# Transformation products as emerging contaminants in soil and water – A case study on TFA and R471811

*Eef De Clercq, VITO, researcher*

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a Multi-stakeholder Network for Emerging Soil Contaminants

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# Transformation products as emerging contaminants in soil and water

Eef De Clercq, VITO

ENSOR 2024

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# 2 case studies to alert for PM-substances

- New hazard classes PMT and vPvM
  - Drinking Water
- The precautionary principle
- 2 examples in Europe
  - R471811
  - TFA
  - Flanders Environment Agency and the Flemish Department of Care

VLAAMSE MILIEUMAATSCHAPPIJ

Vlaanderen is milieu

Vlaanderen is zorgzaam en gezond samenleven

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# It’s in a word - Limit values in water

**Drinking water limit values** EU WFD (2000/60/EC), EU DWD (2020/2184)

- Parametric values
- Health based values
  - Health-related indicator values / precautionary
  - Drinking water guide values

**Groundwater limit values** EU GWD (2006/118/EC)

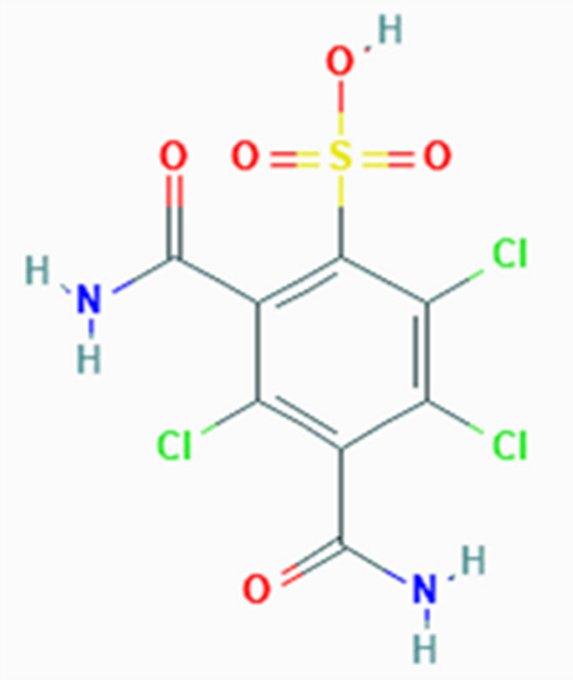
- Groundwater quality standards
- Threshold values

**Surface water limit values** EU WFD (2000/60/EC), EU EQS (2013/39/EU)

- Environmental quality standards

# R471811 – Identification and use

- 2,4-dicarbamoyl-3,5,6-trichlorobenzenesulfonic acid



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- 2,4-dicarbamoyl-3,5,6-trichlorobenzenesulfonic acid
- Main TP (12%) of CHLOROTHALONIL

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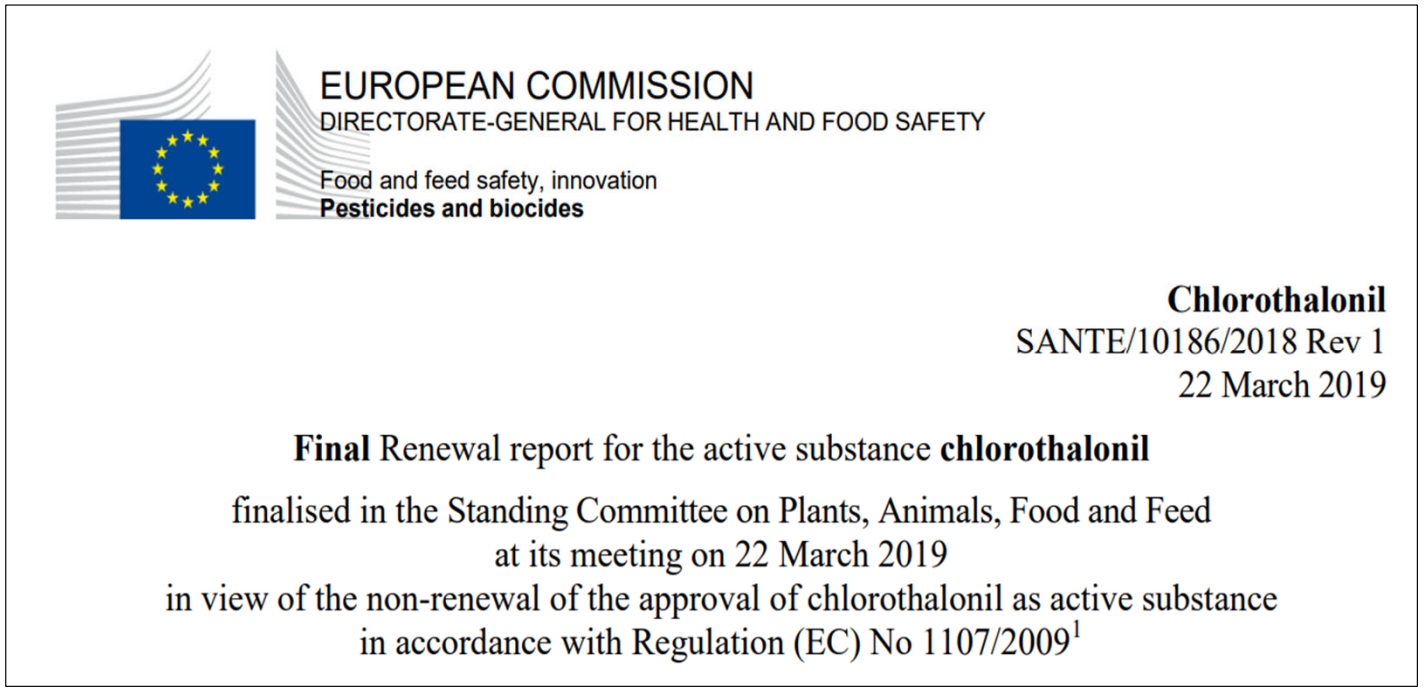

EUROPEAN COMMISSION
DIRECTORATE-GENERAL FOR HEALTH AND FOOD SAFETY

Food and feed safety, innovation
**Pesticides and biocides**

**Chlorothalonil**
SANTE/10186/2018 Rev 1
22 March 2019

**Final** Renewal report for the active substance **chlorothalonil**

finalised in the Standing Committee on Plants, Animals, Food and Feed
at its meeting on 22 March 2019
in view of the non-renewal of the approval of chlorothalonil as active substance
in accordance with Regulation (EC) No 1107/2009[1]

# R471811 – Characteristics and fate

- Persistent (medium to high)
- Very mobile
- Very polar, highly soluble in water (anion)
- Soil → Water

# R471811 – Toxicology

- No toxicological reference values for oral exposure
  - Limited screening of information
- Unlikely to be genotoxic
- Sharing the carcinogenic potential of the parent chlorothalonil ??
  - EFSA has recommended to consider all TPs of chlorothalonil relevant metabolites (EFSA, 2018)

| Sources used for screening for RV | |
|---|---|
| INERIS | France |
| JECFA | WHO |
| EFSA | EU |
| ATSDR | U.S. |
| EPA | U.S. |

# R471811 – Toxicology of mother product

- Toxicological reference values of CHLOROTHALONIL

| Type | Value (mg/kg bw/ d) | Derivation year | Source |
|---|---|---|---|
| ADI | 0,015 | Not specified | EFSA |
| ADI | 0,01 | 1991 | Drinking water guidelines 2022, Australia |
| Health Advisory (HA) | 0,015 | 1988 | US-EPA |

- Harmonized C&L classification: Carcinogenic category 2

→ proposed classification as Carc. 1B by EFSA (2018)

# R471811 – Limit values in drinking water

| Country | Parametric value (µg/l) | | Health based values (µg/l) | |
|---|---|---|---|---|
| Flanders (BE) | 0,1 | VMM, 2023 | 4,5 | Precautionary, 2023 |
| Switzerland | 0,1 | Kiefer et al., 2020 | | |
| France | 0,1 | Anses, 2023 | 3,0 | precautionary; ARS 2023 |
| Denmark | 0,1 | Kiefer et al., 2020 | | |
| Germany | | | 3,0 | Indicator value; UBA, 2021 |

$$QS_{dw,hh} = \frac{0.2 \cdot TL_{hh} \cdot bw}{uptake_{dw}}$$

- Chlorothalonil → QS dw,hh = 105 µg/l

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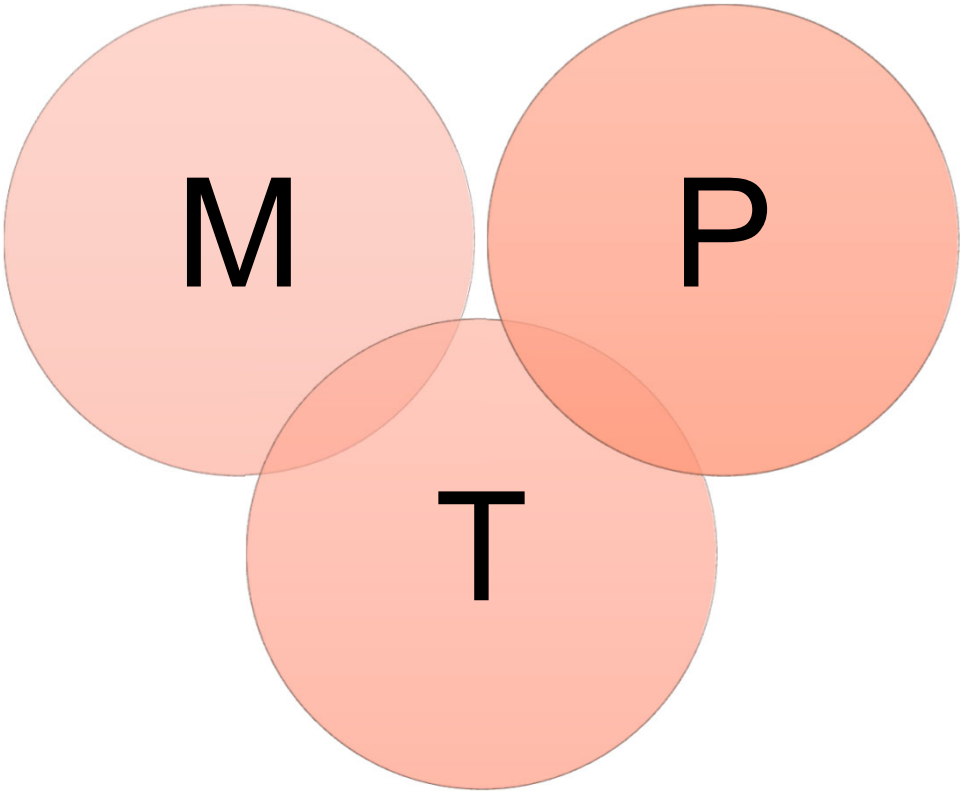
# R471811 – Detection in water

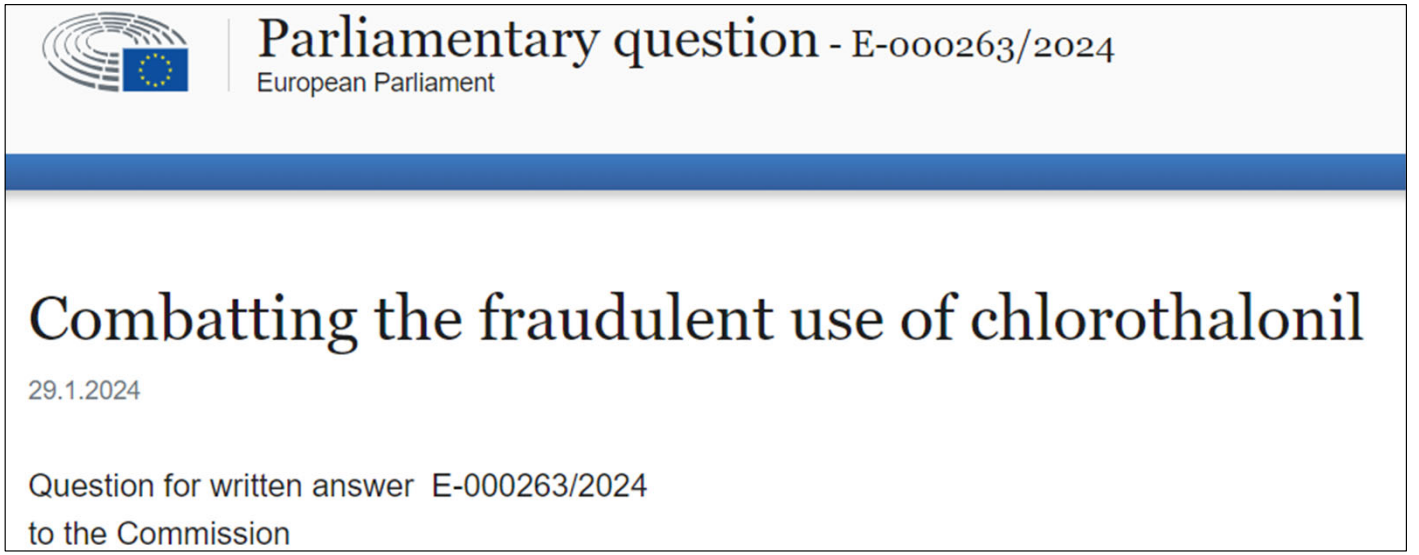
| Country | Samples | Detection | Limit value (0,1 µg/l) exceedance | Max. value |
|---|---|---|---|---|
| Switzerland (Kiefer et al., 2020) | Drinking water resources | 100% of the samples | 52% | 2,2 µg/l |
| France (Anses, 2023) | Raw and treated water | 60% and 57% respectively | 34% | 2 µg/l (raw water) |

# Banning Chlorothalonil - Just in time?

TP R471811

- Monitoring needed
  - Drinking water quality control
  - Uses of (non-approved) fungicide





Parliamentary question - E-000263/2024
European Parliament

# Combatting the fraudulent use of chlorothalonil

29.1.2024

Question for written answer E-000263/2024
to the Commission

Privacy statement | Legal notice | Cook

European Commission

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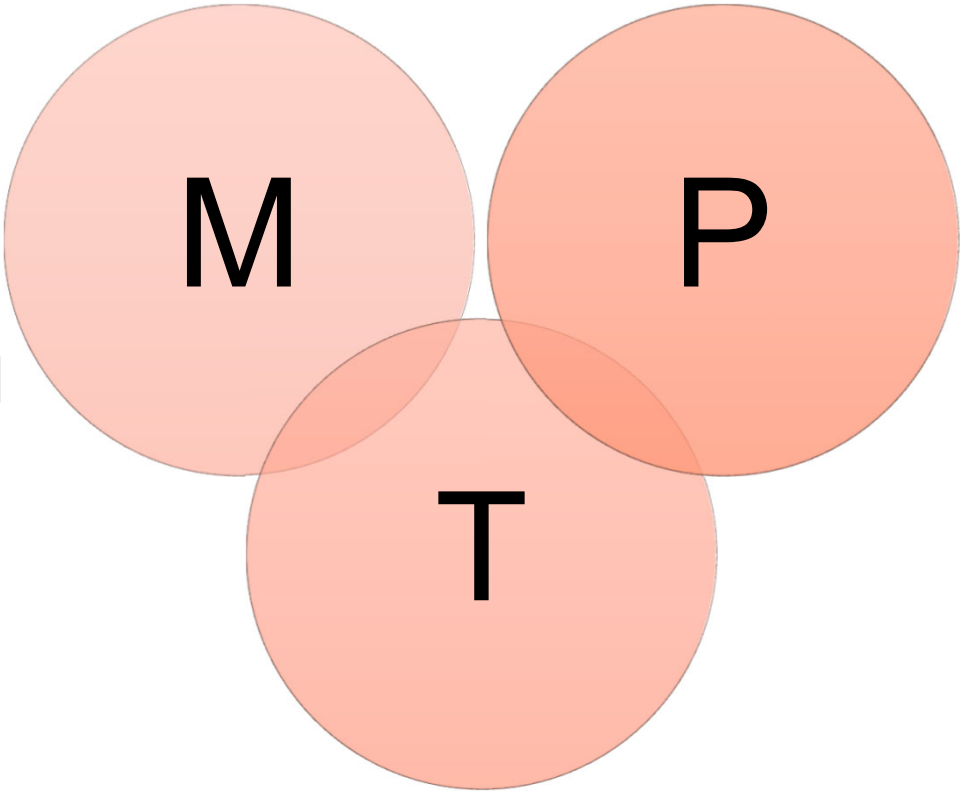
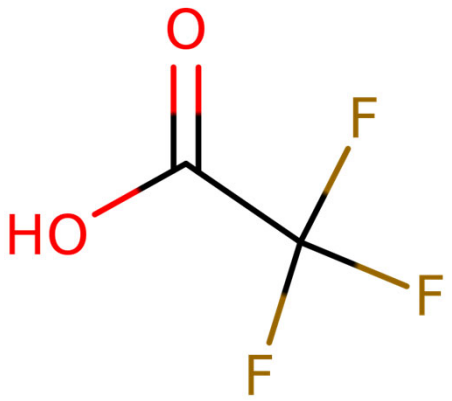
# Banning Chlorothalonil - Just in time?

TP R471811

- Monitoring needed
  - Drinking water quality control
  - Uses of (non-approved) fungicide
- Health Risk assessment needed
  - Toxicity gap

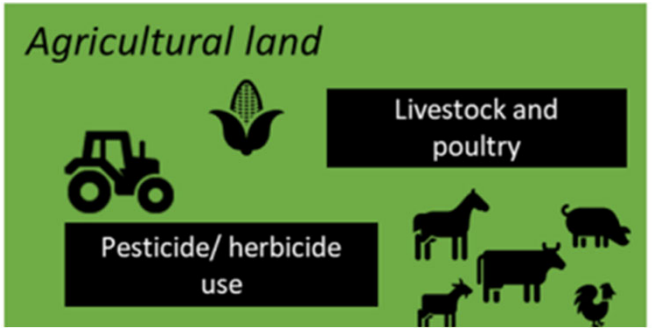


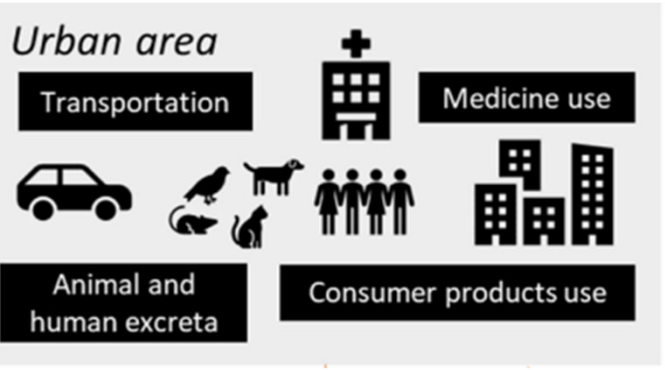
# TFA – Identification and use




- Trifluoroacetic acid
- PFAS – PFAA – PFCA – short chain
- Different sources
  - Production of TFA
    - Regsitered in the EU under REACH (100 – 1000 ton)
  - Degradation to TFA

  - Point sources + diffuse sources





Figures: Hartmann et al., 2023

**PRODUCTION OF PPP**

**METABOLITE OF PPP AND PESTICIDES**

- **EFSA identified 140 pesticides in 2014 potentially leading to TFA formation**

**DEGRADATION OF CF3-SUBSTANCES/**

- **fluorine-anesthetics**
- **medicines**
- **refrigerants, Teflon products**
- **personal care products**

**ANALYSIS OF PEPTIDES**

**PREPARATION OF MEDICINS**

**SOLVENT/CATALYST**

- **for polymerization and condensation reactions**

*"140 pesticides are identified potentially leading to TFA* (EFSA, 2014)

*"a potential breakdown product of a large number (> 1 million) of chemicals"* (Solomon, 2016)

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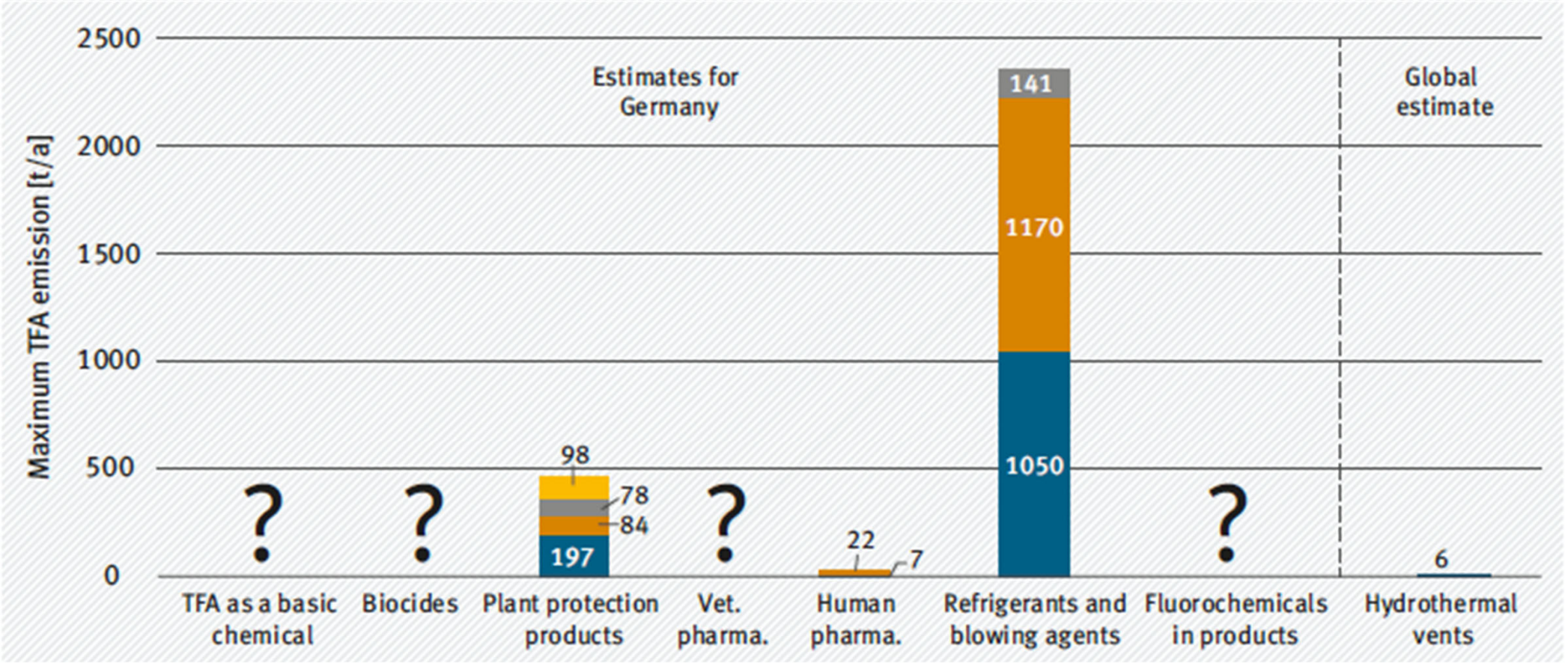
Source: UBA (2021)

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# TFA – Characteristics and fate

- Very persistent
- Very mobile
- Highly soluble in water (anion)
- Low adsorption to organic carbon
- Uptake by plants
- Soil & atmospheric deposition → Water (+ point sources)

# TFA – Toxicology

- Toxicological reference values for TFA:

| Type of value | Value mg/kg bw/ d | Year of derivation | Source |
|---|---|---|---|
| ADI | 0,050 | 2014 | EFSA |
| ADI | 0,018 | 2020 | UBA |

- RIVM (the Netherlands): not sufficient information to confirm both ADI's (2023)

  Relative potency Factor 0,002 (compared to PFOA)

# TFA – Limit values in drinking water

| Country | Parametric value (µg/l) | | Health based values | |
|---|---|---|---|---|
| Flanders (BE) | | | 4,5 | Precautionary; 2023 |
| The Netherlands | 1,0 | halogenated aliphatic hydrocarbons; RIVM (…ILT2022) | 2,2 | Precautionary; RIVM, 2023 |
| Germany | | | 60 | Guideline Value; UBA, 2021 |

$$QS_{dw,hh} = \frac{0.2 \cdot TL_{hh} \cdot bw}{uptake_{dw}}$$

→ QS dw,hh = 305 µg/l or 126 µg/l

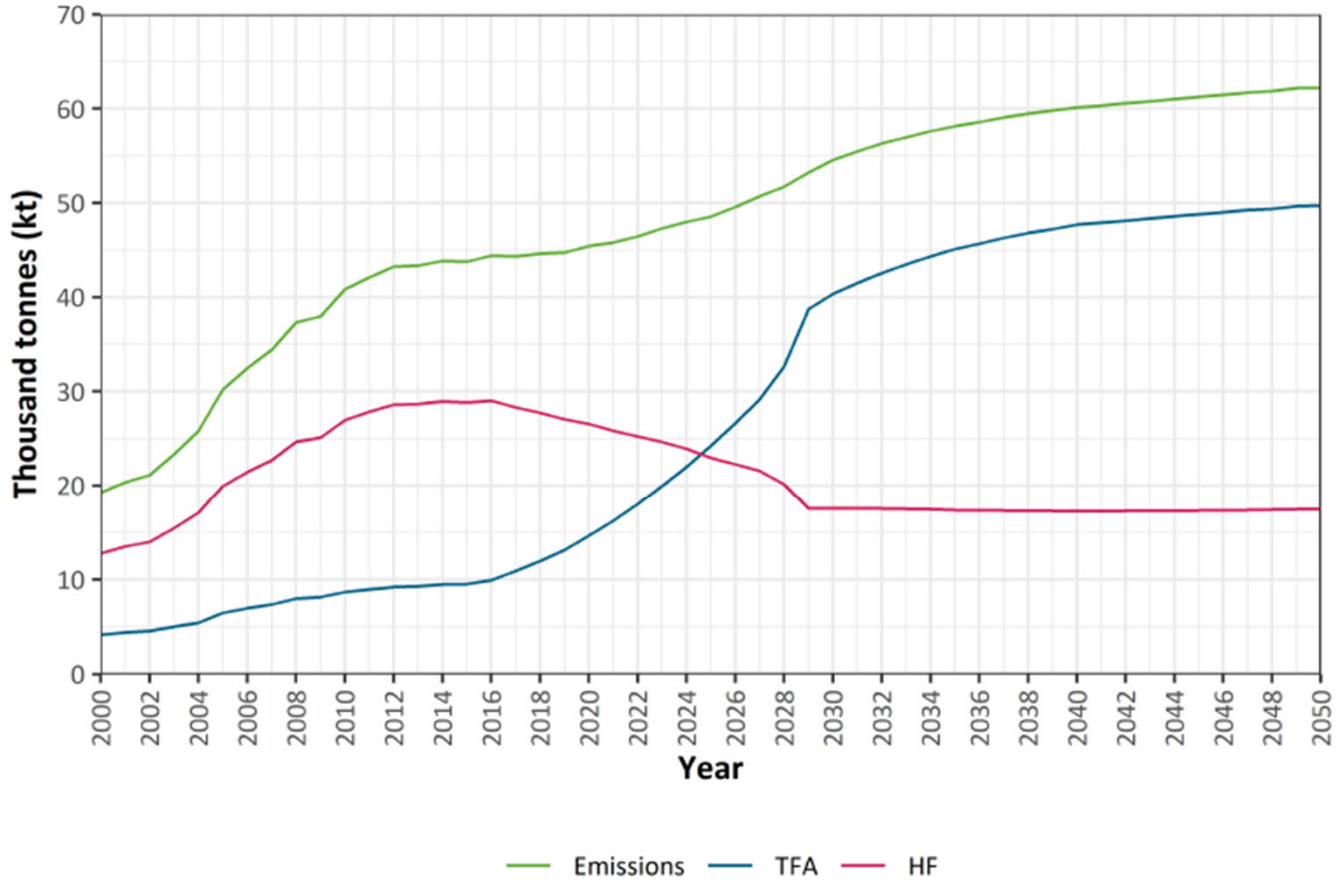
# TFA – Detection in water

| Country | Samples | Location | Max. value or range |
|---|---|---|---|
| Germany (UBA, 2021b) | 19 tap water samples (2018) | Various locations | 2,5 µg/l |
| | Drinking water, Groundwater (2017) | Nearby a wastewater discharge | > 20 µg/l |
| | 29 Groundwater samples (2018) | Nearby intensive agriculture areas | 17 µg/l |
| | 181 Groundwater samples (2019)<br>3 drinking water catchment areas (2018) | Regional<br>Not connected to surface water | > 10 µg/l<br>> 10 µg/l |
| Nederland (RIVM, 2023) | Surface water (Rhine river, 2021) | All locations | 1,4 µg/l |

Source: UBA (2021)



Figure 23: Emissions of TFA-forming HCFC-, HFC-, u-HFC- and u-HCFC-containing refrigerants and propellants in Europe (EU-28) and quantities of trifluoroacetic acid (TFA) and hydrogen fluoride (HF) formed therefrom in metric kilotonnes for the period from 2000 to 2050 for the "u-HFC and u-HCFC maximum scenario".

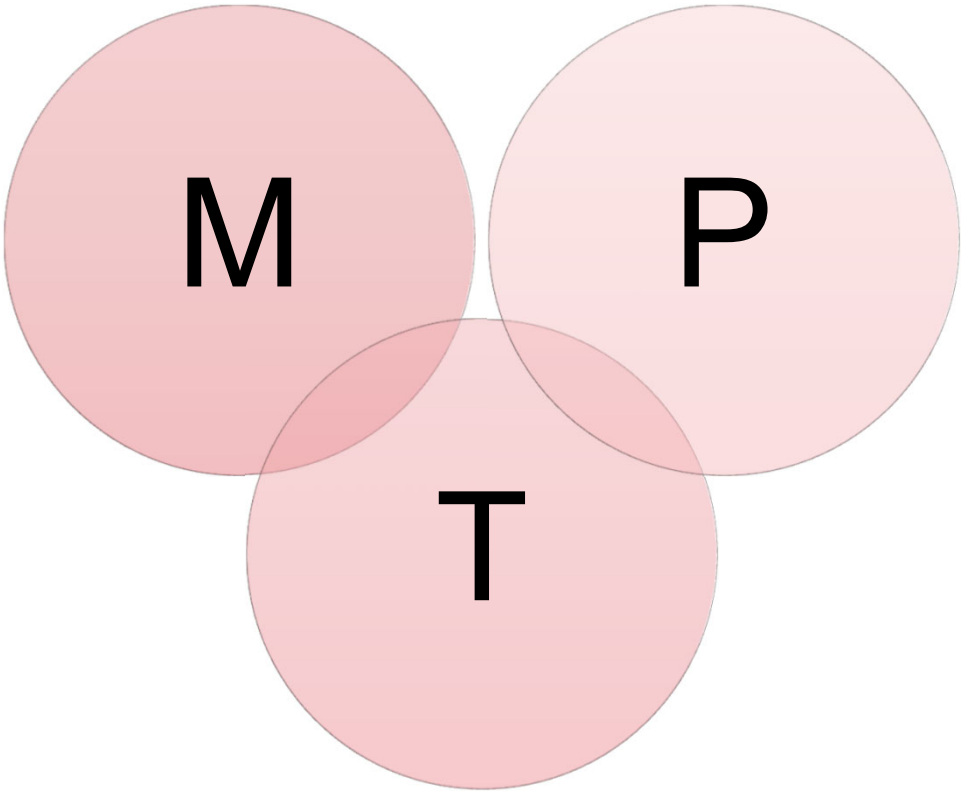


# Should we reduce the inputs of TFA?

- Risk assessment to cover much longer timescales
  - Risk increases and is left for future generations
  - Principle of precaution
- Frictions between sectors
  - TFA cannot be removed by economical means
- *Precautionary principle*

vP as sufficient justification for limiting its input,

even if TFA has a low environmental toxicity”



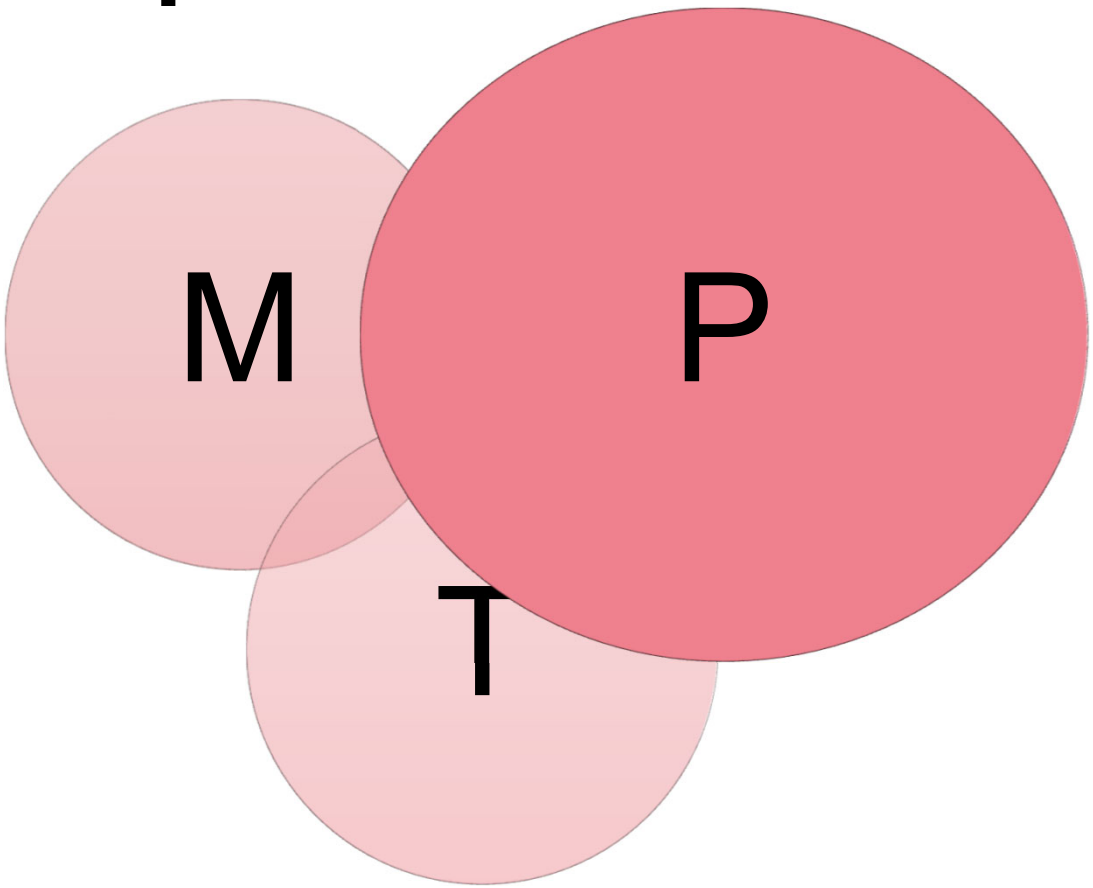
# Should we reduce the inputs of vP?

- Cousins et al., 2019:

*"The concentration of persistent (toxic) substances in the environment cannot be regulated in a timely manner"*

- Hartmann et al., 2023:

*"extremely persistent substances like PFAS—have such long environmental residence times that inevitably exposure concentrations will reach a certain concern level"*



# Literature R471811

- EFSA, 2018
- ARS, 2023
- UBA, 2021
- Kiefer et al., 2020
- Anses, 2023

# Literature TFA

- EFSA, 2014
- Solomon et al., 2016
- UBA, 2021
- UBA, 2021b
- RIVM, 2023
- Hartmann et al., 2023

# Thank you

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