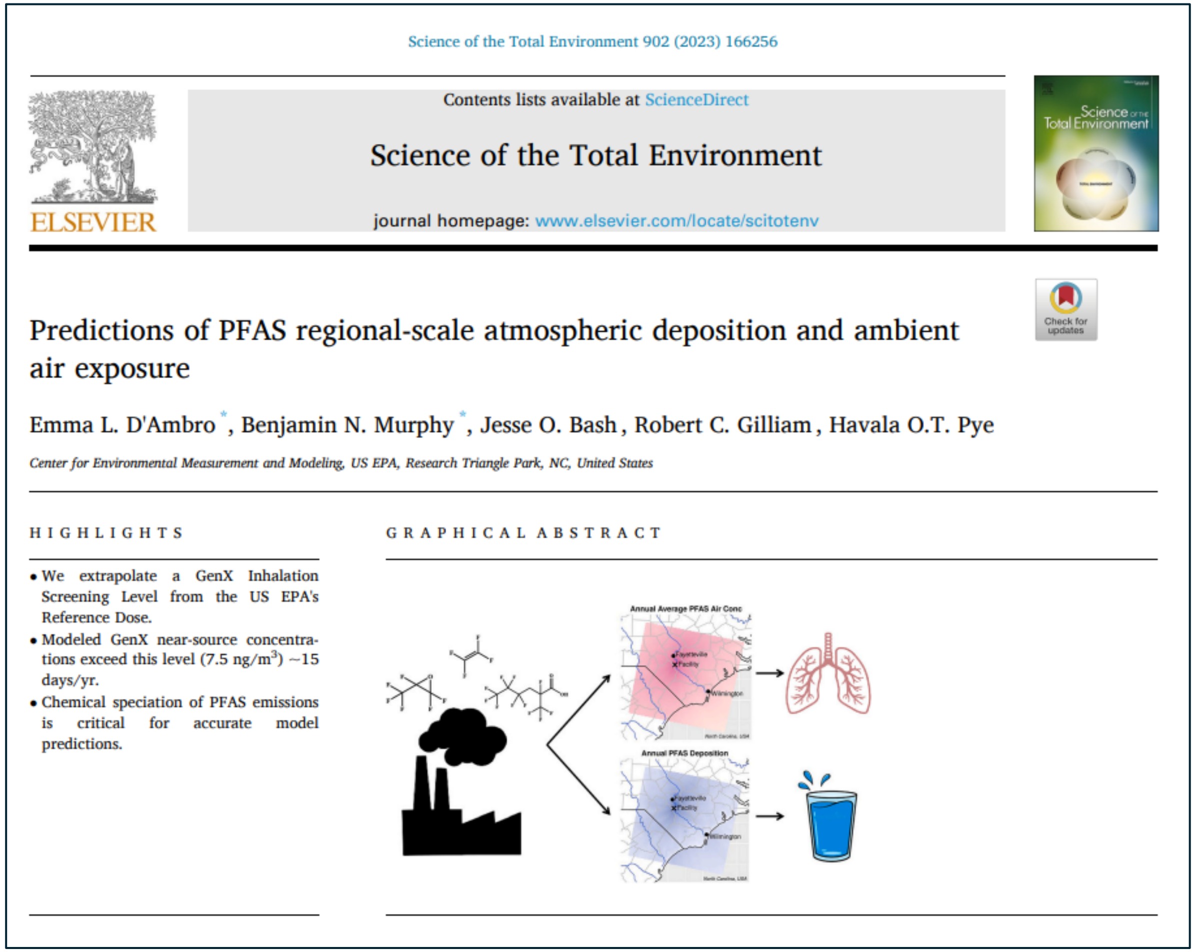


$$\frac{\partial C}{\partial t} = -\underline{\boldsymbol{u}}\nabla C + K\nabla^2 C + R + E - D$$

Change of concentration with time | Advection | Turbulence | Chemical reactions | Emission and deposition

CMAQ-PFAS

- Scientists at the US EPA have recently developed a variant of CMAQ specifically for modelling PFAS emissions to air (CMAQ-PFAS).
- Developed to assess the regional impacts of a group of PFAS (GenX) emitted from the Chemours fluoropolymer manufacturing site in North Carolina.
- Contains physical and chemical properties for 53 compounds calculated using the The Open (Quantitative) Structure-activity/property Relationship App (OPERA).
- Includes the effects of partitioning between different phases using compound specific Henry's law constant and vapour pressure.
- Does not yet include transformation through e.g., oxidation but sensitivity tests applied for complete conversion of pre-cursors to their respective carboxylic acid.



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journal homepage: www.elsevier.com/locate/scitotenv

Predictions of PFAS regional-scale atmospheric deposition and ambient air exposure

Emma L. D'Ambro *, Benjamin N. Murphy *, Jesse O. Bash, Robert C. Gilliam, Havala O.T. Pye

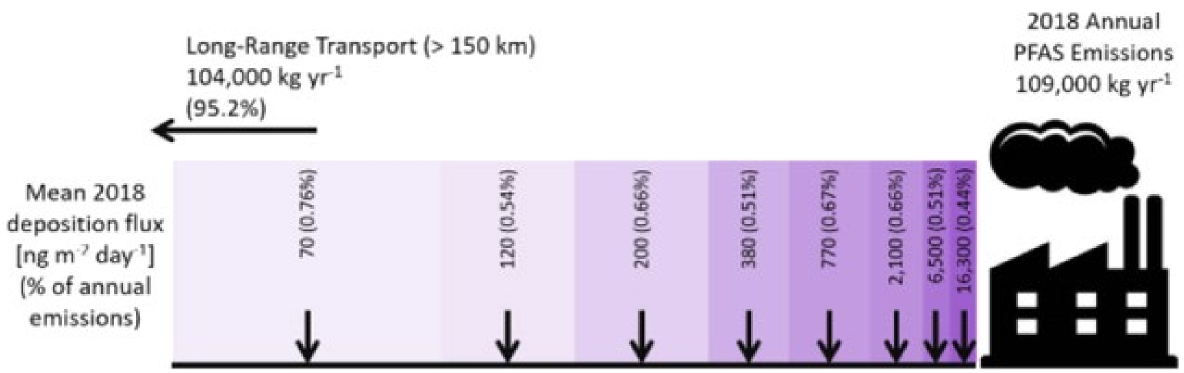
Center for Environmental Measurement and Modeling, US EPA, Research Triangle Park, NC, United States

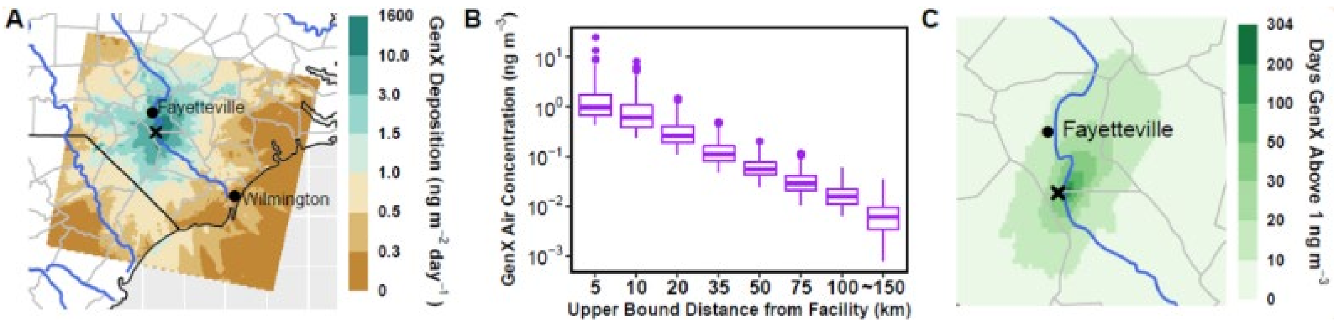
HIGHLIGHTS

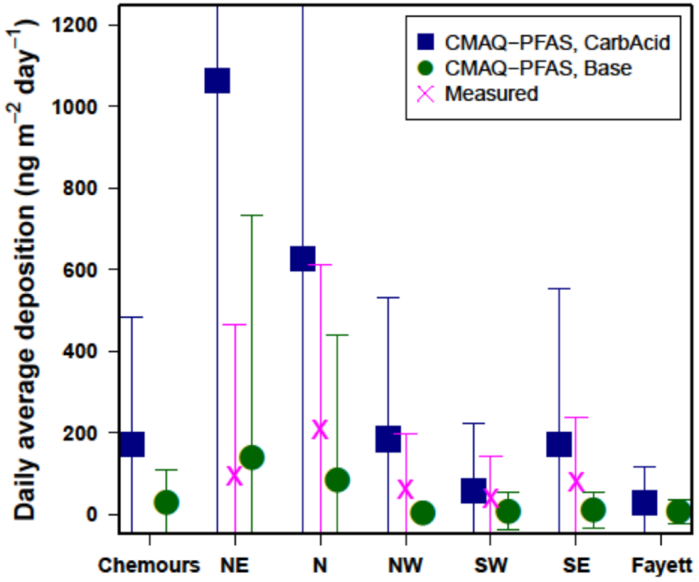
- We extrapolate a GenX Inhalation Screening Level from the US EPA's Reference Dose.
- Modeled GenX near-source concentrations exceed this level (7.5 ng/m^3) ~15 days/yr.
- Chemical speciation of PFAS emissions is critical for accurate model predictions.

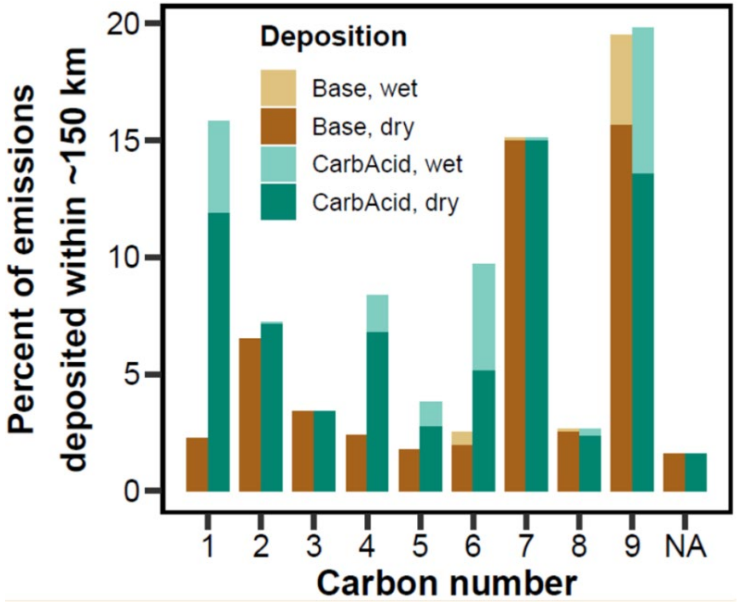
GRAPHICAL ABSTRACT

Some findings









Source: D'Ambro et al., 2021. 'Characterizing the air emissions, transport and deposition of per- and polyfluoroalkyl substances from a fluoropolymer manufacturing facility.' *International Journal of Environmental Science and Technology*, 55(2), 862-870

Concluding remarks

Concluding remarks

Logika GROUP

- PFAS represent a large family of synthetic compounds with significant variability in physical, chemical and toxicological profiles.
- Some PFAS are associated with potential health effects but not all.
- Due to the variability in physical, chemical and toxicological properties, impact assessments should be completed on a substance-specific basis (difficult to assess PFAS as a single group using a proxy compound).
- Screening assessments of short-range impacts considering the inhalation pathway can be made quickly and easily using commonly applied Gaussian plume models.
- Due to their persistence and bioaccumulative properties, long-range transport and deposition to e.g., soil and surface water are also important aspects to support a complete risk assessment.
- Partitioning and chemical transformation should be considered 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.
- Current ‘off-the-shelf’ Gaussian plume models unlikely to be suitable for predicting deposition as they are not typically complex enough to sufficiently represent PFAS partitioning and transformation.
- CTMs provide an opportunity to consider these aspects but obtaining representative compound specific parameters and assessment metrics for deposition is a challenge.

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Thank you

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