

Trifluoroacetate in the water cycle

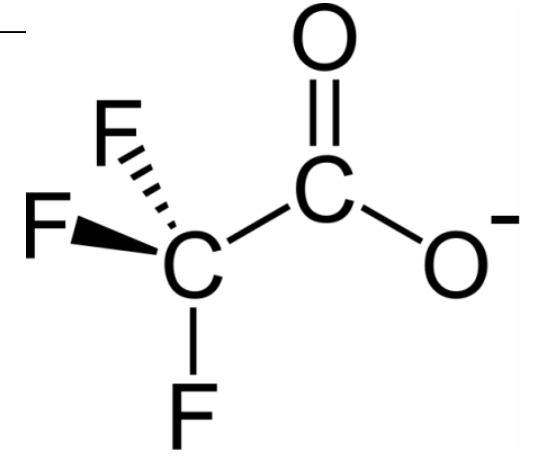
Third PMT Workshop, 25. March 2021

Karsten Nödler & Marco Scheurer



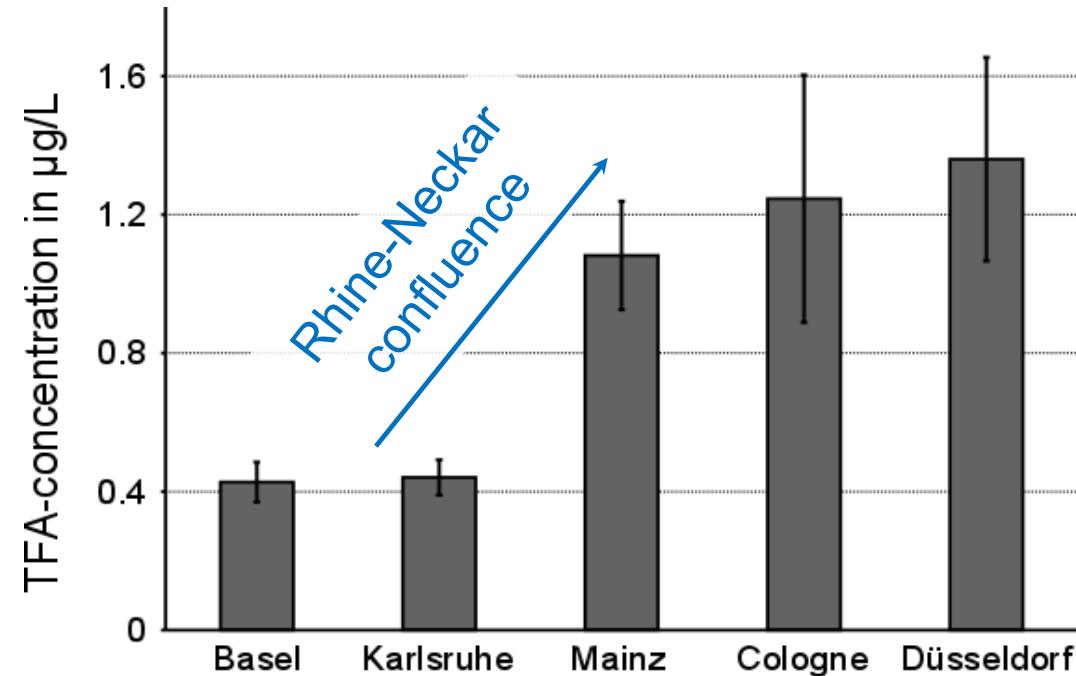
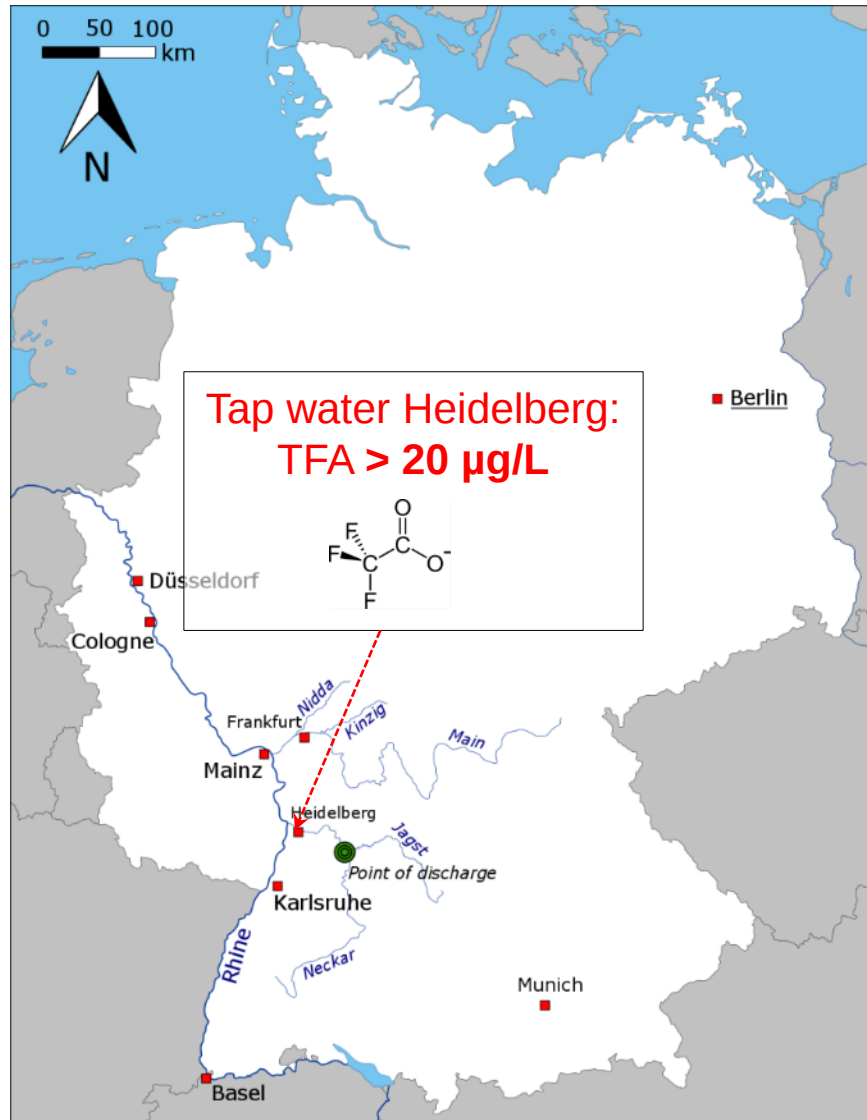
Fact-Sheet *Trifluoroacetate (TFA)*

- Anion of trifluoroacetic acid (CAS 76-05-1)
- Industrial chemical (solvent and building block)
- Tonnage under REACH: 100–1,000 t/a
(1,000–10,000 t/a until recently)
- Highly persistent in the environment, very mobile in the water cycle
 - $t_{1/2}$: many, many (!) years; $\log K_{OC}$: 0.79
- Regulations (Germany)
 - Until 2017: 1 $\mu\text{g/L}$ in drinking water (DW) (health-related indication value)
 - 2017–2020: 3 $\mu\text{g/L}$ in DW (health-related indication value)
 - From 2020: 60 $\mu\text{g/L}$ in DW (guidance value) (Tolerable Daily Intake: 18 $\mu\text{g/kg bw}$)



→ **Precautionary principle!**

2016, how it all began: Industrial discharge at River Neckar



- 100 µg/L at the point of discharge (River Neckar)
- Clear impact on River Rhine
- Water supply >300 km downstream still affected!

2016, how it all began: Industrial discharge at River Neckar



Trinkwasser in Edingen-Neckarhausen
Notfallleitung nach Mannheim wird kommen
Wasserversorgungsverband stimmt Kreditaufnahme von einer Million € Druckerhöhungsanlage erneut ausgeschrieben

Schadensersatzklage weis Neckar – Gemeinde schliesst
VON EDINGER-NECKAR-NEWS & EVENTS (REDAKTION) AM 28. Edingen-Neckarhausen – (edn) Die Chemiefirma Solvay Chemiewerke hat die Trinkwasserleitung (TFA) aus ihrem Chem. Deswegen Konzentration im Trinkwasser ist dadurch deutlich ph. von Edingen-Neckarhausen und Heidelberg ist von der Einleitung.

Trifluoroacetat im Heidelberger Trinkwasser
Die Firma will keinen Filter einbauen
Umweltausschuss diskutiert Thema - "Was übrig bleibt, ist der Frust"

Säure in Trinkwasser gefunden - Das ist jetzt zu tun!

Chemikalie belastet Trinkwasserversorgung am Neckar
Karlsruhe (dpa/IsW) - Ein unerwünschtes chemisches Abbauprodukt belastet die Trinkwasserversorgung am Neckar im Raum Mannheim und Heidelberg. Trifluoressigsäure (TFA) aus dem Flusswasser sei im Uferfiltrat und im Trinkwasser nachgewiesen worden. Das Regierungspräsidium Karlsruhe am Montag mit.

Trinkwasser zwischen Wimpfen und Mannheim verunreinigt
Das müssen Sie zu TFA im Neckar und zur Wasserversorgung wissen
So schön und so schmutzig: Neckar ist einer der verdrecktesten Flüsse im Land. Zum Problem wird das, wenn er Trinkwasserbrunnen beeinflusst

STIMME.de // Heilbronn
11. Oktober 2016, 17:58 Uhr Update: 15. Oktober 2016, 03:33 Uhr
TFA im Neckar: Sechs Fragen und Antworten
Region: Was hat es mit dem Trifluoroacetat im Wasser auf sich? Neckar festgestellt wurde? Behörden beziehen auf Stimme-N

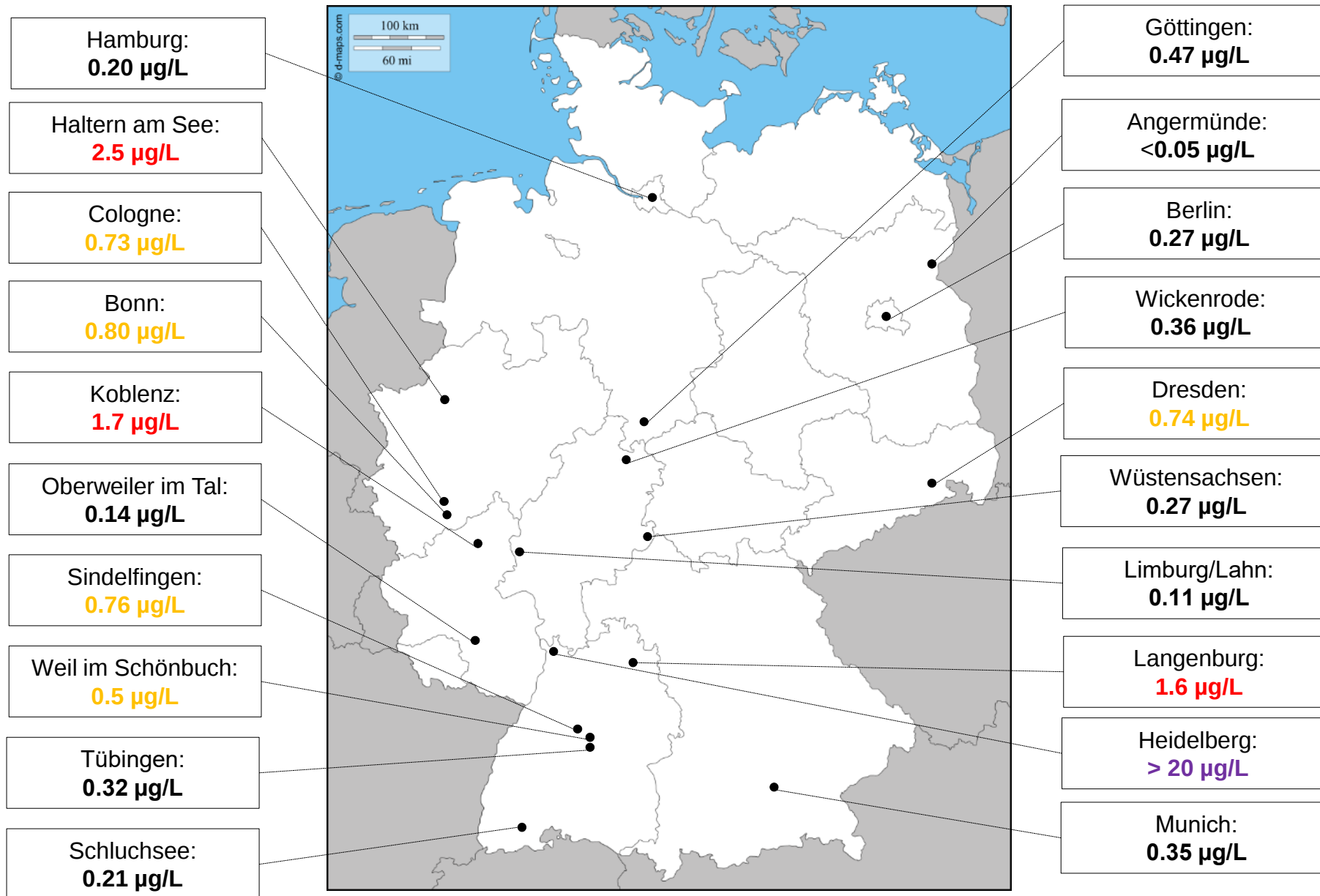
STIMME.de // Heilbronn
10. Oktober 2016, 16:01 Uhr Update: 15. Oktober 2016, 02:23 Uhr
Neckar mit TFA belastet
Bad Wimpfen Ein Chemieunternehmen in Bad Wimpfen soll für die Einleitung des Stoffes Trifluoressigsäure (TFA) verantwortlich sein. Die Firma spricht von ungefährlichem Trifluoroacetat.

Landesschau AKTUELL
Chemische Substanz im Trinkwasser
Zwischen Bad Wimpfen und Mannheim war in den vergangenen Wochen das Trinkwasser teilweise mit einer Fluorverbindung verunreinigt. Verursacher könnte das Chemieunternehmen Solvay sein.

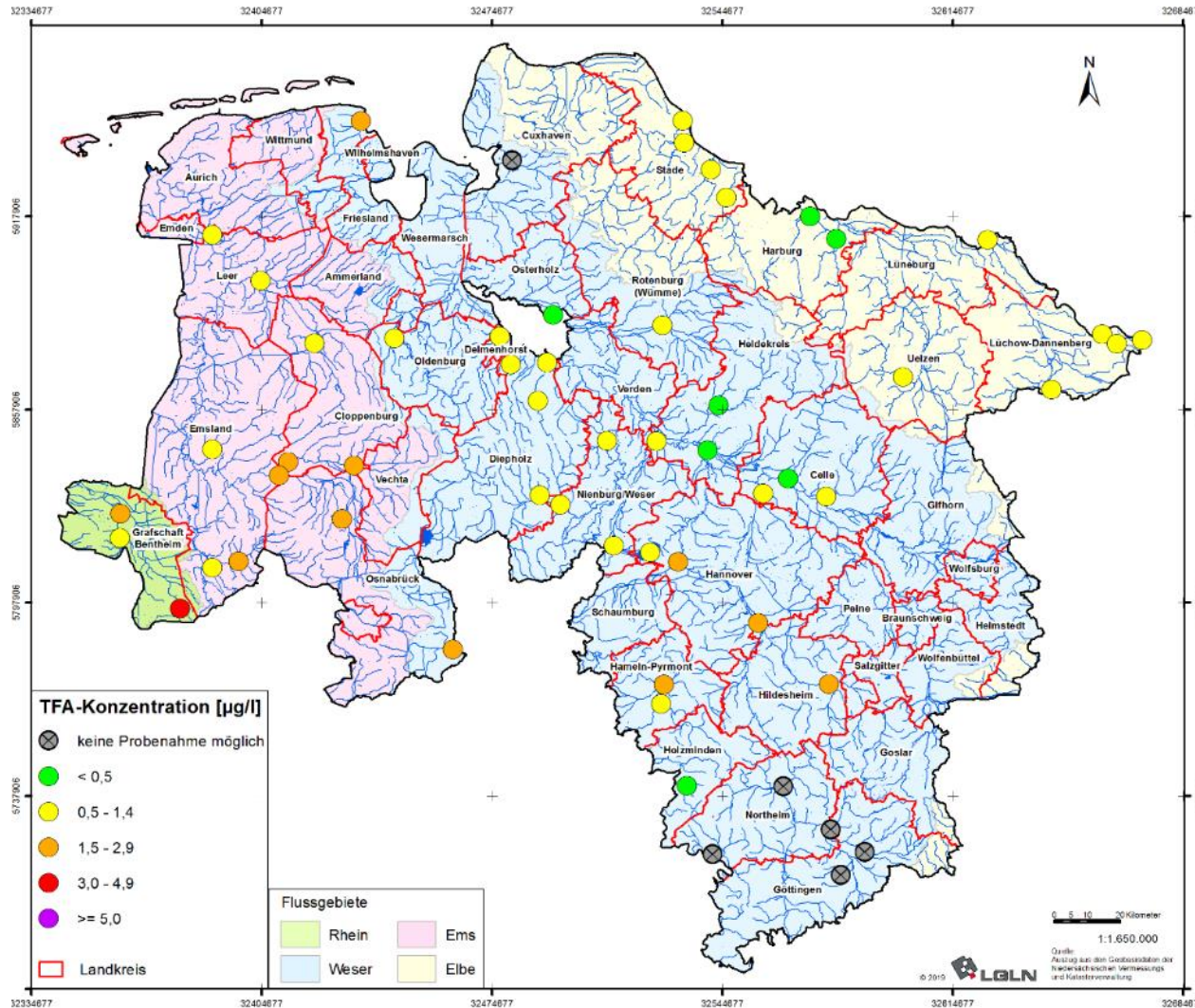
Badische Zeitung
Montag, 10. Oktober 2016
Chemikalie belastet Trinkwasserversorgung am Neckar

RHEIN-NECKAR-ZEITUNG
Trifluores Trinkwasser

TFA concentration in german tap waters (2016)

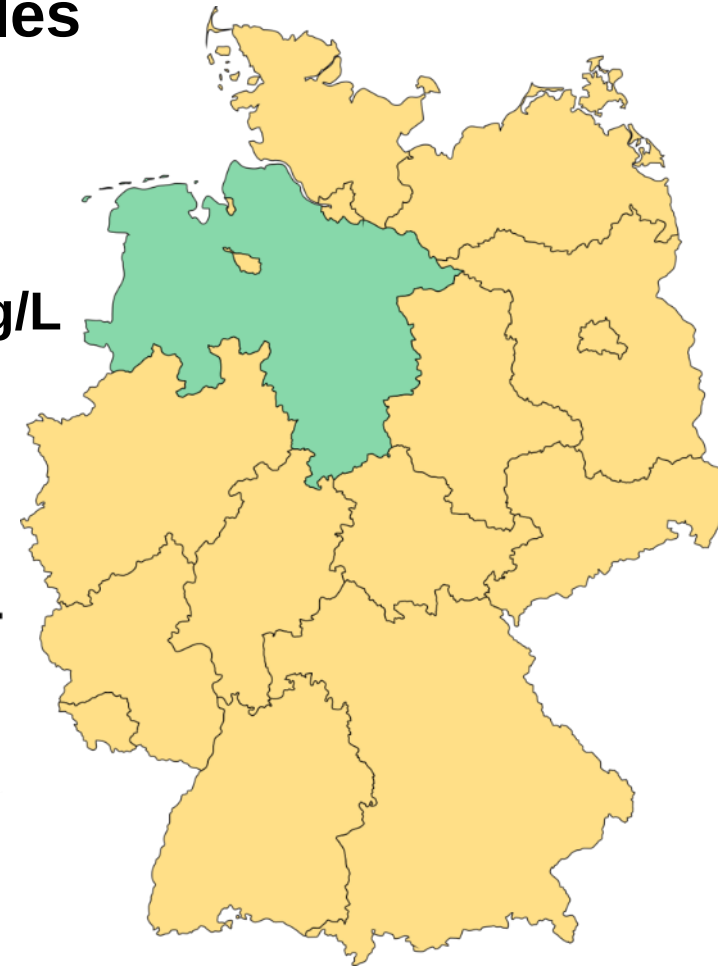
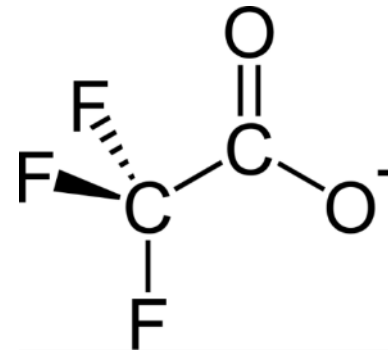


Surface water monitoring (May 2018, Lower Saxony, Germany)



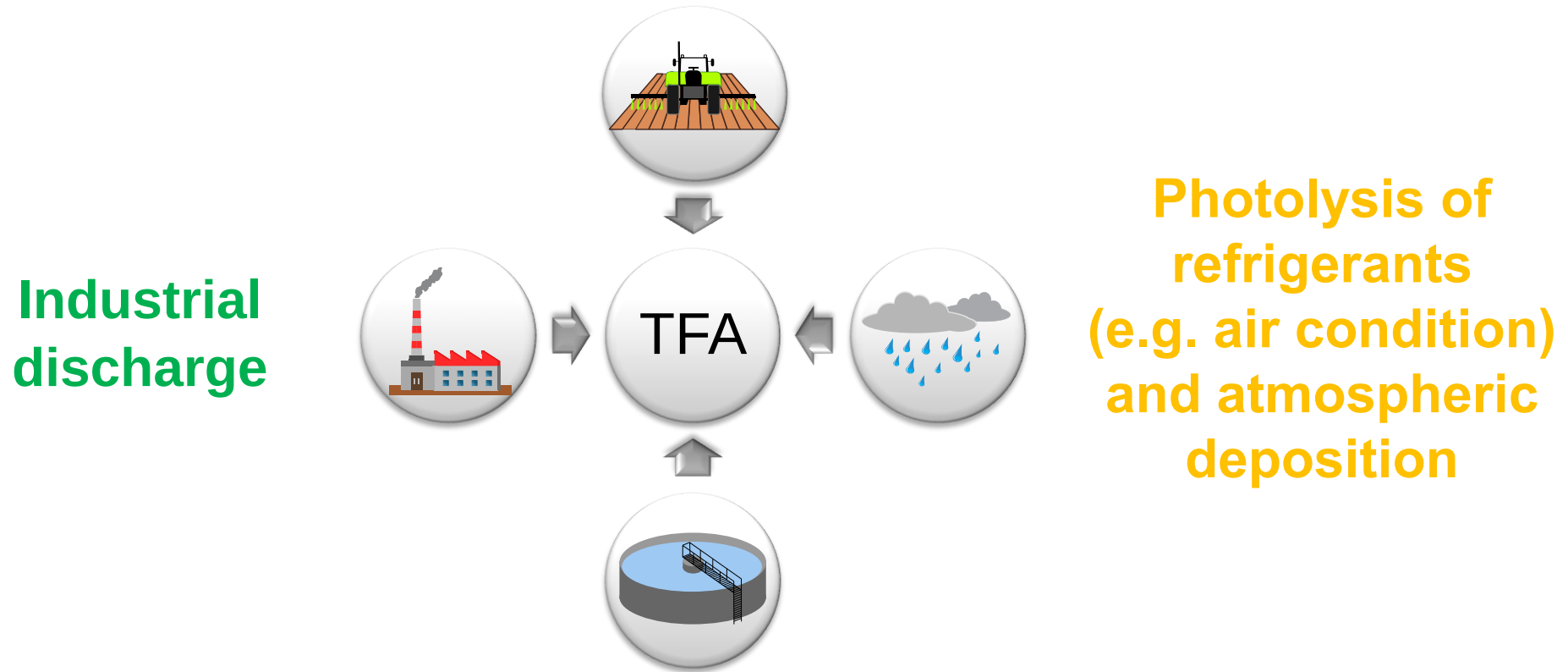
51 water samples

- Min. 0.23 µg/L
- Max. 3.0 µg/L
- Median 0.92 µg/L



- *Primary Source*
- *Secondary Source*

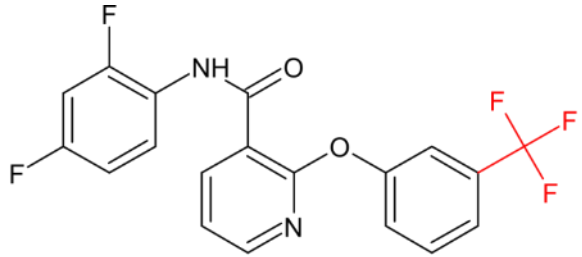
(Bio-)Degradation of selected plant protection products (PPP) → e.g. flufenacet



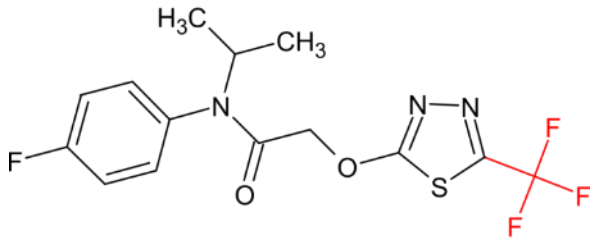
(Bio-)Degradation of selected pharmaceuticals
→ e.g. sitagliptin, etc.

Selected potential precursors to TFA (Part I: PPPs)

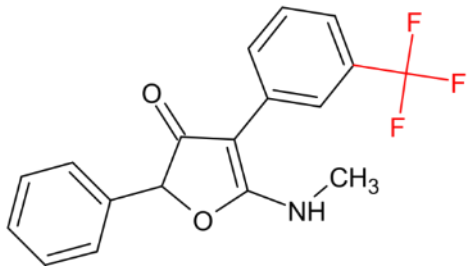
Domestic sales (Germany 2019)



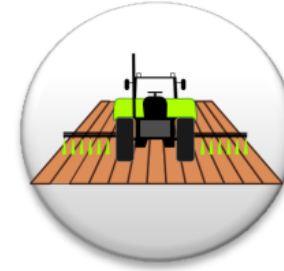
Diflufenican
250–1000 t/a



Flufenacet
250–1000 t/a

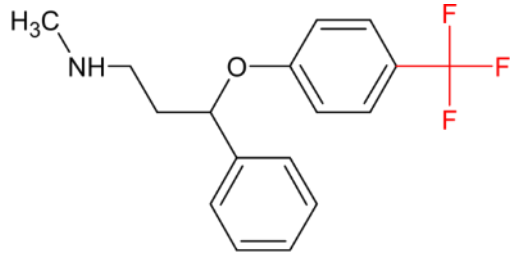


Flurtamone
25–100 t/a

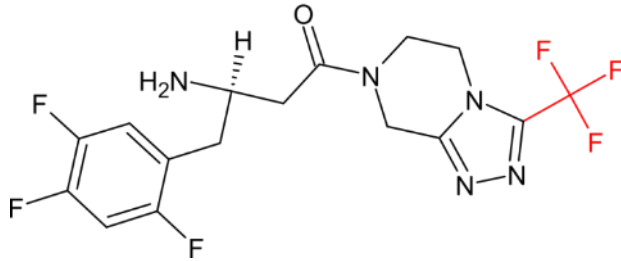


Selected potential precursors to TFA (Part II: Pharmaceuticals)

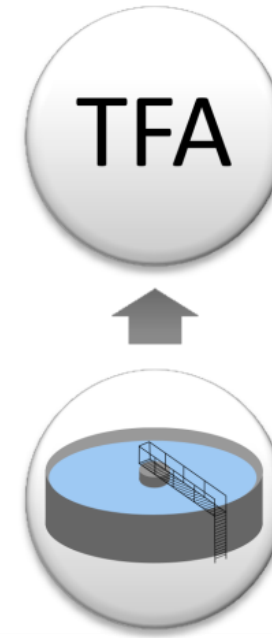
Prescription data (Germany 2019)



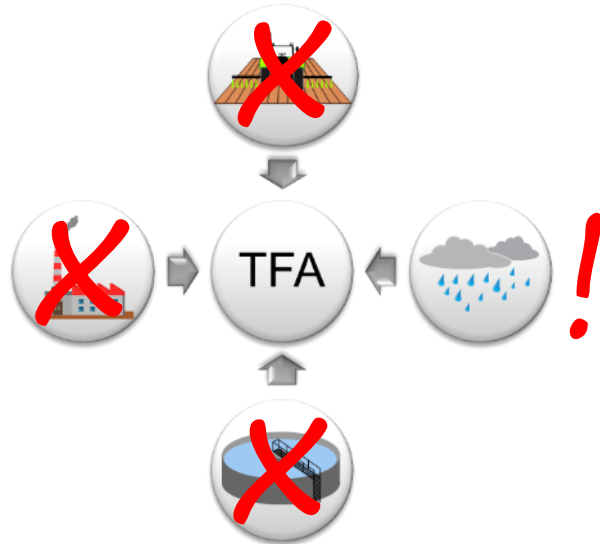
Fluoxetine
1.3 t/a



Sitagliptin
40 t/a

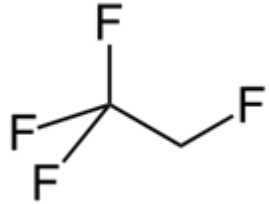
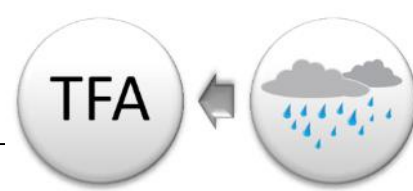


TFA concentration in german tap waters 2016 (excerpt)



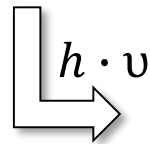
Wickenrode:
0.36 $\mu\text{g/L}$

Refrigerants as precursors to TFA



1,1,1,2-Tetrafluoroethane
(R-134a, Norflurane)

- REACH: 10,000–100,000 t/a
- High global warming potential



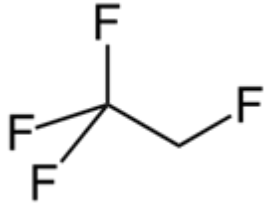
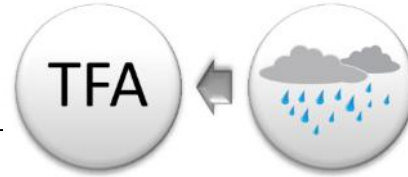
Transformation to TFA 7–20 %

Market forecast



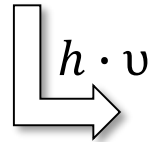
Continuous decline
in Europe

Refrigerants as precursors to TFA



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- REACH: 10,000–100,000 t/a
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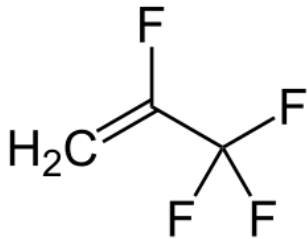


Transformation to TFA 7–20 %

Market forecast

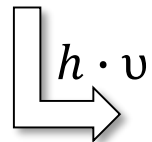


Continuous decline
in Europe



2,3,3,3-Tetrafluoropropene
(R-1234yf)

- REACH: 1,000–10,000 t/a
- Low global warming potential
- Rapid transformation ($t_{1/2}$: 2–11 d)



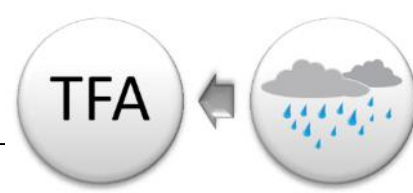
Transformation to TFA **100 %**

Market forecast



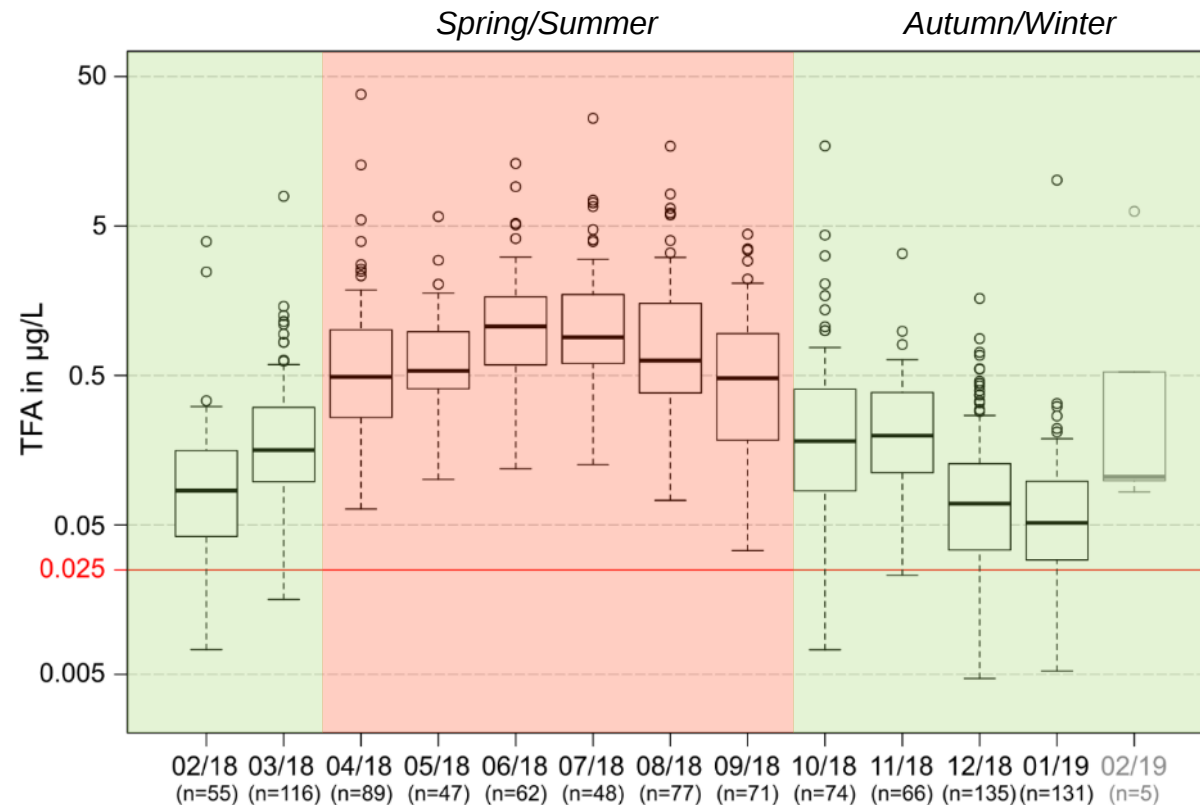
Sharp increase

TFA in precipitation (Germany, 8 locations, 2 years)

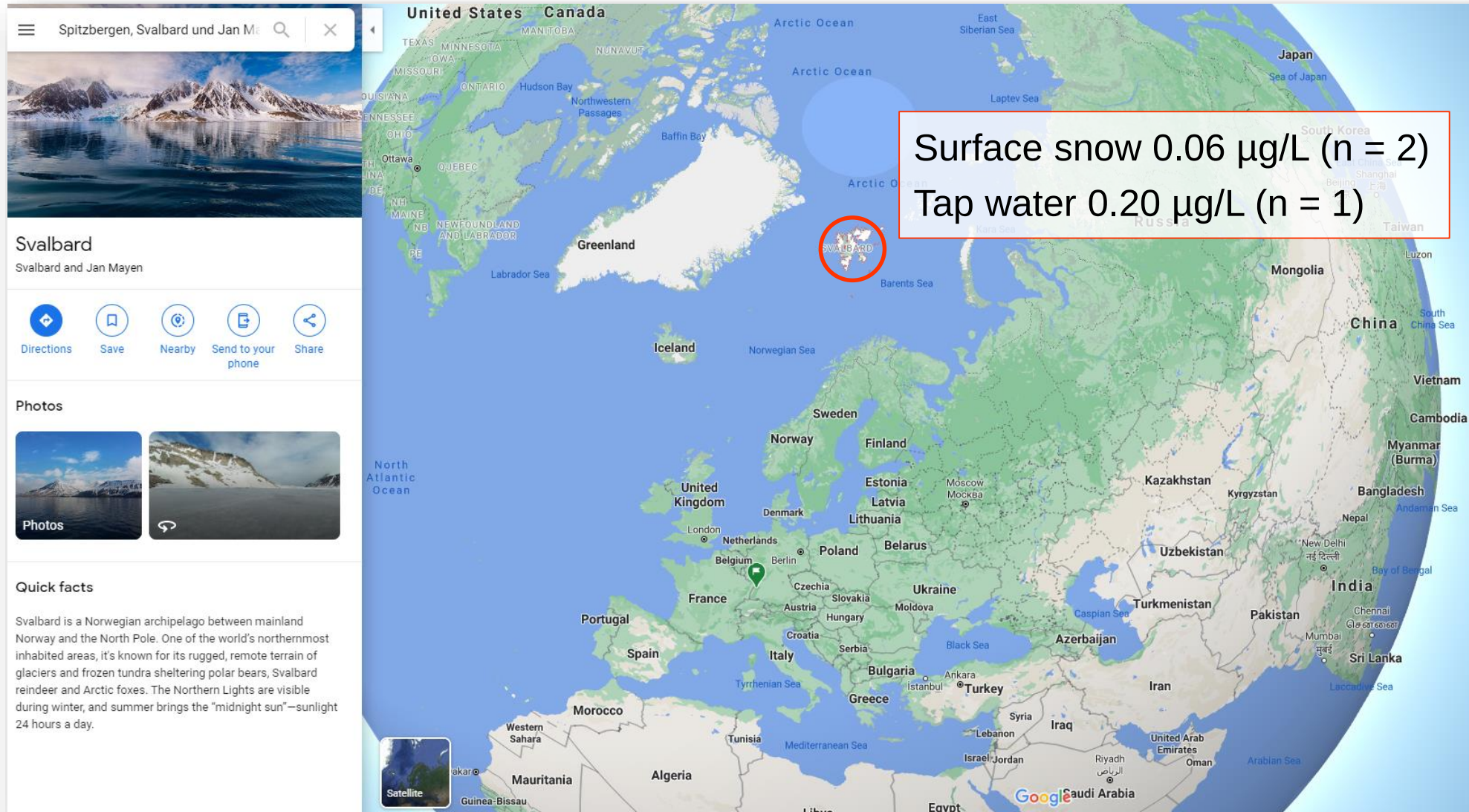
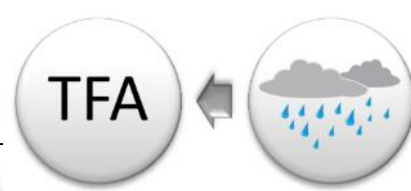


1. *Strong seasonal pattern*
2. *Precipitation-weighted average (PWA) **0.34 $\mu\text{g/L}$** (max. 38 $\mu\text{g/L}$)
→ **98 tons per year** in Germany (based on data from 2018)!*
3. ***Increasing concentration** cmpd. with 1995/1997 (0.08–0.11 $\mu\text{g/L}$ PWA)*¹*

¹ Klein (1997), Dissertation

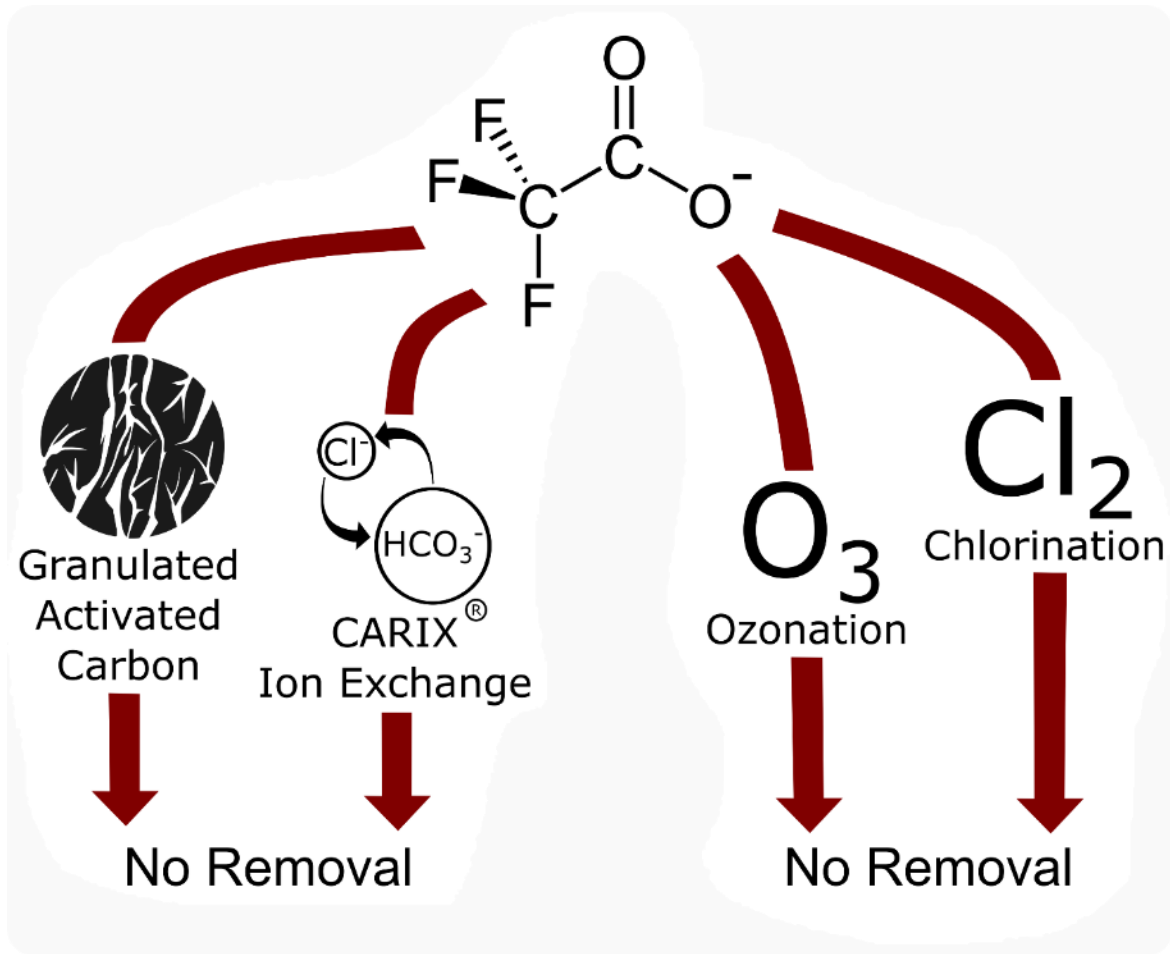
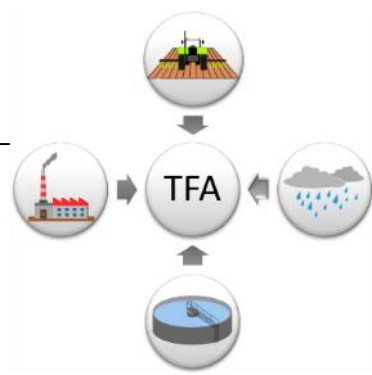


TFA in precipitation / tap water 2017 (Svalbard, Norway)



Thanks to Prof. Roland Kallenborn (Norwegian University of Life Sciences) for the samples!

TFA and drinking water treatment



→ TFA is very mobile!

$\log K_{OC}$: 0.79
no removal by GAC

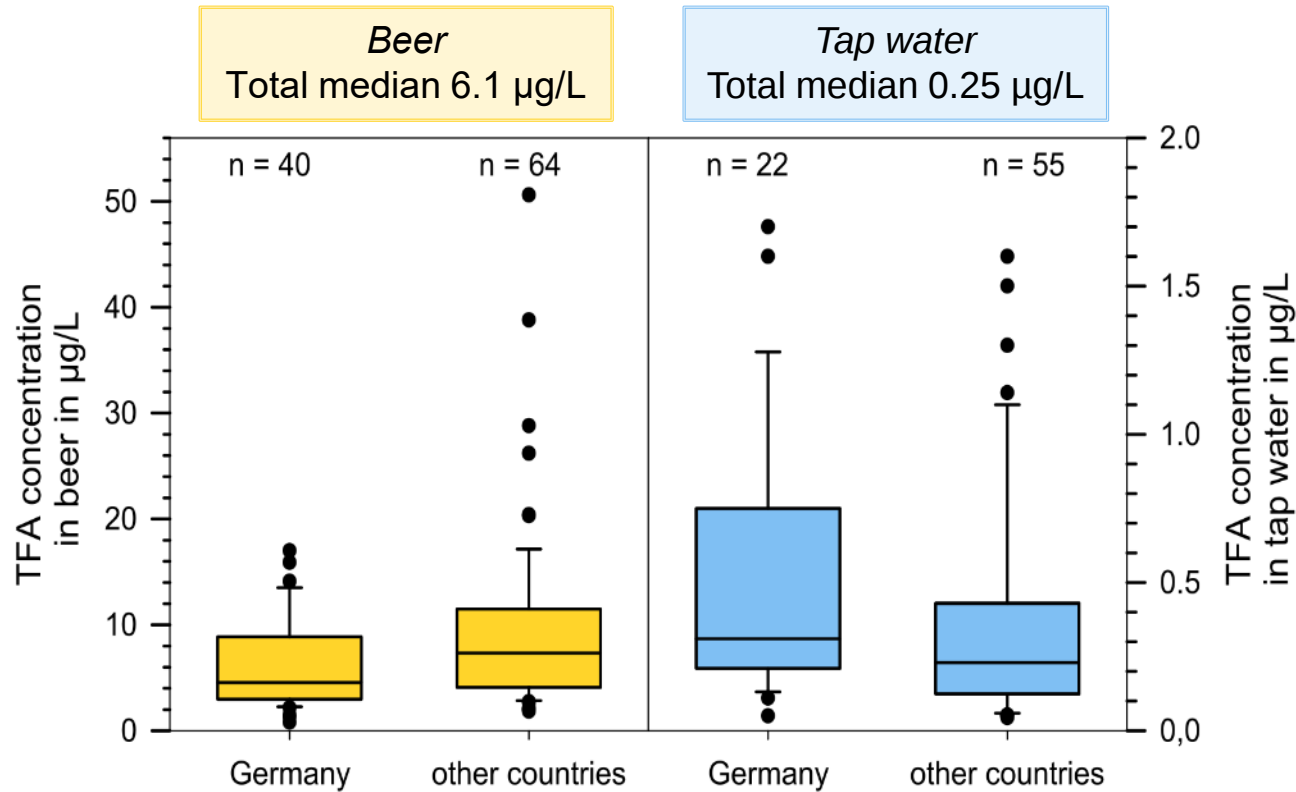
→ Many anions in raw water
ion exchange not economically
feasible

→ C-F bond is highly stable
no removal by oxidative
treatment

Drinking water protection $\rightleftharpoons$ Resource protection!

TFA in food samples and related matrices (I)

TFA

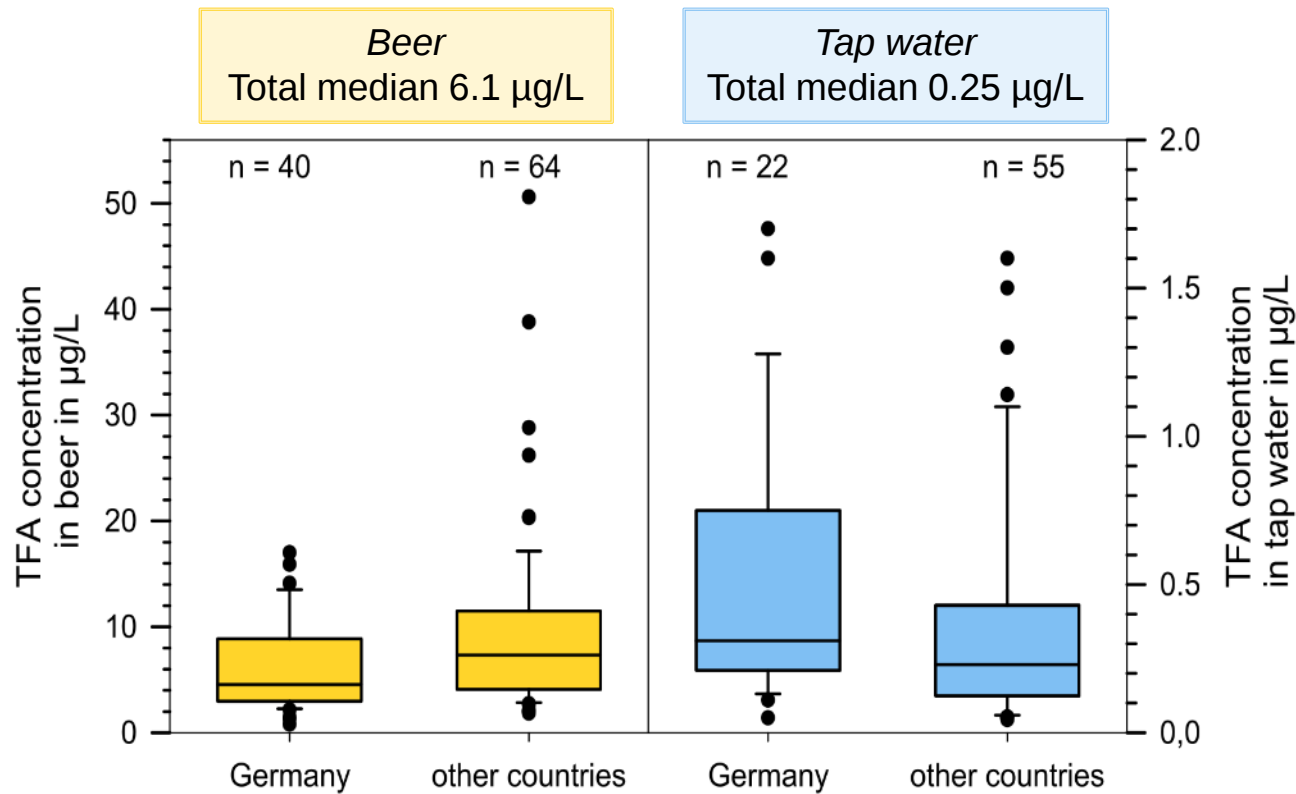
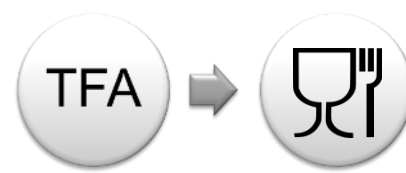


Malt is the major source of TFA in beer!

- *Correlation with K (potassium)*
- *Brewing test*



TFA in food samples and related matrices (II)



Malt is the major source of TFA in beer!

- Correlation with K (potassium)
- Brewing test

MAX. level detected in mg/kg and country of origin
0.23 (Grapes/IT)
0.23 (IT)
0.28 (Rye/Unknown)
0.11 (Orange/IT)
-
0.24 (Mango/ES)
-
0.087 (NZ)
0.10 (ZA)
0.65 (Green Beans/DE)
0.65 (DE)
0.27 (Tomato/DE)
0.12 (ES)
1.2 (Fennel inf./unknown)
4.8 (Rosemary/IL)
0.098 (Grape Juice/unknown)
0.29 (Endive lettuce/DE)
0.29 (DE)
-
-
0.15 (Potato/DE)
0.64 (Soybeans/ DE)
0.64 (DE)
0.47 (unknown)
0.15 (Carrots/DE)
0.15 (DE)
0.094 (Broccoli/DE)
0.075 (DE)
0.094 (DE)
0.076 (Apricot/FR)
0.12 (Wine/DE)
1.3 (Mixed Veg./unknown)

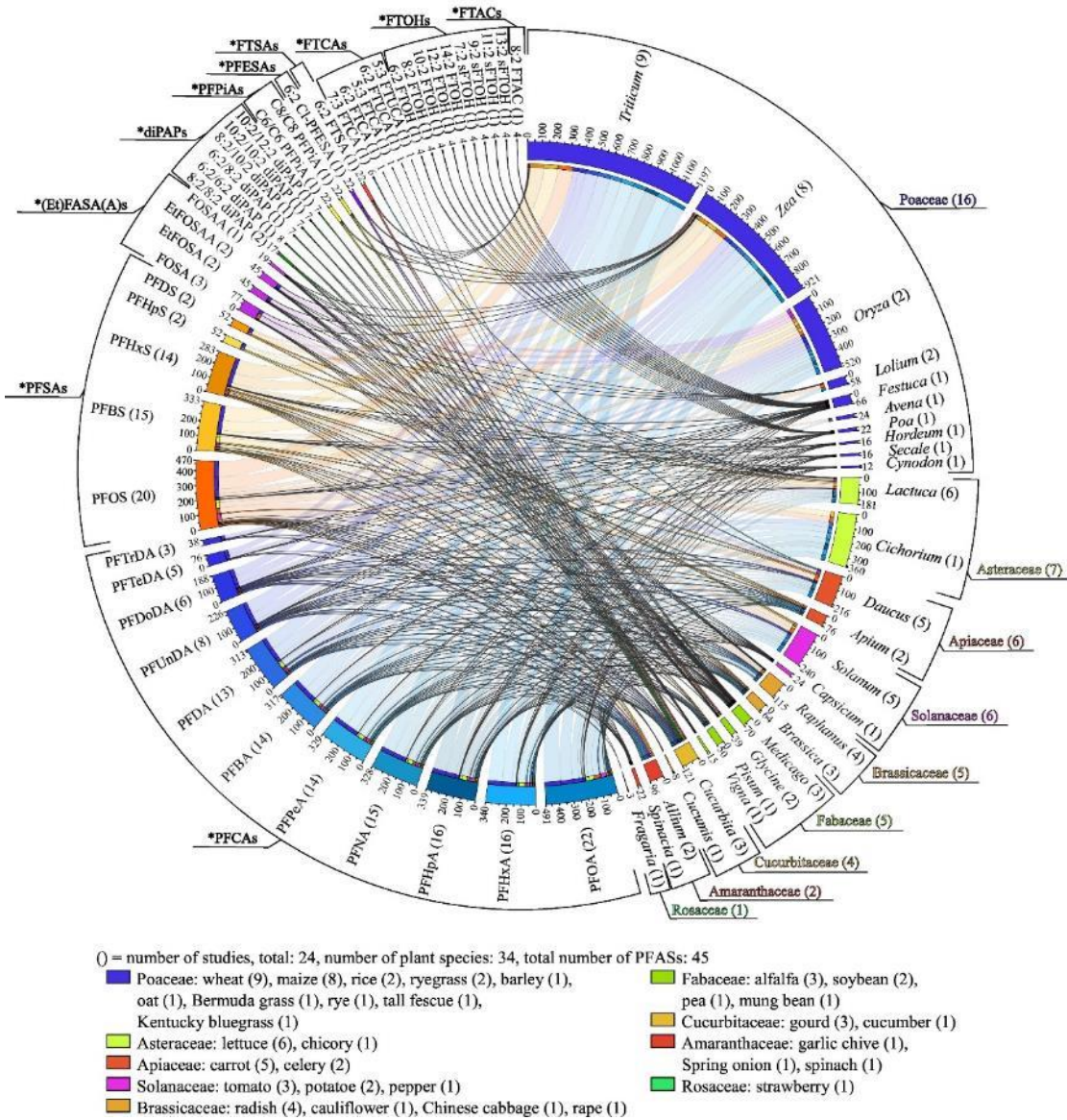
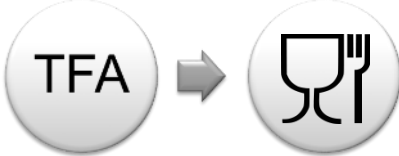
- Human blood: 8.5 µg/L^{*2}
(n = 252)
- Human urine: ~10 µg/L
(n = 1)
- Manure: ~100 µg/L^{*3}
(n = 2)

^{*1} EURL-SRM – Residue Findings Report (2017)

^{*2} Duan et al. (2020), Environ. Int. 134, 105295.

^{*3} Nödler et al. (2019), <https://www.nlwkn.niedersachsen.de/download/141156>

TFA in food samples and related matrices (III)



MAX. level detected in mg/kg*1 and country of origin
0.23 (Grapes/IT)
0.23 (IT)
0.28 (Rye/Unknown)
0.11 (Orange/IT)
-
0.24 (Mango/ES)
-
0.087 (NZ)
0.10 (ZA)
0.65 (Green Beans/DE)
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- Human blood: 8.5 µg/L*2 (n = 252)
- Human urine: ~10 µg/L (n = 1)
- Manure: ~100 µg/L*3 (n = 2)

*1 EURL-SRM – Residue Findings Report (2017)

*2 Duan et al. (2020), Environ. Int. 134, 105295.

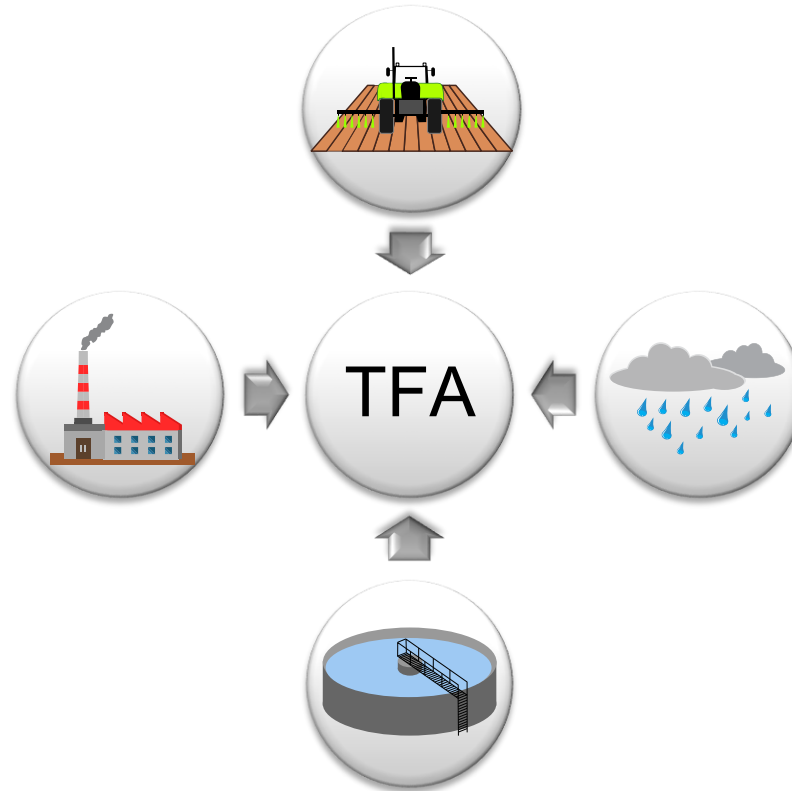
*3 Nödler et al. (2019), <https://www.nlwkn.niedersachsen.de/download/141156>

- **Primary Source**
- **Secondary Source**

(Bio-)Degradation of selected plant protection products (PPP) → e.g. flufenacet, diflufenican, etc.

Manure

Industrial discharge

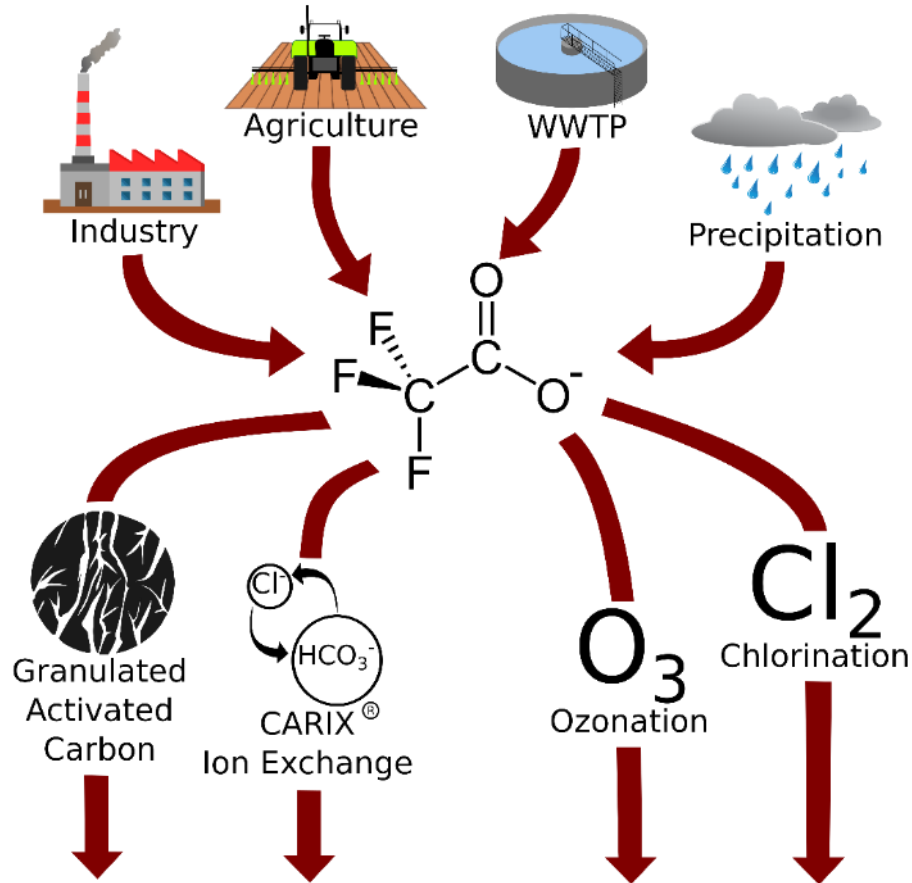


Photolysis of refrigerants (e.g. air condition) and atmospheric deposition

(Bio-)Degradation of selected pharmaceuticals → e.g. sitagliptin, fluoxetine, etc.

Urine

Conclusions



TFA

- is everywhere
- comes from multiple **primary** and **secondary** sources
- in DW-treatment, it cannot be removed in an economically and ecologically sensible way.

Discussion on the essential use of TFA and its precursors is necessary!

Conclusions

CO₂ as a refrigerant instead of TFA-precursors



Das fluoridierte Kältemittel R1234yf wird in immer höheren Konzentrationen in der Atmosphäre nachgewiesen. Es entweicht vor allem aus Pkw-Klimaanlagen und zunehmend auch aus stationärer Kälte-Klima-Technik. Die extrem wasserlösliche, algengiftige und schwer abbaubare Trifluoressigsäure – ein Abbauprodukt von R1234yf – gelangt über Niederschläge in Gewässer. Das UBA rät zum Umstieg auf Alternativen.

TFA

- is everywhere
- comes from multiple **primary** and **secondary** sources
- in DW-treatment, it cannot be removed in an economically and ecologically sensible way.

Discussion on the essential use of TFA and its precursors is necessary!

References in order of appearance

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- Nödler K, Scheurer M (2019): Substances from Multiple Sources (SMS): The presence of multiple primary and secondary sources of persistent and mobile organic contaminants is an upcoming challenge for the drinking water sector and regulatory frameworks. *Environmental Science & Technology* 53, 11061–11062.