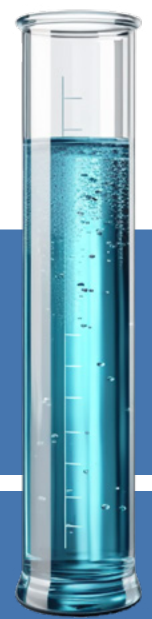
Report

TFA in Water

Dirty PFAS Legacy Under the Radar

May 2024



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TFA in Water

List of Abbreviations

ECHA: European Chemicals Agency

EFSA: European Food Safety Authority

IARC: International Agency for Research on Cancer

PAN: Pesticide Action Network

PFAS: Per- and polyfluoroalkyl substances

PFOA: Perfluorooctanoic acid

PFOS: Perfluorooctane sulfonic acid

REACH: Registration, Evaluation, Authorisation, and Restriction of Chemicals

TFA: Trifluoroacetic acid

UBA: Umweltbundesamt (Federal Environment Agency of Germany)

Key Findings

In February 2024, a joint research by the European Pesticide Action Network (PAN Europe) and its members revealed a sharp increase in the contamination of European fruit and vegetables with pesticides from the problematic chemical group of PFAS, also known as 'forever chemicals'. The current report focuses on their terminal degradation product, the highly persistent chemical trifluoroacetic acid (TFA). We analysed 23 surface water and six groundwater samples from ten EU countries for TFA residues and other PFAS. The extent of the contamination is alarming and calls for decisive action. The key findings are:

A) All water samples analysed contained PFAS. More than 98 per cent of the total PFAS detected were TFA, a known degradation product of PFAS pesticides and other PFAS.

B) 79% of the samples had TFA levels exceeding the proposed[1] EU Drinking Water Directive limit of 500 ng/l (nanograms per litre) for total 'PFAS'.

C) None of the other 23 PFAS analysed in this study exceed their respective limits proposed[2] in the EU Drinking Water Directive.

D) The detected TFA levels ranged from 370 ng/l to 3,300 ng/l with an average of 1,180 ng/l. The average level of the sum of all other 23 PFAS together was 17.5 ng/l.

E) The TFA levels found in surface and groundwater represent the largest known area-wide water contamination by a man-made chemical.

F) PFAS pesticides appear to be the main cause of water contamination with TFA in rural areas, followed by refrigerants, sewage treatment and industrial pollution.

G) The regrettable categorisation of TFA as a 'non-relevant' metabolite under the EU Pesticide Regulation has hindered effective groundwater protection in the EU.

H) The EU Water Framework Directive's 'prohibition of deterioration' should have prevented decades of escalating TFA pollution, yet it has failed to do so.

I) The narrative that short-chain PFAS (like TFA) are harmless originates from the PFAS manufacturing industry but is increasingly challenged by current scientific evidence.

J) Growing resistance from the largest political group in the European Parliament is threatening the proposed group ban on PFAS.

The extent of this contamination is shocking. It is a result of political failure at many levels. What is needed now is swift and decisive action, including: (i) a rapid ban on PFAS pesticides by considering persistence of a synthetic active substance or that of its metabolites as an unacceptable effect on the environment, (ii) the implementation of the new Persistent, Mobile and Toxic (PMT) and very Persistent and very Mobile (vPvM) hazard classes under the EU Pesticide Regulation, (iii) the implementation of the general PFAS restriction under the REACH Chemicals Regulation, (iv) the categorisation of TFA as a 'priority substance' under the Water Framework Directive, and (v) monitoring obligations and limit values for TFA.

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[1] The limit value for «total PFAS» in the EU Drinking Water Directive is 500 ng/l. However, not all EU countries have committed to complying with this upper limit for PFAS in their national regulations.

[2] The limit value «sum of PFAS» in the EU Drinking Water Directive is 100 ng/l. It refers to 20 selected PFAS. TFA is not included.

Background

2.1 Persistent and Toxic

Few categories of chemicals currently pose as significant a challenge for regulatory bodies as per- and polyfluorinated alkyl substances (PFAS), often referred to as 'forever chemicals'. This group of substances combines unparalleled persistence with unpredicted toxicity. Their extensive and unregulated use in industrial and consumer products since the mid-20th century has resulted in PFAS becoming increasingly pervasive in both living organisms and the environment worldwide to levels that raise questions regarding the reversibility of that pollution. At the same time, we are increasingly recognizing the significant hazards and risks PFAS pose to human health.

Health authorities globally have been compelled to revise their assessments of PFAS toxicity multiple times. Until the beginning of 2018, for example, a daily intake of 1,500 nanograms[3] of PFOA[4] per kilogramme of body weight was considered safe in the EU[5]. Currently, the EU food authority EFSA considers a maximum of 0.7 nanograms per kilogram of body weight per day[6] to be tolerable for health reasons – a threshold unfortunately exceeded by significant portions of the European population[7].

The health damage caused by PFAS, as it has been demonstrated in animal experiments, and in some cases, directly in humans, includes malformations in foetuses, testicular and kidney cancer, cardiovascular diseases, impaired fat metabolism, obesity and impairment of the immune system.

In April of this year, the legal drinking water limits applicable in the USA for some widely used PFAS were massively reduced. Specifically, the limits were set to 4 ng/l for PFOA and 4 ng/l for PFOS[8], and to 10 ng/l for PFNA (Perfluorononanoic acid), PFHxS (Perfluorohexane sulfonic acid), and 'GenX Chemicals', respectively. This corresponds to less than one drop in a 5,000 cubic metre swimming pool. And even this extremely small amount is not risk-free, as *there is no level of exposure to these contaminants without risk of health impacts, including certain cancers. A non-enforceable health-based goal, at zero would therefore be desirable from a health perspective,* as the US authority stated in its press release.

3 While in the past toxicological guideline values and legal limits for PFAS were often given in micrograms (µg/kg or µg/l), they are now increasingly given in nanograms per litre or kilogram in the literature and legislation. For reasons of clarity, concentrations are uniformly stated in nanograms per litre or kilogram in this report.

4 PFOA (Perfluorooctanoic acid) is the best-known representative of the PFAS subgroup «perfluorinated carboxylic acids», the same group to which TFA, as its shortest-chain representative, belongs. PFOA is a first-generation PFAS whose toxicological profile - unlike that of TFA - has been very well studied. The risks to health and the environment of PFOA are manifold and meanwhile undisputed and led to EU-wide restrictions in 2020.

5 EFSA (2008); Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts Scientific Opinion of the Panel on Contaminants in the Food chain; https://efsa.onlinelibrary.wiley.com/doi/10.2903/j.efsa.2008.653

6 EFSA (20208); Risk to human health related to the presence of perfluoroalkyl substances in food; https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2020.6223

7 HBM4EU (2022) Policy Brief PFAS https://www.hbm4eu.eu/wp-content/uploads/2022/06/HBM4EU_Policy-Brief-PFAS.pdf

8 PFOS (Perfluorooctane sulfonic acid) is a first-generation PFAS that has been restricted in the EU since 2010. Its negative impact in environment and human health are - as in the case of PFOA - well investigated and well understood.

2.2 Group Ban with a Tricky Exception

PFAS are currently a prominent topic in the media and high on the political agenda. The importance of this focus was underscored by an Europe-wide network of journalists in the Forever Pollution Project, which revealed in early 2023 that nearly 23,000 sites across Europe are verifiably contaminated with PFAS, with an additional 21,500 suspected contamination sites identified.

As part of the European Green Deal, the European Union has committed to gradually ban PFAS chemicals in line with the goal of a pollutant-free environment. Since February 2023, the European Chemicals Agency (ECHA) has had a proposal for a group ban on the manufacture, use and import of PFAS. The proposal applies to all chemicals that fall under the OECD definition of PFAS. This means they have at least one fully fluorinated C atom (without any H/Cl/Br/I attached). This definition includes more than 10,000 PFAS. However, there are some exceptions to the ban. For applications for which there is not yet a functional PFAS-free alternative, time-limited transitional periods are possible. Pesticide and biocide active substances and pharmaceuticals are generally exempt from the PFAS group ban. This is explained by the fact that these subgroups of the PFAS family are regulated in separate regulations. However, there have recently been growing doubts about whether these regulations adequately address the particular dangers resulting from the unprecedented persistence of PFAS.

When asked by EUREAU, the umbrella organisation of European drinking water suppliers, whether PFAS pesticides would be banned under the EU Pesticides Regulation, the European Commission replied that it would *'initiate discussions with Member States regarding the way forward.'* So far not a single pesticide active substance has been banned because it is a PFAS.

Decisive action should be taken on this issue because, as we will see below, PFAS pesticides are among the largest sources of PFAS contamination worldwide, as they are a major source of trifluoroacetic acid (TFA) formation.

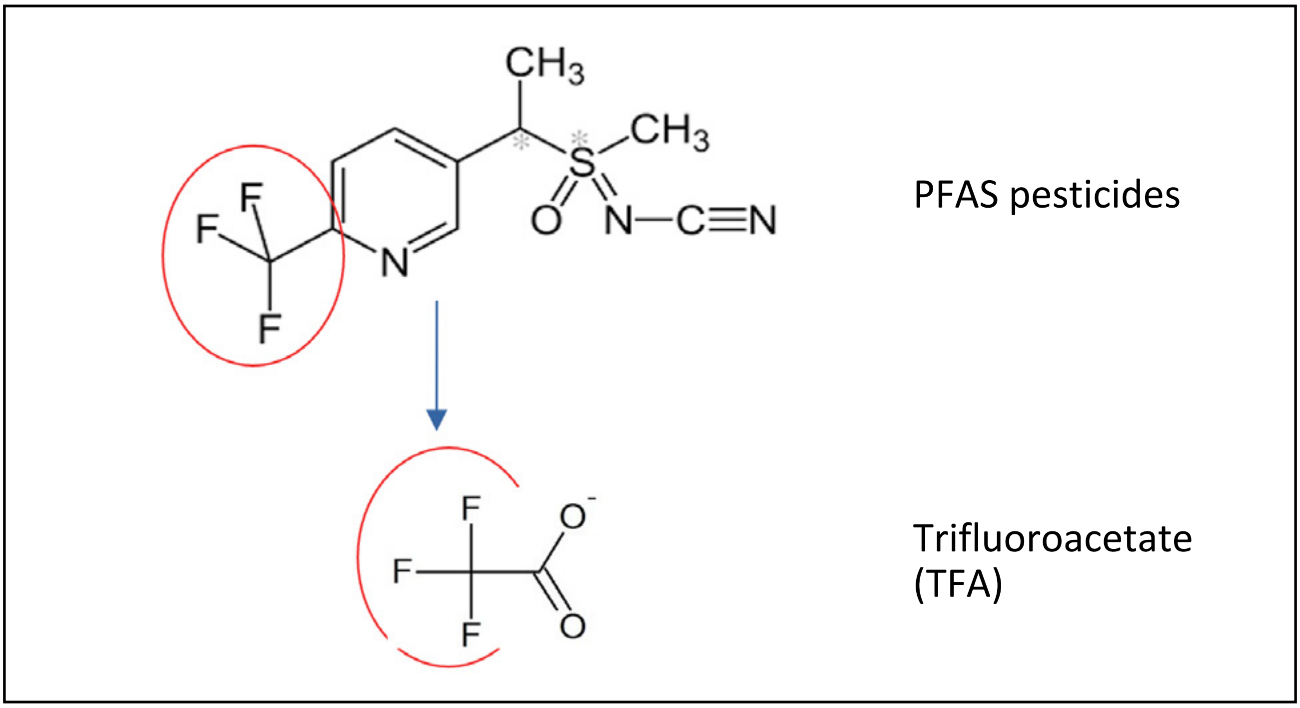

Figure 1. *Carbon-bonded perfluorinated methyl groups in pesticide, biocide and pharmaceutical active ingredients are converted into TFA by oxidative cleavage under environmental conditions.*

2.3 TFA - Threatening our Water

Hardly any man-made chemical is more stable than TFA. In addition, TFA is extremely mobile and highly soluble in water. The combination of these properties makes TFA the 'perfect' groundwater contaminant. The natural filter and buffer function of the soil to remove pollutants from leachate does not work with chemicals such as TFA. They can enter the groundwater almost unhindered and remain there for centuries. Moreover, the usual drinking water treatment processes cannot remove TFA[9].

Among the most important precursors of TFA are the already mentioned pesticides, biocides and pharmaceuticals with perfluorinated methyl groups, but also refrigerants from the PFAS group, so-called ‘F-gases’. The latter are emitted from various cooling systems into the atmosphere, where they undergo photolytic conversion to TFA and then enter the water cycle through rainfall, worldwide. Another potential source of TFA contamination of rivers is the direct discharge of TFA-containing wastewater by the PFAS manufacturing industry, which uses TFA as a raw material for the production of other PFAS.

A recent research project, conducted by the German German Federal Environment Agency (UBA; Umweltbundesamt) estimated the potential emissions of TFA into the environment in Germany from various sources. The modelling considered factors such as the average quantities of pesticide applied to major crops in terms of area, annual sales volumes of PFAS pharmaceuticals, and the annual average concentration of TFA in rain, measured at various monitoring sites and linked to the corresponding regional precipitation quantities.

The results, as shown in Figure 2, indicate that pesticides have the highest potential for TFA release in the water bodies considered, estimated at 434 tonnes per year, followed by F-gases with 96 tonnes, and sewage treatment and liquid manure each contributing around 20 tonnes annually. Data on industrial emissions (direct discharge) were not available, but they are considered 'relevant'.[10]

Based on the available data on agricultural land use, precipitation, wastewater treatment plants and industrial activities, UBA experts calculated that in 303 out of 400 German districts, the dominant pathway for TFA into water bodies is the use of PFAS pesticides, followed by precipitation (51 districts), wastewater treatment plants (38 districts) and industrial contamination (9 districts).

Possible uncertainties in the modelling arise from the assumption that TFA emissions from PFAS pesticides were calculated based on a conservative estimate of 100% molar conversion

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[9] TFA cannot be removed from water by filters (activated carbon) or ozonation; it can only be removed by reverse osmosis. However, this technology requires more resources, leads to higher energy costs, and raises the unresolved issue of disposing of the resulting concentrates.

[10] UBA (2023): Trifluoracetat (TFA): Grundlagen für eine effektive Minimierung schaffen - Räumliche Analyse der Eintragspfade in den Wasserkreislauf: https://www.umweltbundesamt.de/publikationen/trifluoracetat-tfa-grundlagen-fuer-eine-effektive

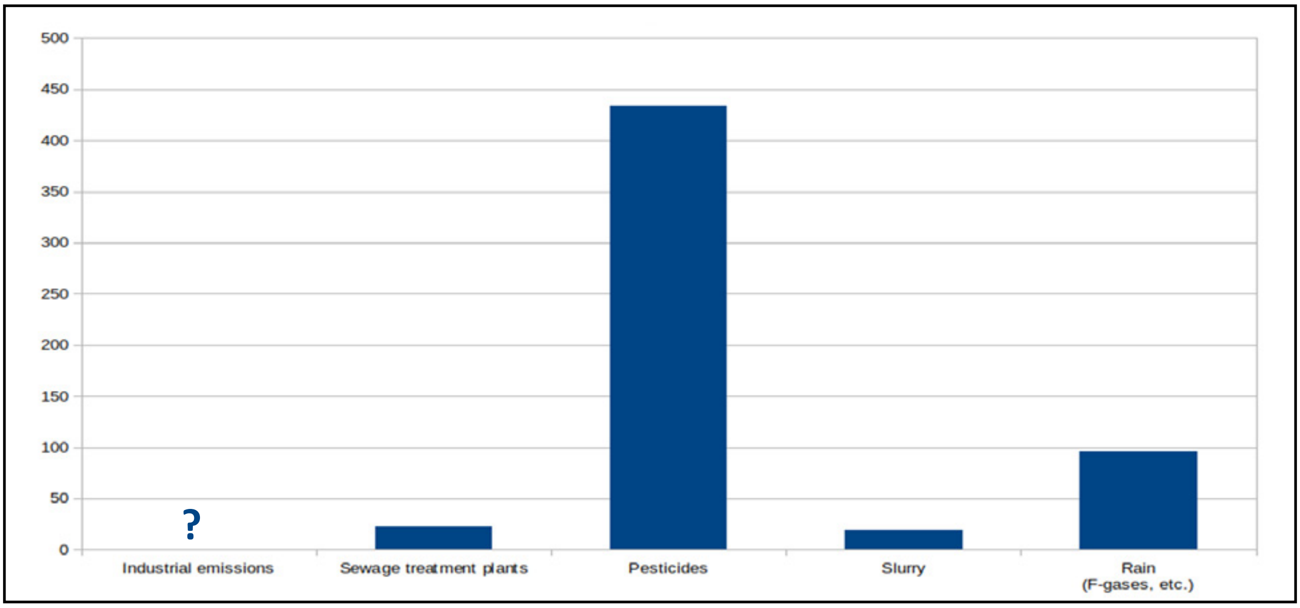

Figure 2. *Average potential annual TFA release from various sources and input pathways (source: [UBA 2023](), p.52)*

of CF3 groups into TFA. This assumption may have led to an overestimation of pesticide-driven TFA emissions. Additionally, pesticide applications were considered only for crops with available data in Germany, potentially leading to an underestimation of emissions.

Despite these uncertainties, the calculations exhibit a strong correlation with real-world average TFA levels measured in surface and groundwater. In regions with a high proportion of arable land, average TFA levels are significantly higher (1,660 ng/L) than in areas where agricultural inputs are not expected but precipitation is the dominant input pathway (670 ng/L), according to the UBA study. The highest average pollution levels measured (2,280 ng/L), however, were found in areas where industrial emissions dominate, which is only the case in a limited number of districts.

Although the aforementioned calculations were conducted using data from Germany, it is reasonable to assume that this holds true for other European countries too. In regions where conventional agriculture is practised, a significant, if not predominant, portion of TFA input into water bodies can be attributed to the use of PFAS pesticides. This conclusion is supported by surveys on the sale of PFAS pesticides in other countries, such as those conducted in France by Generations Futures, which indicate an upward trend in the use of these pesticides.

It is worth emphasising that farmers generally lack information regarding whether plant protection products contain PFAS pesticides, as this information is not provided on product labels or safety data sheets.

2.4 Legal Obligation for Water Protection

Our investigation results show that the "PFAS issue", which first became known to a wider public two decades ago in connection with the Dark Waters scandal and has since been understood primarily as a problem of highly contaminated, but locally limited, ‘contamination hot spots’, has meanwhile become an even greater problem. It has affected all water bodies in Europe. The average concentration of C2-PFAS trifluoroacetic acid is of a magnitude that is reminiscent of the concentrations that were detected at many hot spots with C8 and C6 PFAS as part of the Forever Pollution Project.

In the EU, water is considered a highly protected resource. Various European laws aim to protect water from pollutants. This applies in particular to pesticide active substances and their ‘metabolites’ (i.e. both transformation and degradation products).

According to the EU Pesticide Regulation, pesticides may only be authorised if it has been proven that, under realistic application conditions, the concentration of the active substance in groundwater does not exceed a threshold value of 100 ng/l. In principle, this also applies to its degradation or reaction products, also known as ‘metabolites’. However, with the restriction that these fulfil the criteria for ‘relevant metabolites’ defined in the EU Pesticide Regulation[11]. These criteria require that the metabolites:

a) have inherent properties comparable to those of the starting material with regard to the desired biological activity,

b) or pose a comparable risk to organisms as the parent substance,

c) or have certain toxicological properties that are considered unacceptable.

To our knowledge, the first time that the "metabolite" TFA was assessed as a degradation product of a PFAS pesticide was in 2003 as part of the approval process of the active substance flurtamone which is no longer authorised in the EU since 2018[12]. The decision of the EU authorities was to classify TFA as a ‘non-relevant’metabolite, although they recognised that the toxicological information provided to the competent committee was insufficient. The reason for this was that it was considered that point (a) above was not fulfilled, and in relation to point (b) and especially point (c) - unlike today[13]- no data appeared to be available at the time that indicated unacceptable environmental risks or unacceptable toxicological properties.

The ‘insufficient’ data set is not surprising, as the authorisation procedure does not generally require studies on reproductive toxicity or cancer for the evaluation of metabolites.

Above all, however, the fact that the EU Pesticide Regulation does not recognize the combination of extreme mobility and ultimate persistence as sufficient grounds for classifying a metabolite as 'relevant'—despite this combination being a de facto 'guarantor' of groundwater contamination—has proven to be a terrible mistake.

[11] Additional guidance for interpreting the criteria set out in the regulation is provided in the “Guidance Document on the Assessment of the Relevance of Metabolites in Groundwater of Substances Regulated under Regulation (EC) No 1107/2009”

[12] European Commission, 2013. Review report for the active substance flurtamone. Health and Consumer Protection Directorate-General. [Sanco/10162/2003-Final]

[13] Serious health concerns associated with TFA arose from a two-generation study commissioned by the industry, revealing birth defects (eye malformations) across all three dose groups in rabbits. Subsequently, in spring 2024, Germany proposed to the European Chemicals Agency (ECHA) to classify TFA as toxic for reproduction (category 1B) based on the REACH registration dossier.

Like their pesticide parent substances, 'relevant' metabolites must not be present in groundwater in concentrations of more than 100 ng/litre. This limit also applies to drinking water. If TFA had been recognized as a relevant metabolite, groundwater protection regulations would have prohibited the authorization of all active substances that degrade into TFA, unless it could be assured that groundwater levels would remain below 100 ng/l despite their use, which is obviously not the case. The misclassification of TFA as 'non-relevant' has therefore saved the marketing of PFAS pesticides in the EU. But it has also enabled what is probably the largest systematic contamination of our water with a man-made chemical.

One could now argue that F-gases, which are also a significant cause of TFA contamination in European water bodies (as demonstrated in section 2.3), would not be directly affected by the classification of TFA as a relevant metabolite. That's correct. However, it can be speculated that the EU-wide monitoring obligations for a 'relevant metabolite' TFA, and the resulting data on the ever-increasing TFA pollution, would have triggered the regulation of all relevant sources of TFA contamination, above all F-gases.

This leads us to the Water Framework Directive 2000/60/EC and its daughter directives, the Groundwater Directive 2008/118(EC) and the Directive on quality standards in the field of water policy 2008/105/EC. The central aim of these laws is to achieve 'good status' for Europe's rivers, lakes and groundwater. In particular, water pollution must not increase ('prohibition of deterioration'). Rather, it must be reduced.

To this end, the status of the water bodies in each catchment area must be monitored with regard to the relevant pollutants. If necessary, measures to reduce pollutants must be introduced. This is particularly clearly regulated with regard to groundwater in Article 4 of the Water Framework Directive, which states:

> *"Member States* ***shall implement the measures necessary to reverse any significant and sustained upward trend in the concentration of any pollutant resulting from the impact of human activity*** *in order progressively to reduce pollution of groundwater."*

In the case of TFA, all conditions were met that would have required the introduction of measures to reduce pollution by law. TFA undoubtedly fulfils the criterion of a 'main pollutant' within the meaning of the Water Framework Directive[14] and also shows a 'significant and sustained upward trends' in all water bodies; a creeping but steady increase that has been going largely unnoticed by the public for decades, but which has been predicted or described by scientific experts since the 1990s[15, 16, 17] and has already materialised. In Germany, for example, the measured TFA levels in rainwater have increased fourfold in two

[14] "Organohalogen compounds" are listed at the top of the Water Framewrk Directive's 'non-exhaustive list of key pollutants' (Annex VIII). PFAS belong to the group of organohalogen compounds. Consequently, despite not being classified as a relevant metabolite under the EU pesticide regulation, the pollution by TFA should have been recognised and combated due to the monitoring obligations in the Water Framework Directive.

[15] Likens GE, Tartowski SL, Berger TW, Richey DG, Driscoll CT, Frank HG, Klein A. Transport and fate of trifluoroacetate in upland forest and wetland ecosystems. Proc Natl Acad Sci U S A. 1997 Apr 29;94(9):4499-503. doi: 10.1073/pnas.94.9.4499. PMID: 9114018; PMCID: PMC20751. https://pubmed.ncbi.nlm.nih.gov/9114018/

[16] Ball JC, Wallington TJ. Formation of trifluoroacetic acid from the atmospheric degradation of hydrofluorocarbon 134a: a human health concern? Air Waste. 1993 Sep;43(9):1260-2. doi: 10.1080/1073161x.1993.10467204. PMID: 8217109. https://pubmed.ncbi.nlm.nih.gov/8217109/

[17] Klein, A. (1997) Halogenierte Essigsäuren in der Umwelt. Dissertation zur Erlangung des Doktorgrades der Fakultät Biologie, Chemie und Geowissenschaften der Universität Bayreuth, unveröffentlicht.

decades[18]. Similar and even greater temporal increases in TFA have been reported in studies of surface waters in the USA[19] and China[20], as well as from ice cores in the remote northern regions of Canada[21].

In summary, protecting water from contamination like that caused by TFA is a key goal of European pesticide and water laws. The tools to achieve this goal were in place, namely the legal limits for pesticides and their (relevant) metabolites in groundwater and drinking water, as well as the obligation to monitor halogenated organic pollutants and to contain and reverse their increase in water concentrations through appropriate measures. Governments therefore had not only the opportunity but also the obligation to address the widespread TFA contamination in European waters.

The fact that Member State governments have ignored the TFA problem for decades - and in many countries still do today - turns an environmental scandal into a political scandal.

2.5 The PFAS Playbook

The history of PFAS is a repetitive history of chemicals claimed to be harmless until the evidence to the contrary was so complete that any further denial of their danger was futile. This was the case with the first generation, the now largely banned C8 PFAS, then repeated with their shorter-chain (C6 and C4) substitutes, and today is being played out with the ultra-short-chain PFAS (C1-C3), the most prominent of which is TFA.[22]

The strategies used by PFAS manufacturers are *'common to tobacco, pharmaceutical and other industries to influence science and regulation - most notably, suppressing unfavourable research and distorting public discourse'*. The aim of these tactics is to delay public awareness and regulatory action for as long as possible. This conclusion[23] was reached by a team of scientists analysing internal company documents that DuPont and 3M were required to disclose as a result of legal proceedings in the US.

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[18] Freeling, F.; Behringer, D.; Heydel, F.; Scheurer, M.; Ternes, T. A.; Nödler, K. Trifluoroacetate in Precipitation: Deriving a Benchmark Data Set. Environ. Sci. Technol. 2020, 54 (18), 11210−11219.

[19] Thomas M. Cahill. Increases in Trifluoroacetate Concentrations in Surface Waters over Two Decades. Environmental Science & Technology 2022 56 (13), 9428-9434

[20] Zhai, Z. H.; Wu, J.; Hu, X.; Li, L.; Guo, J. Y.; Zhang, B. Y.; Hu, J. X.; Zhang, J. B. A 17-fold increase of trifluoroacetic acid in landscape waters of Beijing, China during the last decade. Chemosphere 2015, 129, 110−117

[21] Pickard, H. M.; Criscitiello, A. S.; Persaud, D.; Spencer, C.; Muir, D. C. G.; Lehnherr, I.; Sharp, M. J.; De Silva, A. O.; Young, C. J. Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations. Geophys. Res. Lett. 2020, 47 (10)

[22] TFA is the C2 analog of PFOA, a 'C8' PFAS. TFA consists of two carbon atoms, one of which carries three fluorine atoms, while the other carries a carboxyl group.

[23] Gaber N, Bero L, Woodruff TJ. The Devil they Knew: Chemical Documents Analysis of Industry Influence on PFAS Science. Ann Glob Health. 2023 Jun 1;89(1):37

Background

The fact that PFAS manufacturers had to disclose these documents in the year 2000, leading authorities in the US and Europe to address the environmental and health hazards of PFAS for the first time, is due to the tenacity of one individual, the environmental lawyer Robert Bilott. His story is covered in detail in a comprehensive New York Times report, a compelling documentary, and an equally worthwhile feature film. The documents he fought for in court included more than 110,000 pages of internal correspondence, medical reports, and confidential studies by DuPont scientists. They reveal that the PFAS industry knew as early as 1950 that their chemicals could accumulate in our blood, and as early as the 1960s that they could pose health risks. Since 1981, manufacturers knew from their own studies with rats[24] and observations of pregnant workers[25] that their key PFAS compounds at the time, PFOA and/or PFOS (commonly referred to as 'C8' due to the number of carbon atoms), caused birth defects. Specifically, these defects were malformations of the eyes observed both in baby rats whose mothers were exposed to C8-PFAS during pregnancy and in two out of eight babies born to workers involved in C8 production during pregnancy. In the late 1980s and 1990s, manufacturers eventually found increased cancer rates in PFAS workers and increased tumour rates in animal studies with C8.

Instead of informing their customers and the authorities about the potential for birth defects and cancer – as they were legally obligated to do – they concealed these studies and continued to promote the image of their chemicals as harmless and beneficial in their advertising campaigns.[26]

Just how successfully the industry played by the tobacco industry's rules - and how unsuccessful politicians were in protecting the environment and human health - is shown by the fact that first-generation PFASs were not subject to restrictions in the EU until 2010 in the case of PFOS and 2020 in the case of PFOA. Moreover, second-generation PFAS, which are also extremely persistent and have a negative impact on ecosystems and health, but have a shorter, typically C4 or C6 chain length, are still being produced and marketed in an unregulated manner[27].

[24] The DuPont Memo on the 3M rat study with eye malformations is one of countless DuPont documents that US attorney Rob Bilott submitted to US authorities and politicians in March 2001.

[25] The DuPont Memo on the company's internal investigation into the pregnancies of C8 workers is one of countless DuPont documents that US attorney Rob Bilott submitted to US authorities and politicians in March 2001.

[26] Stephanie Soechtig (2018) The Devil We Know Film Documentary

[27] COUSINS, I.T., G. GOLDENMAN, D. HERZKE, R. LOHMANN, M. MILLER, C.A. NG, S. PATTON, M. SCHERINGER, X. TRIER, L. VIERKE, Z. WANG und J.C. DEWITT, 2019. The concept of essential use for determining when uses of PFASs can be phased out [online]. Environmental Science: Processes and Impacts, 21(11), 1803-1815.

2.5.1 The Myth of Harmless Short-Chains

A masterpiece from the PFAS playbook is currently being showcased by the industry regarding TFA. Two narratives stand out prominently.

Narrative No. 1 claims that the TFA pollution measured in rain and global water bodies is not industry-made but of natural origin. This stance by the PFAS industry[28] is strikingly reminiscent of the denial of man-made climate change, organised and financed by the fossil fuel industry. But the fluorochemical industry even seems to have invented this narrative. In the 1970ies, when their chlorofluorocarbons (CFCs) - and with them a thriving two-billion-dollar halogenation industry - came under pressure because of depleting the ozone layer[29], they posited a volcanic origin for ozone-depleting gases. Today, the fluorochemical industry and its affiliated scientists are once again promoting a volcanic origin for a chemical they produce, the regulation of which would seriously harm their business. They claim that 'hydrothermal vents' are significant natural emitters of TFA. Although this narrative is not supported by the facts[30, 31], this narrative does its job to obscure and distort public and scientific discourse and delay policy action.[32]

Narrative No. 2 builds on a myth that has been propagated since the shift from longer-chain PFAS (C8 and higher) to shorter-chain compounds (often C6 or C4): the narrative of comparatively harmless short-chain PFAS. According to this TFA, as an ultrashort-chain (C2) compound, is simply not comparable to other PFAS. Examples of this strategy by the fluorochemical industry have been compiled by Belgian environmental researcher Thomas Goorden in his publication The Dark PFAS Hypothesis - Strategies of Deception. Some of these examples are quite astonishing: for instance, when a publication[33] funded by PFAS manufacturer 3M claims, citing another publication[34] also funded by 3M, that *'ultra-short-chain PFAS such as TFA and PFPrA should not be grouped with other perfluoroalkyl carboxylates and perfluoroalkyl sulfonates'* when it comes to regulating PFAS.

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[28] EFCTC, 2021. The case for a large natural source of TFA in the oceans is extremely strong, well- documented, and scientifically supported Position Paper

[29] Goorden Thomas (2023); The Dark PFAS Hypothesis - Strategies of Deception

[30] Industry's argument that large quantities of TFA measured in the environment (fresh and sea surface water, rain and air) cannot be explained by the known industrial sources is contradicted by the simple fact that measured TFA loads in rain, surface and groundwater fit very well with the estimated environmental emissions of well known TFA precursors (as demonstrated above). Moreover, TFA is not detectable in ice core and groundwater samples of pre-industrial freshwater from Greenland and Denmark, and a plausible mechanism of natural TFA formation is lacking.

[31] Nielsen et al, 2001. Trifluoroacetic acid in ancient freshwater. Atmospheric Environment 35:2799-2801

[32] What makes this narrative so successful and enduring is that, even though the known material flows and degradation pathways of chemicals explain the measured pollution in global waters well, refuting the claim that deep-sea volcanoes produce TFA is difficult and associated with considerable effort, if not impossible. Consequently, the industry can repeatedly bring up this argument to distract from the true causes and solutions - and it does so.

[33] Racz, L., 2023. Evaluation of Approaches for Assessing PFAS Mixtures, Retrieved from https://policycommons.net/artifacts/4845526/evaluation-of-approaches-for-assessing-pfas-mixtures/5682240/

[34] T. Colnot and W. Dekant, "Commentary: Cumulative risk assessment of perfluoroalkyl carboxylic acids and perfluoralkyl sulfonic acids: What is the scientific support for deriving tolerable exposures by assembling 27 PFAS into 1 common assessment group?" Archives of Toxicology, vol. 96, no. 11, pp. 3127–3139, Nov. 2022

Background

Actually, it is no great surprise that the PFAS industry is keen to portray TFA as harmless. TFA is not only an important starting product for the production of many PFAS, but it is also the persistent terminal degradation product of an estimated 2,000 PFAS. This includes a large number of commercially important PFAS compounds, such as F-gases, pharmaceutical, biocide, and pesticide active ingredients.

Scientists involved in the dissemination of these questionable narratives often have a history of defending industrial chemicals that have come under regulatory pressure. It is not uncommon for them to adopt scientifically dubious positions in defence of industrial interests. Notable examples include coordinated attacks organised and financed by Monsanto against the IARC's classification of glyphosate as a probable human carcinogen[35], as well as efforts to prevent a general ban on hormone-disrupting pesticides[36]. These activities, although often lacking in substance, are frequently very effective: industry-sponsored publications are all too often taken at face value by regulatory authorities, and sometimes even by respected scientists, finding their way into IPCC reports.[37]

If it turns out in the end that the industry's assurances were false, it is usually the citizens who bear the cost. Unfortunately, this scenario is exactly what is looming with TFA. The narrative of harmless short-chain PFAS was recently shattered by a study commissioned by the industry itself to investigate TFA's reproductive toxicity. In this study, eye malformations occurred in all three dose groups of rabbits administered TFA, reminiscent of the similar malformations in rats and humans mentioned above, linked to C8-PFAS exposure.

One might almost get the impression that this is a 'cat-and-mouse' game between an industry pushing the boundaries of what is permissible to defend its economic interests, and authorities that sometimes lack the means or the will to hold the industry accountable.

That's why we should keep reminding ourselves that this is not a game. The consequences are real-life human suffering, affecting thousands or even millions of people since PFAS entered our lives more than seventy years ago. This includes children born with deformities, cancers, obesity, and cardiovascular diseases, to name just a few of the most well-documented PFAS-associated illnesses.

In view of these fatal consequences, it would be desirable for authorities and courts to refrain from treating industry strategies of suppressing unfavourable research results and distorting public discourse[38] in order to 'defend' their products as if they were trivial offences. They are not.

[35] Burtscher H, Clausing P, Robinson C: Buying Science: How industry strategized (and regulators colluded) in an attempt to save the world's most widely used herbicide from a ban. GLOBAL 2000, March. 2017

[36] Corporate Europe Observatory 2015: A toxic affair: How the chemical lobby blocked action on hormone disrupting chemicals.

[37] Goorden Thomas (2023); The Dark PFAS Hypothesis - Strategies of Deception

[38] Gaber N, Bero L, Woodruff TJ. The Devil they Knew: Chemical Documents Analysis of Industry Influence on PFAS Science. Ann Glob Health. 2023 Jun 1;89(1):37

2.6 Water Protection Stopped by Court

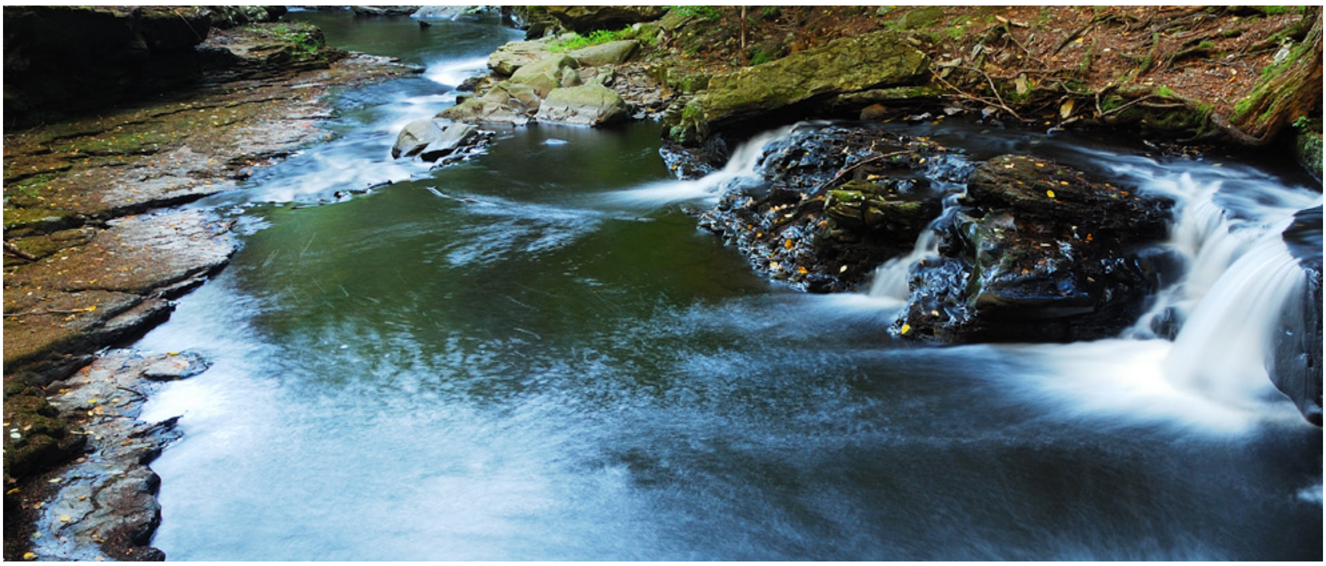
In February 2022, the German Federal Environment Agency (UBA), which is responsible for assessing environmental risks as part of the pesticide approval process in Germany, published an article on its website titled: 'Pesticide Approvals Undermine Environmental Protection.'

This article, which arguably deserved more media attention than it ultimately received, begins with the following words:

> ***"'Under current law, pesticides are approved in Germany even though scientific evidence shows they harm the environment. German authorities are currently unable to effectively protect the environment from harmful pesticides. This needs to be re-regulated at the European level."***
> ***(UBA, Feb. 2022)***

The background to this remarkable statement from an authority responsible for the authorisation of plant protection products is succinct: The UBA detected TFA contamination in groundwater within an intensively farmed region, threatening to exceed the groundwater threshold value for 'non-relevant' metabolites of 10,000 ng/l, or had already done so. The herbicide flufenacet, which is known to break down into TFA, has been identified as a significant source of this water pollution. Therefore, the UBA has capped the annual quantity of flufenacet-containing pesticides used.

However, the authorisation holders legally challenged this decision and won in a German court, which ruled that Germany had to align with other EU countries that do not impose restrictions based on environmental data (and do not even analyse TFA in groundwater). Consequently, the restrictions imposed by the UBA on all pesticides containing flufenacet were lifted, allowing the continued contamination of German groundwater with TFA.



2.7 Protecting Industry

PFAS are a prime example of what's known as regrettable substitution. Regrettable examples include the extremely climate-damaging F-gases, which succeeded the ozone-depleting CFCs and were then replaced by less climate-damaging F-gases, which in turn cause trifluoroacetic acid (TFA) to 'rain' from the sky, while in the Teflon industry, highly hazardous C8 chemicals were replaced by highly hazardous C6 chemicals. These examples illustrate that the PFAS problem cannot be solved by only banning individual substances. The 'group ban' as proposed by the Netherlands, Germany, Denmark, Norway, and Sweden, is therefore the only feasible way to protect the environment and public health from these extremely dangerous substances.

Unfortunately, in recent months, resistance has been mounting within the strongest group in the European Parliament, the European People's Party (EPP). Their environmental spokesperson argues against what he calls a 'blanket ban' on PFAS. He claims that the group ban approach would 'go too far,' especially since not all sub-components of PFAS and all applications are equally hazardous to health.

How serious the EPP is about its opposition to a PFAS ban was recently demonstrated when its environmental policy spokesperson told reporters that his party would 'consider' a 90% target for reducing greenhouse gas emissions by 2040 only in exchange for other concessions, such as permanently abandoning a ban on PFAS chemicals. Recently, the EPP's environmental policy spokesperson also expressed opposition to the proposed PFAS ban in a letter to the President of the European Commission.

TFA in Water Test Results

3.1 Study Approach

The objective of this sampling study was to gain insight into TFA pollution in European surface and groundwaters. Partner organisations of the Pesticide Action Network (PAN) Europe were invited to collect water samples from watercourses in their respective EU countries for random sample analysis. PAN members from the following ten EU countries participated in this survey by contributing one or more water samples from their country: Austria (GLOBAL 2000), Belgium (Nature & Progrès), Bulgaria (Via Pontica Foundation), Croatia (Earth Trek), France (Generations Futures), Germany (PAN Germany and BUND), Luxembourg (Mouvement Ecologique), Netherlands (PAN Netherlands), Spain (Ecologistas en Acción), and Sweden (Naturskyddsforeningen).

The project partners received suitable sampling tubes (BITEFU, 50ml centrifuge tubes for laboratory chemistry) and instructions for sampling by mail. Sampling took place during April 2024. A total of 23 surface water samples and 6 groundwater samples were collected and sent to the Water Technology Centre in Karlsruhe for analysis.

Individual analyses for TFA were carried out on all 29 water samples. Additionally, three composite samples were prepared, which were analysed for 23 additional PFAS[39] besides TFA. For this purpose, the 6 groundwater samples were mixed in equal parts to form the 'groundwater composite sample'. Aliquots of the 10 Austrian river samples were combined to form the 'Austrian composite sample,' and corresponding aliquots of the remaining 13 surface water samples were combined to form the 'European composite sample'.

The reason for choosing an approach in which individual determination was only carried out for TFA, while the bigger set of 24 PFAS was determined as an average contamination by analysing composite samples, lies in the specific focus of this study on investigating TFA contamination in European waters. TFA is a PFAS that receives far less attention in water analyses of many member states compared to other PFAS listed in the EU Drinking Water Directive (cumulative limit for 20 PFAS) or the EU Water Framework Directive (PFOS as a priority substance).

The analysis was carried out using HPLC-MS-MS. The respective quantification limits were 50 ng/l for Trifluoroacetic acid (TFA), 1 ng/l for the 20 PFAS regulated in the EU Drinking Water Directive, 2 ng/l for Perfluoropropionic acid (PFPrA), 1 ng/l for Perfluoropropane sulfonic acid (PFPrS) , and 50 ng/l for Perfluoroethane sulfonic acid (PFES).

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[39] The composite samples were analysed for the ultrashort-chain PFAS, Trifluoroacetic acid (TFA) Perfluoroethane sulfonic acid (PFES), Perfluoropropionic acid (PFPrA), and Perfluoropropane sulfonic acid (PFPrS) as well as for the 20 PFAS regulated as «Sum of PFAS» in the EU Drinking Water Directive: Perfluorobutanoic acid (PFBA), Perfluoropentanoic acid (PFPA), Perfluorohexanoic acid (PFHxA), Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorobutane sulfonic acid (PFBS), Perfluoropentane sulfonic acid (PFPS), Perfluorohexane sulfonic acid (PFHxS), Perfluoroheptane sulfonic acid (PFHpS), Perfluorooctane sulfonic acid (PFOS), Perfluorononane sulfonic acid (PFNS), Perfluorodecane sulfonic acid (PFDS), Perfluoroundecane sulfonic acid, Perfluorododecane sulfonic acid, Perfluorotridecane sulfonic acid

3.2 Individual Determination of TFA

The survey showed that TFA was present in all water samples, with concentrations ranging from 370 ng/l to 3,300 ng/l. The average TFA concentration across all samples was 1,180 ng/l. In surface water, the average concentration was slightly higher at 1,220 ng/l compared to groundwater samples, where it measured 1,025 ng/l. Refer to Figures 3 and 4 for details.

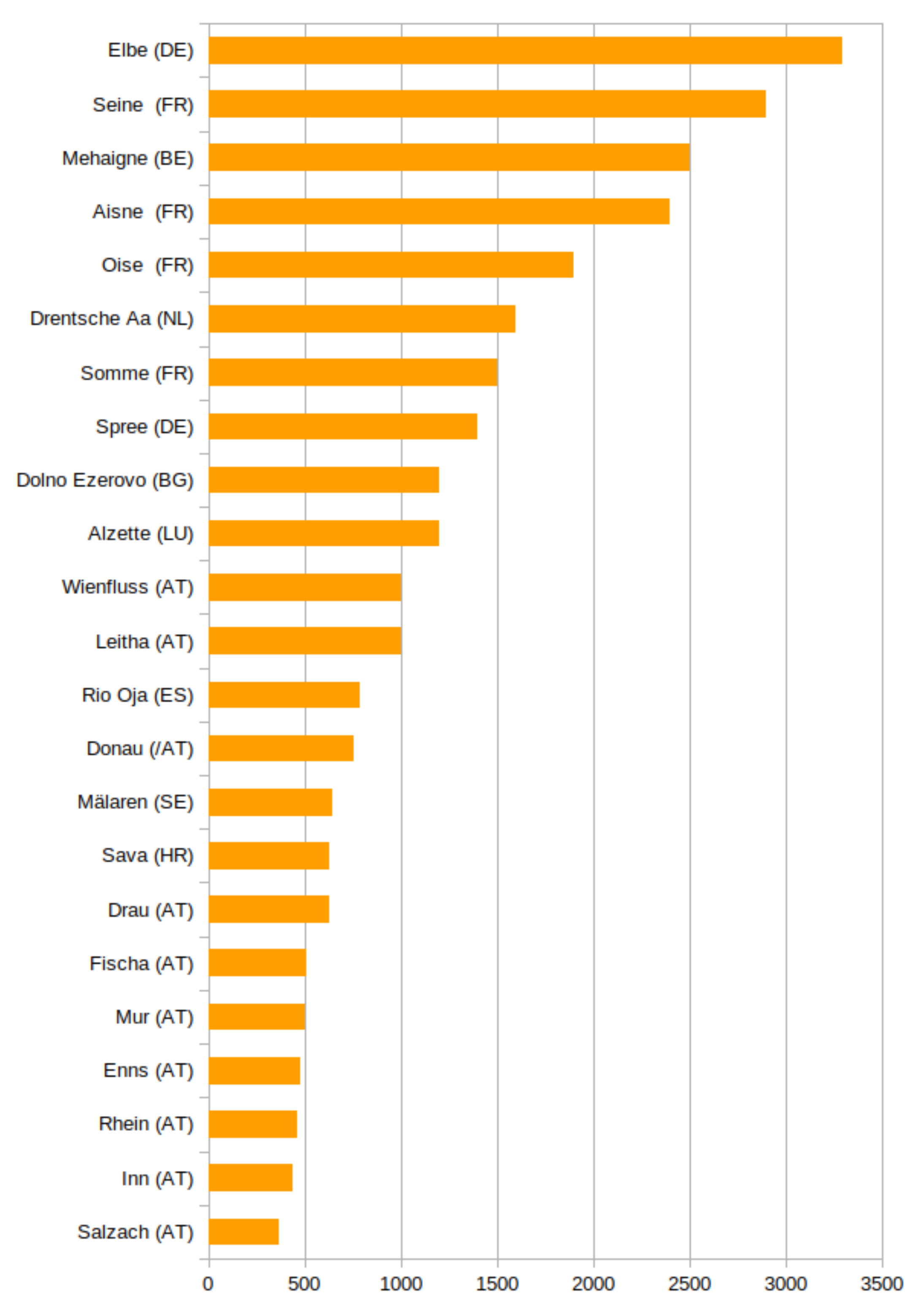

Figure 3. *TFA loads in 23 European surface water samples*

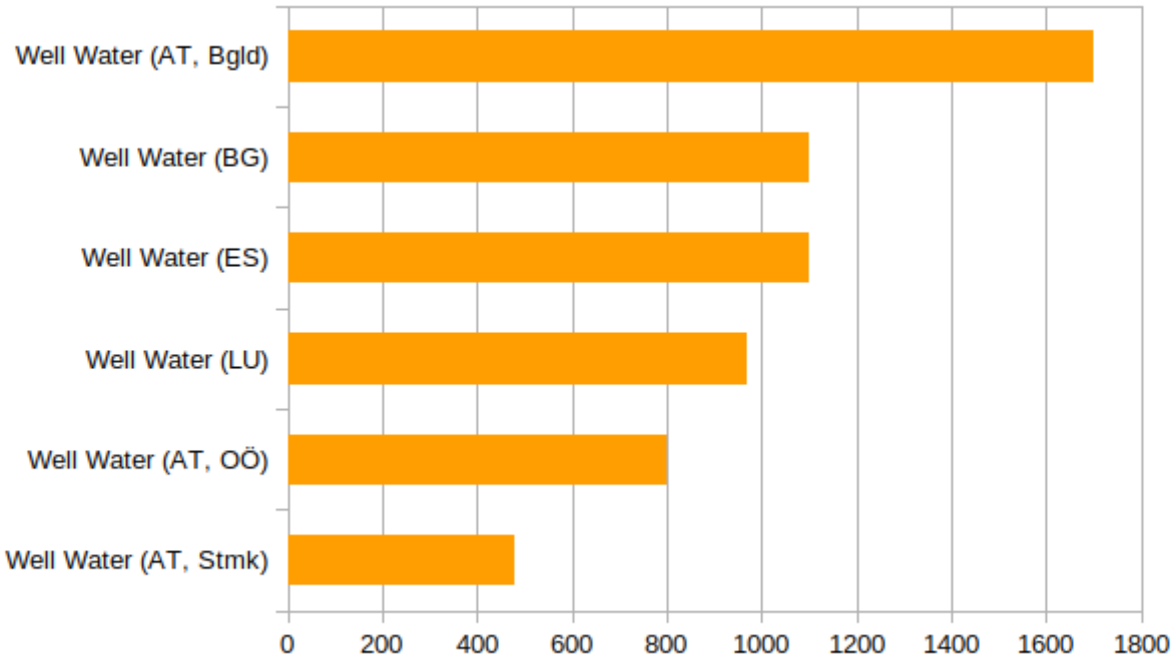

Figure 4. *TFA loads in 6 European groundwater samples*

3.3 Multi-PFAS Determination in Composite Samples

To enhance the understanding of TFA contamination, three composite samples were prepared alongside the individual analyses. These composite samples, named 'Composite Sample Groundwater' (Figure 5), 'Composite Sample Europe' (Figure 6), and 'Composite Sample Austria' (Figure 7), were analysed for TFA and underwent additional analyses for those 20 PFAS regulated in the EU Drinking Water Directive. In addition to these 20 PFAS, another three ultrashort-chain PFAS, Perfluoroethane sulfonic acid (PFES), Perfluoropropionic acid (PFPrA), and Perfluoropropane sulfonic acid (PFPrS) were analysed in 'Composite Sample Groundwater' and 'Composite Sample Europe.'

The striking finding from this comparison is that the average TFA load[40] accounts for about 99% of the total PFAS contamination when including the 20 PFAS regulated in the Drinking Water Directive (and an additional 3 short-chain PFAS, as we did with 'Composite Sample Groundwater' and ‘Composite Sample Europe,')

[40] The value determined directly in the composite sample was used

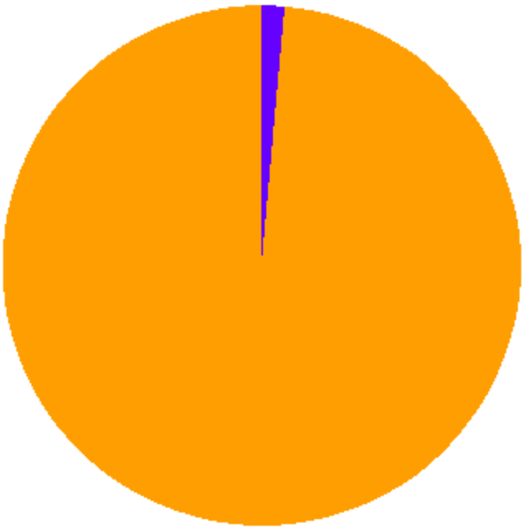

Figure 5. *'Composite Sample Groundwater': Comparison of the mean contamination by the sum of 23 PFAS (**purple**) with the mean contamination by TFA (**orange**) in 6 groundwater samples*

The composite sample from from 6 groundwater sources detected 10 ng/l Perfluoropropionic acid (PFPrA), 3.6 ng/l Perfluorobutanoic acid (PFBA), 1.3 ng/l Perfluorobutane sulfonic acid (PFBS), and 1,800 ng/l TFA. 99.1 % of the total PFAS contamination detected in this sample originates from TFA.

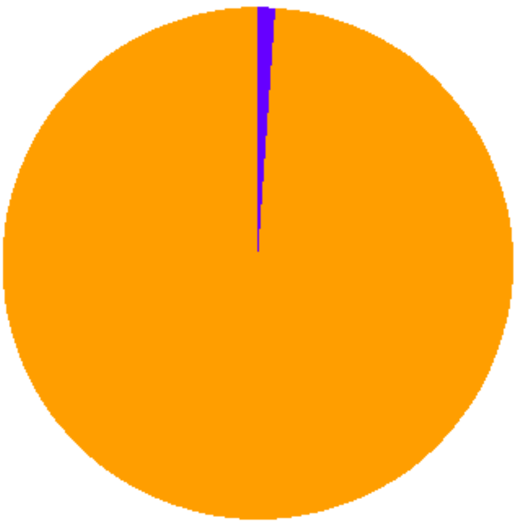

Figure 6. *'Composite Sample Europe': Comparison of the mean contamination by the sum of 23 PFAS (**purple**) with the mean contamination by TFA (**orange**) in 13 European surface waters 'Composite sample Europe'*

The composite sample from 13 European surface waters detected 11 ng/l Perfluoropropionic acid (PFPrA), 2.2 ng/l Perfluorobutanoic acid (PFBA), 1.5 ng/l Perfluoropentanoic acid (PFPA), 1.5 ng/l Perfluorohexanoic acid (PFHxA), 1.0 ng/l Perfluorobutane sulfonic acid (PFBS), 1.5 ng/l Perfluorooctane sulfonic acid (PFOS), and 2,100 ng/l TFA. 99.1 % of the total PFAS contamination detected in this sample originates from TFA.

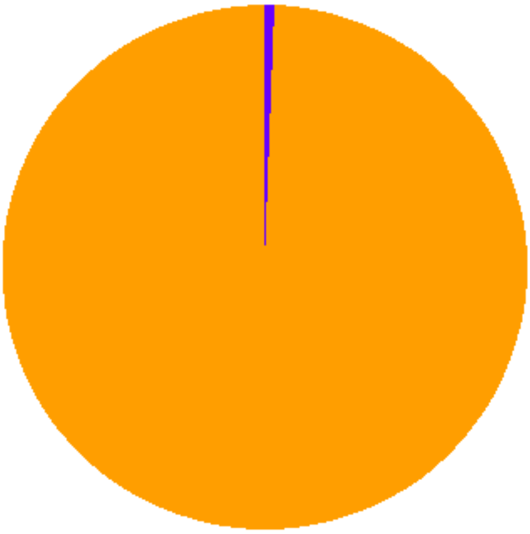

Figure 7. *'Composite Sample Austria': Comparison of the mean contamination by the sum of the 20 PFAS (purple) with the mean contamination by TFA (orange) in 10 Austrian surface waters*

The composite sample from 10 Austrian surface waters detected 1.1 ng/l perfluorooctanoic acid (PFOA), 1.1 ng/l perfluorooctanesulfonic acid (PFOS), 1.2 ng/l perfluorobutanoic acid (PFBA), and 650 ng/l TFA. 99.5 % of the total PFAS contamination detected in this sample originates from TFA.

Summary and Conclusion

Our investigation results reveal that the 'PFAS issue' which first came to broader public attention around the Dark Waters Scandal two decades ago, and has since been primarily understood as a problem of highly contaminated but locally confined contamination hotspots, has meanwhile evolved into an even larger issue. It has affected all water bodies in Europe. The average contamination levels of European waters by C2-PFAS trifluoroacetic acid are on a scale reminiscent of the concentrations detected at countless hotspots with C8 and C6 PFAS within the framework of the Forever Pollution Project.

European pesticide and water legislation contains both the instruments to protect water from pollutants and the clear obligation of governments to ensure this protection. Our findings show that political leaders have not fulfilled this important legal duty. The result of this collective failure is the largest known Europe-wide water contamination by a man-made chemical. A dirty legacy that will be passed onto future generations. This is, in itself, a highly unpleasant and disturbing outcome.

Adding to this is the certainty that pollution will increase with each passing day unless decisive action is taken to curb TFA inputs—first and foremost through a swift ban on PFAS pesticides and F-gases. According to recent modelling by the German Federal Environment Agency, pesticides are the dominant source of TFA pollution in rural areas. This is likely to apply equally to a relevant part of the European land area and the surface and groundwater bodies there. From a global perspective, F-gases from refrigerants are likely to have an even higher pollution potential.

Apart from the fact that any contamination of surface and groundwaters by pollutants (especially with regard to potential use as drinking water) is undesirable and must be prevented by law, there are three further complicating factors in the case of contamination with TFA.

Firstly, TFA is the epitome of a persistent chemical. To date, there is no evidence that any form of degradation takes place in the environment for this substance. Secondly, TFA cannot be removed from water using any of the established[41] drinking water treatment processes. Thirdly, TFA is a PFAS whose toxicological profile still leaves many questions unanswered.

Unfortunately, a recent industry-conducted study on TFA, which found malformations in rabbit offspring[42] raises concerns that the narrative of harmless short-chain PFAS may be false in the case of TFA.

Of the more than 10,000 chemicals that fall under the OECD definition of PFAS, 2,000 are likely to be precursors of TFA. This means that there are other relevant entry pathways for TFA that we do not yet know about. And it shows how necessary and correct the EU's chosen approach of a group ban on all PFAS is.

We do not need to prove the toxicity of every single one of the more than 10,000 PFAS

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[41] The only technology capable of removing TFA from water is reverse osmosis. However, implementing this method requires significant technical expertise, high energy consumption, and water usage, and may alter the mineral composition of the water. Additionally, scaling up reverse osmosis systems can be challenging.

[42] https://echa.europa.eu/fr/registration-dossier/-/registered-dossier/5203/7/9/3/?documentUUID=bbe1c0df-91db-4cef-a965-89ded98a88c8

[43] This figure was presented by German and Dutch experts when presenting the restriction proposal: https://www.https://www.youtube.com/watch?v=CXAZ3ath3To (9 min 50 sec)

Summary and Conclusion

chemicals. Their ultimate persistence alone is sufficient to justify a general ban. In 2020 alone, 75,000 tonnes of these substances were emitted into the environment[43], where they or their degradation products cannot be removed, creating a toxic legacy for future generations. This is both irresponsible and self-destructive. The urgency of action is further underlined by the fact that the handful of PFAS that have been more intensively researched have all proven to be very toxic. They exhibit reproductive toxicity, carcinogenic, immunological and endocrine-disrupting properties. These harmful effects can occur even at very low concentrations and thousands of people have already fallen ill or died as a result of contact with these substances.[44, 45]

For all these reasons, political interventions aimed at derailing the planned PFAS group ban, such as those undertaken by the largest political group in the European Parliament in recent months, are incomprehensible and reprehensible.

What we need to get the environmental problem of TFA contamination under control is a package of measures that must be implemented quickly and decisively:

- Ban all pesticides that fall under the OECD definition of PFAS under the EU Pesticide Regulation by:
    - Considering persistence of a synthetic active substance or that of its metabolites as an unacceptable effect on the environment in light of its intrinsic toxic properties and the cumulative nature of the PFAS pollution.
    - Revising Annex II of the Pesticide Regulation to ban Persistent, Mobile and Toxic (PMT) and very Persistent and very Mobile (vPvM) active substances.
- Implement the general PFAS restriction under REACH,
- Classify TFA as a priority hazardous substance under the Water Framework Directive,
- Establish environmental quality standards and EU-wide monitoring obligations for TFA in water.

The starting point of this investigation was the question of whether and in what concentrations TFA, the persistent terminal degradation product of most PFAS pesticides, can be found in the environment. The answers we have received are worrying and raise further questions. One of them is what these results mean for the quality of our drinking water. Therefore, we have started to collect drinking water samples (tap water and bottled water) from different European countries to be analysed for TFA and other PFAS. The results will be presented as soon as they are available.

Last but not least, we appeal to all politicians – especially the political groups that have so far opposed the PFAS group ban – to take a responsible stance in the face of this serious threat to our water resources. Prioritise the protection of health and the environment over short-term economic interests. Support all necessary measures to protect our water and secure it for the future!

[44] Biggeri, A., Stoppa, G., Facciolo, L. et al. All-cause, cardiovascular disease and cancer mortality in the population of a large Italian area contaminated by perfluoroalkyl and polyfluoroalkyl substances (1980–2018). Environ Health 23, 42 (2024)

[45] Nicole W. PFOA and cancer in a highly exposed community: new findings from the C8 science panel. Environ Health Perspect. 2013 Nov-Dec;121(11-12)

TFA in Water

Dirty PFAS Legacy Under the Radar

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