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Reducing the input of chemicals into waters: trifluoroacetate (TFA) as a persistent and mobile substance with many sources

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substance with many sources**

Sources, input pathways,
environmental contamination
of TFA and regulatory approaches

List of Figures

Figure 1	Structure of the background paper	p. 7
Figure 2	Maximum possible TFA emission from plant protection products in Germany by the 28 active substances that can theoretically form TFA	p. 12
Figure 3	Increase in emissions from refrigerants and blowing agents (HFC and unsaturated HFC) in important sectors in Germany from 1990 to 2019, in tonnes	p. 16
Figure 4	Estimated maximum TFA emissions in t/a for the relevant groups of chemicals*	p. 18
Figure 5	The most important sources and input pathways leading to TFA contamination in surface waters and groundwater	p. 19
Figure 6	Comparison of estimated local TFA inputs through plant protection products,* liquid manure, sludge from wastewater treatment and precipitation	p. 21
Figure 7	Monthly input of trifluoroacetate through precipitation in Germany between February 2018 (02/18) and February 2020 (02/2020)	p. 22
Figure 8	Interactions of sources, input pathways and contamination	p. 24

List of Tables

Table 1	Summary of available (eco)toxicological indicators for TFA	S. 31
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Contents

List of Figures and Tables	4
Motivation and objective	6
Summary	6
1 Substance properties	9
2 Sources	10
3 Input pathways	19
3.1 Localised input	19
3.2 Diffuse input	21
4 Contamination	25
4.1 Marine environment	25
4.2 Rivers, lakes and estuaries	26
4.4 Drinking water	28
4.5 Soil	28
4.6 Biosphere	28
5 Impact	30
5.1 Human health and ecosystems	30
5.2 Limits of the risk assessment and dealing with uncertainties	30
5.3 Water supply	34
6 Measures	37
6.1 Statutory restrictions	37
6.2 Political strategies and collaborative approaches	41
6.3 Local co-operations	43
7 Outlook	44
References	48

Motivation and objective

Trifluoroacetate (TFA) is a chemical that has been more and more frequently detected in waters in Germany in recent years. It is formed by many substances but is not itself subject to degradation. The great number of its possible precursors is one of the causes of the extensive input of the substance into the environment. Due to its physical and chemical properties – as a very persistent and very mobile substance – TFA easily finds its way into the water cycle, where it accumulates over time. So far, there are no practicable and economical options for its subsequent removal. Therefore, the inputs of TFA should be reduced. The objective of this paper is to provide a collection of information on TFA as a basis for developing a preventive minimisation strategy. The

diversity of its sources and input pathways requires a cross-sectional analysis and integrated co-operation to regulate TFA effectively and reduce its inputs into the environment. Therefore, this paper addresses both policymakers such as the federal government as legislator, regulatory authorities, state and local authorities, and those concerned in practice, such as water suppliers, agriculture, and environmental and water associations. Our objective is to enable the different stakeholders to design and implement a co-ordinated and effective minimisation strategy. This paper will also serve as a basis for developing appropriate regulatory options within the remit of the German Environment Agency.

Summary

Trifluoroacetate (TFA) is a substance of great concern for environmental protection: due to its high solubility in water and its mobility, TFA easily finds its way into the water cycle, which acts as its primary medium of distribution in the environment. TFA is not degradable, very persistent and remains in the environment once released. For that reason, its long-term impact on the environment cannot be fully predicted. An effective subsequent removal of TFA from waters is not feasible using established and extensively used techniques, particularly in drinking water production. TFA is introduced into waters from various sources and through different pathways. Knowledge of where TFA may come from and which sources lead to increased concentrations is currently still limited. This background paper gives an overview of the current state of knowledge, in particular on sources, input pathways, environmental impact, and measures to reduce the input.

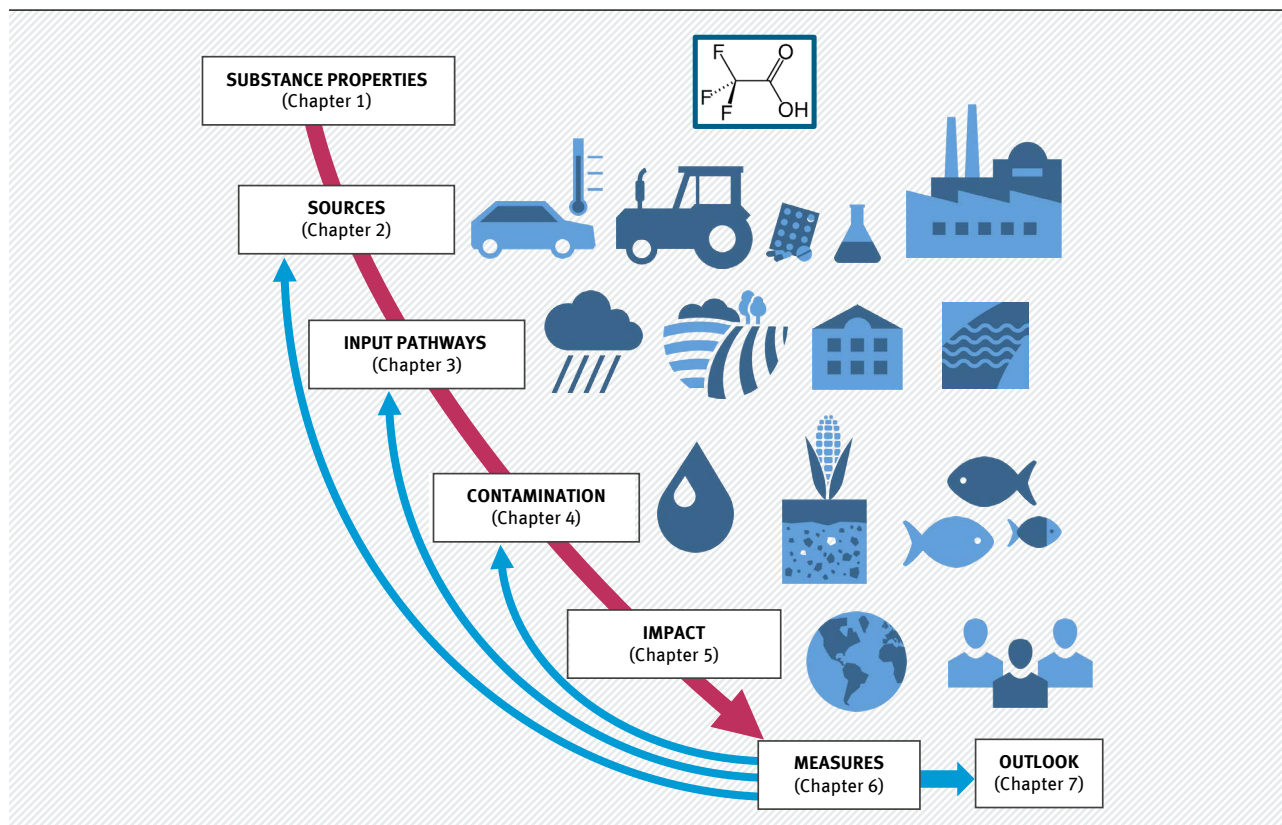
TFA is used as a basic chemical in the production of fluorinated compounds. In addition, TFA is a degradation product of various fluorochemicals from a variety of applications, such as halogenated refrigerants and blowing agents, plant protection products, pharmaceuticals, and biocides. Depending on the input pathway, the precursors of TFA degrade in different environmental compartments (air, soil, water). For input pathways, a distinction is made between isolated, localised

inputs and diffuse, extensive inputs of TFA into the environment. At the local level, input pathways may play a different part in TFA contamination in each case. In this paper, to give a quantitative estimate of the potential inputs, we calculate the maximum possible emissions of TFA across Germany based on sales figures and other data on the use of the respective chemicals. Monitoring data are used to determine current levels of TFA in surface waters, groundwater and drinking water in Germany. On the basis of these data, we discuss the current and expected impact of this chemical. We also present existing statutory and administrative regulations, political strategies and local minimisation efforts.

Figure 1 shows the structure of this background paper and the different areas considered.

Figure 1

Structure of the background paper



Source: own diagram, German Environment Agency

Key points

- ▶ TFA is very mobile and very persistent in the environment. According to current knowledge, toxicological and ecotoxicological effects are only detected at very high concentrations. However, the long-term impact of TFA in the environment is very uncertain.
- ▶ Based on the quantities sold and used, the main sources for TFA in the environment in Germany are refrigerants and blowing agents as well as plant protection products, all with a rising trend. Pharmaceuticals account for a relatively low quantity. The proportion accounted for by veterinary drugs and industrial production is unknown. The contribution made by biocides and fluorinated chemicals for consumers is not known in detail, but is assumed to be low. TFA inputs from natural sources such as deep-sea vents are very low.
- ▶ TFA is dispersed in the environment through the main input pathways of precipitation (as a result of atmospheric degradation of refrigerants and blowing agents), leaching on agricultural land (through the application of plant protection products and fertilisers), industrial discharge (by industries producing and using fluorochemicals), and municipal sewage treatment plants (through the discharge of pharmaceuticals, biocides and other fluorinated chemicals).
- ▶ TFA is not yet measured regularly nationwide in Germany. However, it has already been detected in many surface waters and in groundwater. Concentrations range from < 0.1 to > 10 µg/L; at point sources, they are significantly higher.
- ▶ TFA has also been found in significant quantities in other environmental compartments and products: soils, agricultural crops, food, beer, tea, wildflowers. An increase in contamination is to be expected, e.g. as a result of a significant upward trend in the use of TFA-forming refrigerants and plant protection products.

- ▶ Removing TFA from water takes great effort. In drinking water production, no practicable and economical method exists for its removal. Hence, the high levels of contamination cause conflict between drinking water production, agriculture and other sectors of the economy. Reverse osmosis can be used in the treatment of industrial wastewater to reduce TFA contamination to a minimum before it is discharged into the environment. So far, this is barely practised.
- ▶ TFA and its many precursors are currently rarely controlled in any legislative area, and where administrative requirements exist, they are not necessarily consistent with each other. In the interest of sustainably controlling contamination of natural and drinking waters, TFA inputs need to be regulated. Given the wide variety of sources, this may be done both by using sector-specific or application-specific approaches (substance-related laws and regulations) and by medium-specific control (water law). The German Environment Agency has started an assessment considering the options for regulating the various input sources using the regulatory instruments within the remit of the Agency. It would not be appropriate to shift the problem wholly to the end of the input chain (especially water suppliers), not least because of the chemical properties of TFA.
- ▶ First steps towards reducing TFA inputs into the environment have been initiated. The Federal Republic of Germany, together with four other states (the Netherlands, Denmark, Sweden, Norway) is currently (mid-June 2022) working on a restriction proposal under the European chemicals regulation (REACH; Regulation (EC) No 1907/2006) for regulating the manufacturing and application of the large group of per- and polyfluoroalkyl substances (PFAS) whose working definition would also include TFA. In terms of the EU strategy for the sustainable use of chemicals, it is now being assessed to what extent fluorinated refrigerants and the manufacturing and application of TFA-forming plant protection products, pharmaceuticals and biocides can be addressed by a REACH restriction.



1 Substance properties

TFA is short for trifluoroacetic acid ($\text{CF}_3\text{-COOH}$; EC No. 200-929-3, CAS No. 76-05-1) and its anion, trifluoroacetate ($\text{CF}_3\text{-COO}^-$). TFA is formed through degradation from a large number of fluorinated substances containing one or more trifluoromethyl groups (C-CF_3). In the environmentally relevant pH range, the molecule occurs as trifluoroacetate. TFA is highly soluble in water and adsorbs poorly to soil, sediment and organic matter. Thus, the substance is very mobile; it is introduced into the natural water cycle very rapidly from the atmosphere, soils and through wastewater, and is thereby dispersed in the environment. As a result, TFA can be detected even in waters at some distance from input sources.

Given the strong carbon–fluorine bond and its poor oxidisability, TFA is very stable. Even microorganisms able to break up carbon–fluorine bonds by means of the enzyme fluoroacetate dehalogenase only succeed in doing so with compounds containing a single fluorine atom, such as monofluoroacetate. Due to their relatively high stability, di- and trifluoroacetate, however, cannot be degraded by this enzyme (Boutonnet et al., 1999). Therefore, there are no currently known environmental conditions in which TFA degrades. TFA is thus a very persistent substance.¹

¹ According to the criteria of Annex XIII of the REACH Regulation, TFA fulfils the criteria for a very persistent substance, as standardised tests in various soils and sediment showed no evidence of degradation. However, there are indications of some potential for degradation by certain microorganisms under specific laboratory conditions. A study by Visscher et al. (1994) showed microbial degradation of TFA in sediments under both aerobic and anaerobic conditions. Under aerobic conditions, the formation of the potent greenhouse gas fluoroform (CHF_3) was observed during TFA degradation (Visscher et al., 1994; Castro et al., 2014). However, these studies were carried out under specific laboratory conditions and have so far not been reproduced. Thus, they only offer an indication that a transformation of TFA might be possible under certain conditions. This has not yet been observed under environmental conditions.

2 Sources

This section discusses the sources that may cause the input of TFA into the water cycle. Where sufficient data are available, an estimate is given of the maximum possible emission of TFA from each source across Germany.

Besides being emitted as a basic chemical, TFA can in principle be formed from all chemicals whose molecular structure includes a C-CF₃ group. In the atmosphere, TFA can be formed from volatile precursors by photochemical oxidation. In soils, water and sediments, chemicals can degrade into TFA biologically and photolytically (Solomon et al., 2016; Sun et al., 2020). Nearly 2,000 potential precursors are currently known. Of the utmost significance seem to be chemicals which are discharged into the environment in large quantities during their application and then degrade in the environment. These chemicals include, in particular, plant protection products, refrigerants and blowing agents, biocides, but also veterinary and human pharmaceuticals. According to current knowledge, these groups of substances, containing a total of about 150 TFA-forming chemicals, contribute significantly to TFA contamination in the environment, given the high environmental exposure associated with them and their applications (see also Chapter 3).

To date, there has been no comprehensive overview at the national level of the input of TFA from its use as a basic chemical, of the quantities of TFA actually formed from various chemicals, and of the contribution of individual sources to the concentrations detected in the environment. Empirical data concerning the potential for TFA formation are available for certain plant protection products and for the atmospheric degradation of some refrigerants.

In this chapter, we use available information about the quantities sold and/or used to calculate the annual quantity of TFA introduced into the environment in Germany from various sources. This calculation is based on the conservative assumption that a precursor will release the potential quantity of TFA completely (unless otherwise stated) and rapidly (within a year). This is done for various groups of chemicals. In some instances it is not possible to estimate the quantities of TFA at the national level (e.g. the input of

TFA from hydrothermal vents); here, we will present a global estimate instead.

TFA as a basic chemical

Any chemical manufactured in the EU or imported to the EU by individual companies in quantities > 1 t/a must be registered according to Regulation (EC) 1907/2006 (REACH Regulation). A substance may only be placed on the market in the EU once successfully registered. Along with the substance properties, registrant companies submit a generalised description of the planned use(s) of the substance and the annual quantity used (based on their own calculations). According to the information available in the publicly accessible section of the ECHA registration database, TFA as a substance is registered in the EU under REACH at a substance quantity of 100–1,000 t/a (ECHA, 2020a). In addition, TFA is registered as an isolated intermediate for the synthesis of other chemicals, with no tonnage given. For this specific kind of registration, less stringent requirements apply to the data submitted on substance properties. However, making use of this privileged type of registration comes with specific requirements for the containment of the technical facilities and minimisation of potential emissions.

TFA as such is widely used as a parent substance or solvent in synthesis processes. Other applications include the surface treatment of glass on an industrial scale and use as a laboratory chemical (ECHA, 2021). Given the EU-wide scope of validity of the substance registration, specific information on the quantities manufactured and used in Germany is not available. Since TFA as a basic chemical is not used outdoors, its emissions are likely to be limited to wastewater from industrial applications. This (potential) source of emissions cannot currently be quantified for Germany, but can play a major role at the local level (see Chapter 3.1).

Biocides

A total of six biocidal active substances containing a C-CF₃ group are approved at the EU level: chlorfenapyr, tralopyril, bifenthrin, lambda-cyhalothrin, flocoumafen and fipronil. In Germany, only biocidal products with these active substances approved at the EU level may be sold. At present, no biocidal products with the already approved active substances chlorfenapyr (only for product type (PT) 8: wood preservatives; although the active substance has also been notified in PT 18: insecticides, approval has not yet been granted) and tralopyril (PT 21: anti-fouling coatings) are authorised in Germany (ECHA, 2020). Furthermore, the authorisation for the only bifenthrin-containing product (PT 8) authorised so far has expired in Germany (and other EU member states). The remaining three approved biocidal active substances are contained in a total of 12 authorised products in Germany. These twelve products with the active substances lambda-cyhalothrin (PT 18: insecticides), fipronil (also PT 18) and flocoumafen (PT 14: rodenticides) are used both indoors and outdoors and may therefore be released into the environment.

Besides the products authorised through the EU assessment, the notification register of the German Federal Institute for Occupational Safety and Health (BAuA) lists a further 41 products containing an active substance relevant under the Biocidal Product Regulation, but these are subject to transitional arrangements until 2024 (BAuA, 2020). No environmental exposure assessment has yet been carried out for these products.

The approval of one other originally notified active substance expired in 2017 (flufenoxuron, PT 8), and no application for renewal has been made so far for this agent. According to the BAuA notification register, there are no more products with this active substance on the market in Germany, apart from three products whose marketability will end in 2024. No environmental exposure assessment has been carried out for these products either.

As a result of the approval of active substances which precedes the authorisation of products, data on the degradation of individual active substances are available. Given the complex structure of the parent substances, only potential TFA precursors were identified in the simulation studies submitted. In one case, there was an elimination of the C-CF₃ group, but in the absence of a specific radioactive marker for the C atom,

it was not possible to detect TFA as a degradation product (metabolite) here either. Since metabolites are only included in the environmental risk assessment under certain conditions (e.g. detection of the metabolite of > 10% of the active substance at any point in time of measurement in the course of the study; evidence of (eco-)toxicological relevance of a detected metabolite), TFA has not so far been considered in the environmental exposure and risk assessments of biocides and their metabolites.

There is currently no central registration of the quantities of biocidal products sold in Germany. Therefore, it has not been possible to estimate the theoretical maximum TFA emission potential of biocides.

Plant protection products

There are currently 45 active substances containing a C-CF₃ group approved for use as plant protection products in the EU. 26 of them are used in plant protection products authorised for use in Germany. For the pesticidal agents flurtamone and flufenacet, degradation studies were submitted as part of the approval process, showing the formation of TFA. TFA was also detected in various field studies for other active substances – without the exact degradation pathway being known (EFSA, 2014; EFSA, 2017; EFSA, 2017a). In ozonisation – a process used in treating wastewater and drinking water – the formation of TFA from the active substances tembotrione, flufenacet, flurtamone and fluopyram was observed. However, a quantitative derivation of the formation rate was not possible (Scheurer et al., 2017).

Plant protection products are intended primarily for use on farmland; a generally high level of environmental exposure may therefore be assumed. This chapter focuses on the 26 active substances contained in plant protection products authorised in Germany. In addition, flurtamone and flutolanil, though no longer approved active substances in the EU, are also included in the analysis due to their high quantities of application in recent years; thus, 28 active substances are considered (Figure 2). The applied quantities of these active substances range from 0.8 to 629 t/a (BVL, 2019; average values for 2016–2018). No clear trends are apparent in the sales figures for the past 10 years – they either stagnate or fluctuate around a constant mean. The only exception is flufenacet, which shows the largest tonnages sold. Both the sales figures and the number of plant

protection product applications for this active substance have been steadily increasing in Germany for some years. In the period from 2008 to 2018 alone, the sales figures increased by about 80% (BVL, 2019). At present, there are 31 authorised plant protection products with this active substance, with applications pending for several more (BVL, 2021; as of July 2021).

On the basis of the sales figures and considering all 28 active substances, a maximum of 504 t of TFA per year can be emitted in Germany through plant protection product applications (457 t max. without flurtamone and flutolanil). The three active substances that represent the most important sources with regard to TFA can emit a maximum of 197 t (flufenacet), 84 t (diflufenican), and 78 t (fluazinam) of TFA, respectively.

Thus, flufenacet is the most significant plant protection product with respect to the emission of TFA across Germany. In addition, flufenacet is one of the

few substances for which the formation of TFA is not only a theoretical assumption, but has been proven in laboratory studies. Therefore, regulating the production and use of flufenacet is an important lever for managing TFA emissions into the environment (see Infobox 6).

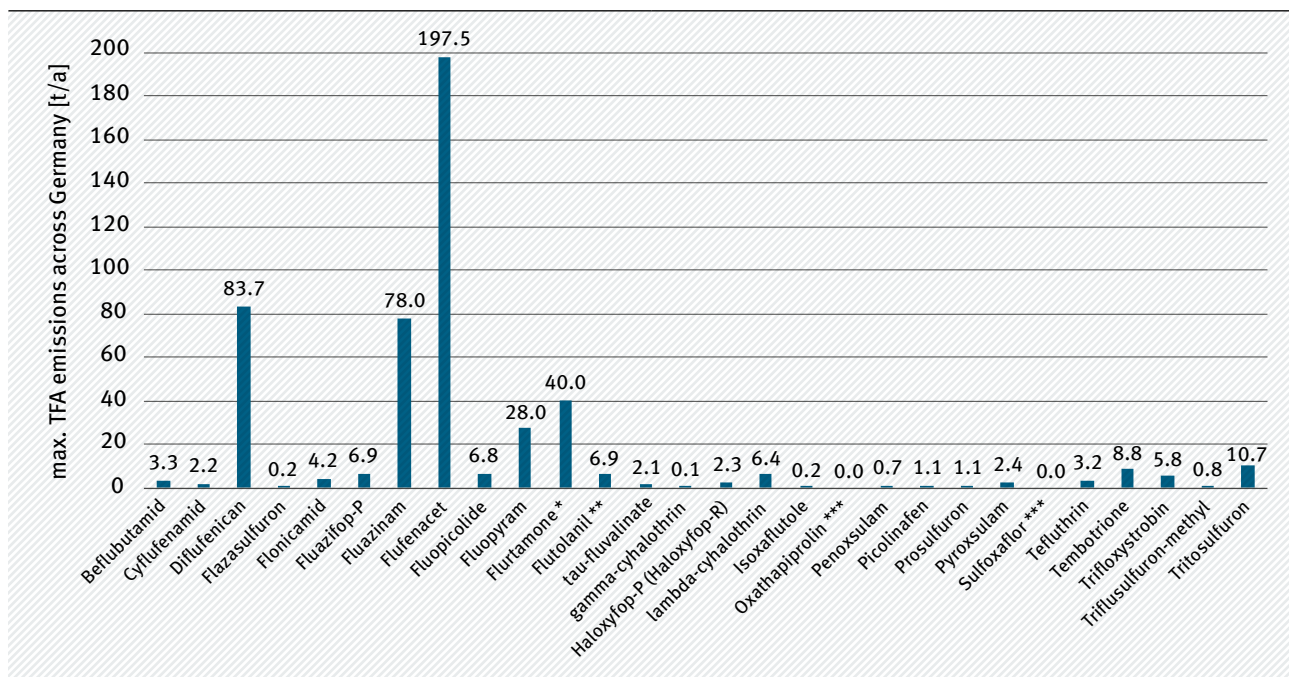
Veterinary pharmaceuticals

A total of eight active ingredients of veterinary pharmaceuticals contain a C-CF₃ group; seven of them are authorised in Germany. In detail, there are the analgesic flunixin and its meglumine salt, the inhalational anaesthetic isoflurane and the antiparasitics fipronil, pyriprole, metaflumizone (no longer authorised), fluralaner and esafoxolaner. Due to the high vapour pressure and type of application, isoflurane is mostly introduced into the atmosphere through air (see also Human pharmaceuticals). All five antiparasitics are used for pets (dogs, cats, etc.); hence, a diffuse input mostly through surface runoff is to be expected. Fluralaner is also approved for the treatment

Figure 2

Maximum possible TFA emission from plant protection products in Germany by the 28 active substances that can theoretically form TFA

On the basis of the quantities of the active substance sold, taken as a mean for the three years 2016, 2017 and 2018.



■ Maximum TFA emission across Germany, calculated on the basis of quantities sold in Germany [t/a] – mean for 2016–2018

* No approval at the EU level (must be used up by 2020)

** Currently no products authorised in Germany (tuber treatment before sowing)

*** Products containing the active substance are authorised but not sold

Source: own diagram, German Environment Agency (data from BVL, 2019, and BVL, 2021)

of chickens, so an input through the application of manure on fields is possible. Flunixin and/or its meglumine salt is approved for use in horses, pigs and cattle; input therefore occurs directly on pastures and indirectly through manure application on fields.

With only the consumption of antibiotics being systematically recorded in Germany, and the active ingredients mentioned not belonging to that class, it is currently not possible to estimate the potential input of TFA into the environment from veterinary pharmaceuticals. However, it may be assumed that the consumption of the anaesthetic gas isoflurane has been increasing significantly since January 2021. Since then, the castration of male piglets – to avoid boar taint – without anaesthesia has been banned, leading to an increased demand for anaesthetics. There are funding programmes to aid pig breeders in purchasing castration devices using isoflurane (BLE, n.d.). This will lead to a maximum additional TFA emission of 2.5 t/a (BT-Drs. 19/9723). For the other active ingredients, consumption is expected to remain constant.

Human pharmaceuticals

Research in DrugBank (Version 5.1.1) showed that 51 human pharmaceuticals contain C-CF₃ groups, of which 39 are approved in Germany. A comparison with the quantities consumed in 2020 shows that these could release a maximum of about 29 t/a of TFA (data from the IQVIA Inc.,² unpublished). Here, an unrealistically high rate of formation of 100% is assumed for the active ingredients discharged through sewage treatment plants. While there are indications suggesting that a small proportion of TFA may be formed from human pharmaceuticals in sewage treatment plants (Scheurer et al., 2017) it must be assumed that the bulk of human pharmaceuticals is introduced unchanged into surface water. The active ingredients degrade very slowly in surface waters, so the release of TFA may be assumed to be greatly delayed and fairly small. However, by introducing an oxidative fourth treatment stage, the release of TFA from human pharmaceuticals may shift towards effluents from sewage treatment. As already mentioned above, it has been shown that TFA may be formed from active ingredients containing a C-CF₃ group after ozonisation (Scheurer et al., 2017).

Of the maximum quantities of TFA formed, about 23% derive from the halogenated inhalational anaesthetics (anaesthetic gases) isoflurane, sevoflurane and desflurane. Their main input pathway is through exhaust air into the atmosphere, where TFA is formed from anaesthetic gases through various degradation processes and transported into waters through precipitation. In Germany, a total of about 180 t of these gases is used per year, of which 176 t find their way into the atmosphere (average for 2011 to 2018; ZSE, 2020). Taking into account the rates of formation of TFA – 95% for isoflurane, 7% for sevoflurane and 3% for desflurane – this will result in a maximum of about 7 t/a of TFA (Behringer et al., 2021). All three anaesthetic gases have relatively long residence periods in the atmosphere: 3.2 years for isoflurane, 14 years for sevoflurane and 1.4 years for desflurane (Vollmer et al., 2015). This means that the anaesthetic gases are dissipated globally, making an exact quantification of specific TFA inputs from anaesthetic gases in Germany highly difficult and unreliable.

A further 73% of TFA derives from six active ingredients: the diabetes medication sitagliptin, the analgesic celecoxib, the heart medication flecainide, the antidepressant fluoxetine, the cancer medication bicalutamide and the HIV medication efavirenz. The remaining active pharmaceutical ingredients each contribute less than 0.5% and just over four per cent in total. Human pharmaceuticals and their degradation products are transported from toilets to sewage treatment plants and from their effluent into surface waters – where they tend to degrade rather slowly. Small amounts may be discharged in sedimentation sludge as fertiliser on agricultural land (see Chapter 3.2).

As a result of demographic change, the consumption of pharmaceuticals is likely to have an upward trend. This is particularly true for diabetes, cancer and heart medication. Furthermore, there is a tendency towards using halogens in drug development. For instance, a skilful substitution with halogens may have a beneficial effect on the pharmacokinetics (uptake) and the metabolism of an active ingredient in the body (Wei Zhu et al., 2014). It is therefore to be expected

² For us to be able to share these data publicly, IQVIA requests the publication of the following pre-drafted text, which need not necessarily reflect the opinion of the German Environment Agency: "IQVIA MIDAS data combine country-level data, healthcare expertise and therapeutic knowledge in 90+ countries to deliver data in globally standardized forms to facilitate multi-country analyses, acting as a leading source of insight into international market dynamics relating to the distribution and use of medicines. IQVIA MIDAS data are designed to support multi-country analyses of trends, patterns and similar types of analyses. All of the calculations, algorithms and methodologies used to produce these estimates of real-world activity make the data highly reliable for these intended uses."

that further pharmaceuticals from which TFA can be formed will be put on the market. In sum, however, the small inputs of the active ingredients and the slow formation of TFA from human pharmaceuticals suggest that these constitute a rather negligible source.

Halogenated refrigerants and blowing agents

An important area of application of halogenated gases is their use as refrigerants in stationary and mobile refrigeration and air-conditioning units, as a blowing agent for plastic foams, and as an aerosol propellant. Halogenated gases are still used in high tonnages: according to Behringer et al. (2021), nearly 8,000 t were used in Germany in 2018.

These gases are emitted to varying extents in manufacturing, application and disposal. Data concerning the quantities used and emissions of halogenated refrigerants and blowing agents in Germany are available in the national inventory reports under the UN Framework Convention on Climate Change (UNFCCC). Figure 3 gives an overview of the emissions. Some of these halogenated gases degrade in the atmosphere to form TFA which, due to its very high solubility in water, is then transported into soils and waters through precipitation.

In 2018, the quantity of refrigerants and blowing agents with a potential for TFA formation amounted to about 5,800 t (ZSE, 2020). The refrigerant currently most in use, particularly in stationary and mobile refrigeration and air-conditioning systems, is HFC-134a (1,1,1,2-tetrafluoroethane, CH_2FCF_3). TFA is also formed from gases such as HFC-143a (1,1,1-trifluoroethane, $\text{C}_2\text{H}_3\text{F}_3$) and HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane, C_3HF_7), which are often components of refrigerant blends, whereas HFC-227ea is also a foam blowing agent and propellant. Since 2013, HFC-1234yf (2,3,3,3-tetrafluoropropene, $\text{CF}_3\text{CF}=\text{CH}_2$) has increasingly been used, often as a substitute for HFC-134a, particularly in motor vehicle air-conditioning units and also in refrigerant blends. Another relatively new substance is the fluorinated gas HFC-1234ze(E) (1,3,3,3-tetrafluoropropene, $\text{CF}_3\text{CH}=\text{CHF}$), which is increasingly being used as a refrigerant, as a blowing agent for extruded polystyrene (XPS) insulation foams, and as an aerosol propellant.

The atmospheric lifetime of fluorinated gases can range from a few days for unsaturated HFCs (such as R-1234ze(E) and R-1234yf) to several thousand years for perfluorinated gases. Rates of TFA formation also vary. For example, HFC-134a is very stable in the atmosphere, with only about 7 to 20% very slowly converted into TFA over many years, while more than 99% of HFC-1234yf degrades to TFA within a few days.

In a maximum scenario for Germany developed in a study by Behringer et al. (2021), it was calculated that a TFA formation potential from projected refrigerant and blowing agent emissions was about 2,300 t for 2020, which could triple by 2050, depending on future choices of refrigerants. The main cause for the increase in future quantities of TFA is the switch from HFC-134a to HFC-1234yf.

As the gases emitted into the atmosphere are dispersed across large distances and even across the seas, only part of their degradation products (such as TFA) is introduced back into the environment in Germany. Besides the atmospheric lifetime of the gases, local TFA input is determined by other factors such as season, air-mass flow, geographical location and level of precipitation. The balance of the input of these gases will therefore be more accurately represented in global or Europe-wide models.

On the basis of models using actual atmospheric concentrations of refrigerants and blowing agents, Behringer et al. (2021) estimate that in 2018, about 50% of the precipitation-induced input of TFA was attributable to known refrigerants and blowing agents, in particular HFC-134a. As a result of European bans and restrictions on halogenated gases with a high global warming potential, many long-life fluorinated gases are now being replaced by substances with a short atmospheric lifetime. With an increased use of HFC-1234yf, the absolute input of TFA and likely also its share in the total input will continue to increase by 2050. Detailed information on measurements and models for Germany and Europe regarding the input of TFA and refrigerants and blowing agents can be found in the papers by Freeling et al. (2020) and Behringer et al. (2021). The development of the use and environmental compatibility of halogenated refrigerants is summarised in Infobox 1.

Fluorochemicals in household and commercial products and on the move

The group of per- and polyfluoroalkyl substances (PFAS), also known by the synonymously used term per- and polyfluorocarbons (PFCs), comprises more than 4,700 different substances. About 2,000 of them have the potential for TFA formation. Many of these potential precursors of TFA are used in consumer products. Given their high stability and water-, oil- and dirt-repellent properties, they are found in various

materials coming into contact with food (e.g. paper cups, pizza boxes, baking paper, non-stick frying pans), outdoor clothing and workwear, carpets, and fire-fighting products. When using consumer products, for example as washing them, PFAS can find their way into wastewater and later, through sewage treatment plants, into the environment (Lenka et al., 2021). They may also contaminate the environment directly, as when PFAS-containing fire-fighting products are used.

INFOBOX 1: Environmental compatibility of halogenated refrigerants

The environmental compatibility of halogenated refrigerants and blowing agents has been questioned since the 1980s. In household refrigerators, aerosol cans and some plastic foams, chlorofluorocarbons (CFCs), which damage the ozone layer, have by now been replaced worldwide by halogen-free hydrocarbons (UBA, 2017). For other applications, chlorofluorocarbons were replaced mostly by hydrofluorocarbons (HFCs) (Figure 3). Since the 2010s, due to their global warming potential, these have frequently been replaced by unsaturated HFCs with a lesser global warming potential. However, unsaturated HFCs degrade in the atmosphere to halogenated substances such as TFA to an even greater extent. But substances such as carbon dioxide, ammonia and hydrocarbons already exist as natural, halogen-free alternatives for most applications such as refrigeration systems in supermarkets and in industry, air conditioning and heat pumps (UBA, n.d.; Eckert, 2019). There are funding programmes such as the German Ordinance on the promotion of refrigeration and air conditioning systems to support the transition (BAFA, 2020).

In mobile air-conditioning systems, the European car industry had been developing innovative systems using the non-inflammable refrigerant carbon dioxide as a replacement for HFC-134a with its very high global warming potential since the late 1990s. Since about 2006, tests for their introduction into series production were under way. However, with international car manufacturers in the end agreeing on the inflammable and more

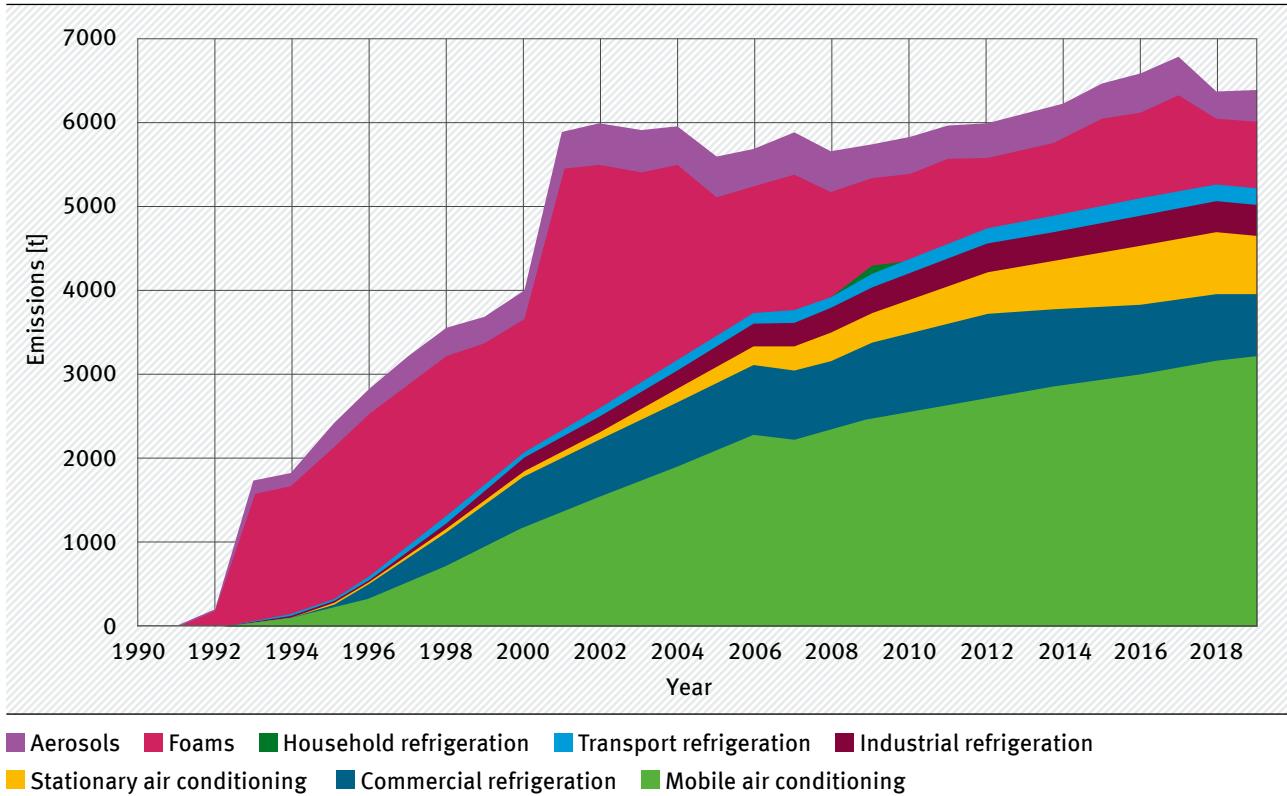
expensive halogenated refrigerant HFC-1234yf, the transition to the safe natural refrigerant carbon dioxide was abruptly cancelled in 2010 in Germany as well. By using HFC-1234yf, the input of TFA from refrigerant emissions is now increasing by a multiple compared to HFC-134a.

The feasibility of carbon-dioxide air-conditioning systems was demonstrated by some car models from Germany introduced since 2016. They had been developed in response to safety concerns arising from tests of some car air-conditioning units using HFC-1234yf in 2012 (NTV, 2013). The first electric car models with an optional carbon-dioxide air-conditioning unit with a heat-pump function for heating have been offered since 2020 (VW, 2020). TFA input can be reduced if manufacturers of cars with new drive systems opt for natural refrigerant solutions for mobile air conditioning systems in the medium term and do not use halogenated liquids for battery cooling.

Mobile carbon-dioxide air-conditioning systems with efficient heat pumps are already available for electric buses, replacing additional diesel-powered heaters in winter (Konvekta, 2020). Some trains, for instance, are cooled using air-based systems entirely without separate refrigerants (UBA, 2019). Air-conditioning systems using carbon dioxide or hydrocarbons are also being tested for trains. Further information on mobile air conditioning focussing on refrigerants can be found on the website of the German Environment Agency (UBA, n.d. a).

Figure 3

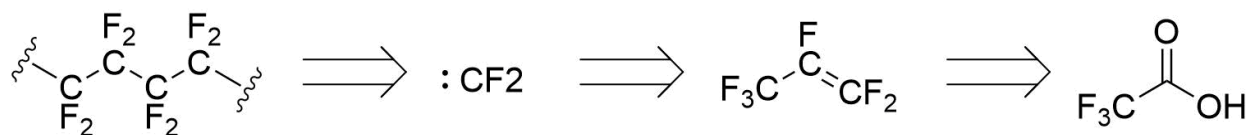
Increase in emissions from refrigerants and blowing agents (HFC and unsaturated HFC) in important sectors in Germany from 1990 to 2019, in tonnes



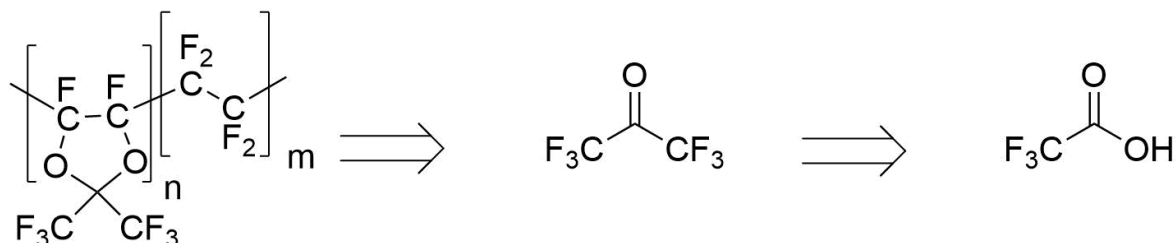
Source: own diagram, German Environment Agency, (data from ZSE emissions database of the German Environment Agency as of 11/2020; ZSE, 2020)

Many instances of PFAS contamination in soils and in groundwater have already been documented in Germany. In North Rhine-Westphalia, fire-fighting products were identified as the primary source (73%) of PFAS contamination in soils and groundwater, followed by effluents from electroplating (10%) and polluted sludge from wastewater treatment (6%) (MULNV NRW, 2019). But it is usually unknown in these cases whether and to what extent soils and groundwater have also been polluted with TFA, as in most cases only PFAS with a longer carbon chain are analysed ($\geq C4$).

Fluoropolymers, e.g. Teflon® as one of the best known substances in this group, have found a wide range of applications as insulation for cables, protective coating for textiles and metals, medical protection equipment, chemically inert seals and membranes in functional clothing. Semicrystalline fluorinated polymers make up a major part of the market, with a trading volume of approx. 220,000 t globally in 2012. The largest share of this is represented by polytetrafluoroethylene (PTFE) at 126,000 t/a. A much smaller share (< 1 t/a) is made up of amorphous Teflon variants (e.g. Teflon® AF) which find special applications due to their excellent optical properties and low refractive index (Gardiner, 2015; Teng, 2012; Dams and Hintzer, 2016).



(from: Ellis et al., 2001)



(from: Blakey et al., 2007; Jackson et al., 2011)

As early as 2001, Ellis et al. (2001) reported that thermolysis of PTFE yields 8% TFA. The conditions used in the study resembled the temperatures at which PTFE is processed (sintering process). The proposed degradation mechanism assumes a decomposition of PTFE into carbene radicals, from which hexafluoropropylene (HFP) is produced, which in turn can be converted into TFA (Ellis et al., 2001).

For the less widespread amorphous fluoropolymer, photochemical degradation was observed by Blakey et al. (2007), detecting hexafluoroacetone (HFA) as a main degradation product of Teflon® AF. HFA is a volatile compound which can be converted into TFA by photolysis, e.g. in the atmosphere. In addition, HFA can also be converted into TFA under alkaline conditions (e.g. by contact with alkaline detergents; a related process is called haloform reaction) (Blakey et al., 2007; Jackson et al., 2011).

Thus, a degradation of fluoropolymers into TFA is detectable. The photolytic degradation of amorphous polymers seems more relevant at first, as it can occur solely by UV radiation. However, given the small quantities of Teflon® AF (and other amorphous fluoropolymers) produced, this process is likely to be less significant for the quantities of TFA in the environment. While the formation of TFA from PTFE (and other semicrystalline fluoropolymers) has only been detected at very high temperatures and is therefore less relevant in the environment, the high production volumes do present a certain potential for TFA emission.

PFAS therefore constitute a significant group of substances used in large quantities. However, they are usually not easily degradable under environmental conditions and produce TFA very slowly and in small quantities, if at all. A recent study by Sun et al. (2020) suggests that at least short-chain fluorotelomer alcohols (4:2 FTOH and 6:2 FTOH) can be degraded into TFA by certain microorganisms under specific laboratory conditions.

Natural sources

Geological and biological sources in the sea seem to be responsible for small but continuous inputs of TFA (Frank et al., 2002). Increased concentrations of TFA have been measured in the vicinity of deep-sea vents in particular (Scott et al., 2005). According to Scott et al. (2005), about 6 t/a of TFA are produced by hydrothermal vents under the sea.

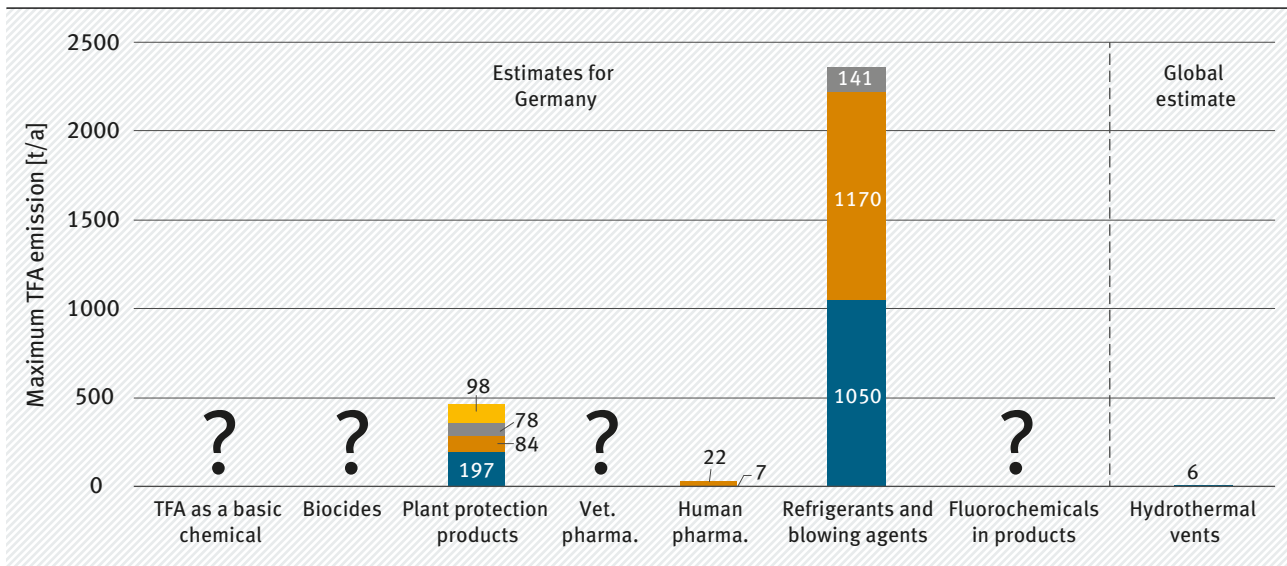
By comparison to the chloride discharge from the seas, Nödler et al. (2019) and Behringer et al. (2021) show that only very small quantities of TFA are likely to be transported to the shore from the seas.

Overview of TFA sources

The results of Chapter 2 are summarised in Figure 4, which lists the estimated maximum TFA emissions per area of chemicals.

Figure 4

Estimated maximum TFA emissions in t/a for the relevant groups of chemicals*



* Calculated from the respective quantities sold or the emissions (refrigerants and blowing agents), or taken from published model-based estimates (hydrothermal vents)

Source: own diagram, German Environment Agency (data basis: see Notes on Fig. 4)

Notes on Figure 4

Germany

TFA as a basic chemical: Here, the tonnage of 100–1,000 t/a is given as the quantity put on the market at EU level (REACH); no specific figure for Germany is available, as well as for the amount of TFA emitted into the environment as a result of the manufacture and application of the substance itself. The use of TFA as a basic chemical is assumed to be largely limited to enclosed spaces and sealed containers in laboratories and synthesis facilities, so TFA is not usually emitted into the environment directly from the place of use, but may be released from wastewater treatment plants acting as a catchment for indirect release from various connected emitters and point sources.

Biocides: Sales figures for biocidal products are not known; therefore, no quantitative estimate can be given.

Plant protection products: A major part of the maximum TFA emissions is due

to three approved active substances: Flufenacet (blue), Diflufenican (orange) and Fluazinam (grey). The potential for TFA formation from all 23 other potentially TFA-forming substances is given as a sum in yellow.

Veterinary pharmaceuticals: Sales figures for veterinary pharmaceuticals are not known; therefore, no quantitative estimate can be given.

Human pharmaceuticals: For human pharmaceuticals, a distinction can be made between drugs that find their way into the water cycle through wastewater (orange; mostly the drugs sitagliptin, celecoxib, flecainide, fluoxetine, bicalutamide, efavirenz) and those that, as anaesthetic gases, are emitted into the environment via the atmosphere (blue; isoflurane, sevoflurane, desflurane).

Refrigerants and blowing agents: Estimate of the potential quantity of TFA from refrigerants and blowing

agents for the year 2020 on the basis of expected emissions in Germany and rates of TFA formation (Behringer et al., 2021). A further increase is to be expected for the coming years as a result of the increased proportion of the refrigerant R-1234yf, in particular, which is converted into TFA at almost 100% (blue: TFA from refrigerant R-134a; orange: TFA from refrigerant R-1234yf; grey: TFA from other refrigerants).

Fluorochemicals in products: An estimate is not possible here; however, the emission is likely to be negligible.

global

In the absence of data for natural sources (hydrothermal vents) for Germany or Europe, we here present estimates of the global TFA emissions from these sources instead.

Hydrothermal vents: estimate of the global TFA emission per year from hydrothermal vents by Scott et al. (2005).

3 Input pathways

In Chapter 3, we investigate input pathways, taking a local perspective depending on the pathway. A distinction is made between isolated, localised input pathways and diffuse, more extensive input pathways. In this chapter, the individual input pathways will be discussed in detail.

Figure 5 shows the most important input pathways into the water cycle and their interactions.

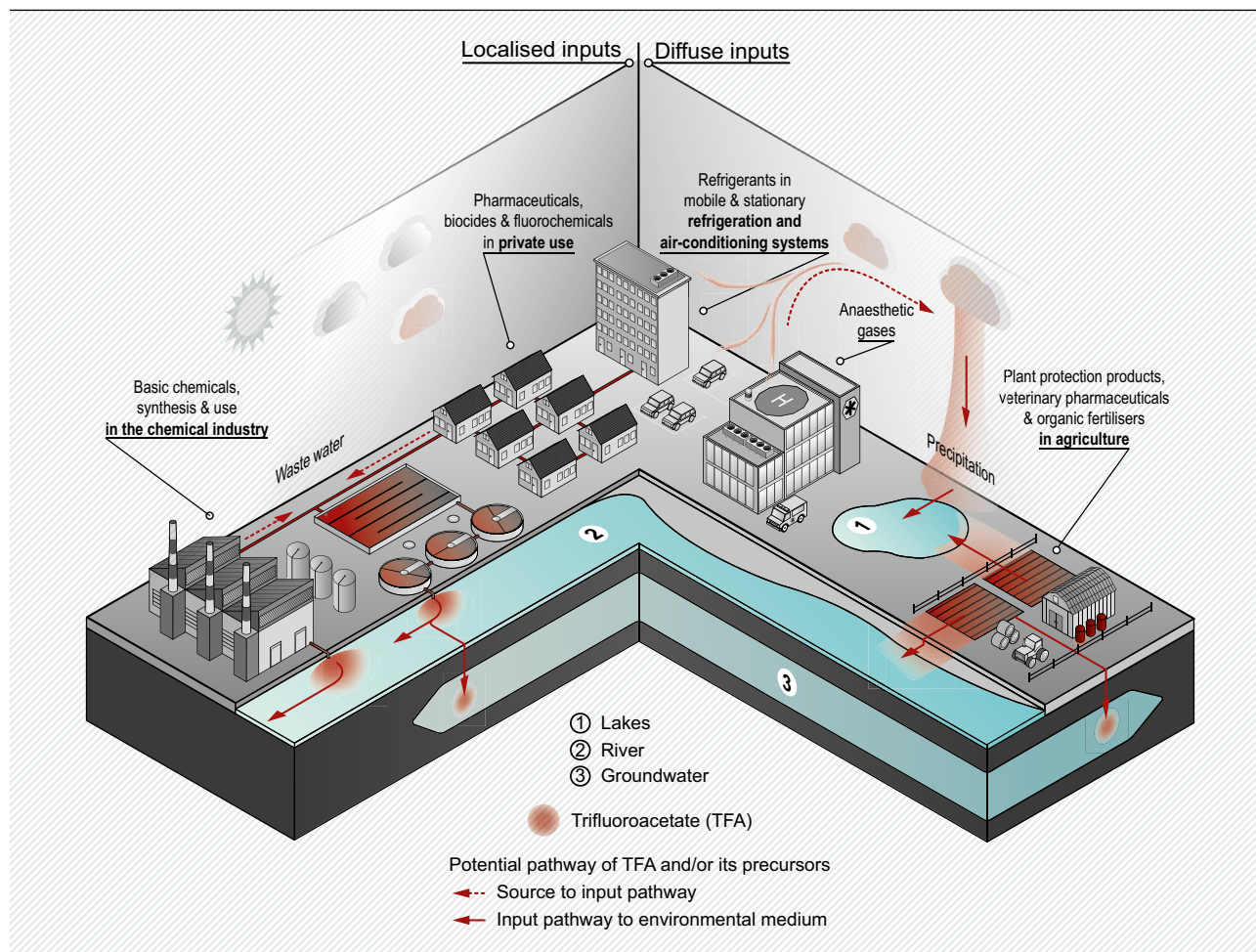
3.1 Localised input

Localised input occurs through the discharge of wastewater from industry and municipalities into surface waters – often major rivers. Its effect on local concentrations can be very high. In Germany, industrial

discharge in the majority of cases requires a permit, which is issued at the local level on the basis of local environmental conditions and their reception capacity. In a typical case, such a permit would impose an obligation on the applicant to use the best available technology (BAT) and respect the requirements set under immission control legislation (e.g. German Federal Immission Control Act; German Technical Instructions on Air Quality Control) and medium-dependent environmental legislation (e.g. German Wastewater Ordinance; environmental quality standard (EQS); see Infobox 5) relevant to the specific type of industrial installation. The final emission permit would usually involve considering known pollutants and common sum parameters for the specific industrial sector. Given the around

Figure 5

The most important sources and input pathways leading to TFA contamination in surface waters and groundwater



Source: own diagram, Anika Lehmann

2,000 potential precursors of TFA and the intangible number of applications, it is not possible to estimate the amount of local releases of TFA from industrial facilities and wastewater treatment plants – this is also because TFA is not covered by reporting obligations under EU industrial plants legislation (Directive 2010/75/EU – Industrial Emissions Directive (IED)) or under medium-based environmental law. Direct TFA discharges are known in only two cases – a chemicals manufacturer on the River Neckar (Infobox 2) and on the River Alz in Bavaria (Scheurer et al., 2017).

Other releases of TFA at the local level can result from waste treatment processes, such as landfill. Various transformation processes occur on (in-situ) landfill sites, which may lead to the formation of TFA and its emission into the environment. To our knowledge, there have been no studies of relevant release pathways or quantities of emissions from landfill sites. Therefore, no quantitative estimate can be given.

Chemicals from human pharmaceuticals, biocides and from commercial and private applications typically accumulate in municipal wastewater treatment plants. Just as their sales volumes (Chapter 2), their inputs are difficult to quantify and likely to be rather small. Predictions regarding concentrations in surface waters of human pharmaceuticals show that a concentration significantly greater than 0.01 µg/L is expected only for the drug sitagliptin – the other five substances, celecoxib, flecainide, fluoxetine, bicalutamide and efavirenz, are estimated at < 0.01 µg/L (UBA calculations on the basis of IQVIA consumption figures). The water of the River Rhine takes about 10 days to flow from Lake Constance to the mouth (ARD, 2015). Given the average half-life periods of human pharmaceuticals, if a wastewater treatment plant discharges into the Upper Rhine, the river will transport the greater part of TFA precursors into the sea before they can degrade into TFA.

Effluents from four wastewater treatment plants were tested for TFA in measurements conducted by the State

INFOBOX 2: Release from industrial production – TFA in the River Neckar

It was releases from the production of fluorochemicals that set the TFA ball rolling: in 2016, the Karlsruhe-based Technologiezentrum Wasser (TZW) coincidentally measured TFA in the River Neckar in south-west Germany and reported it to the Baden-Württemberg State Institute for the Environment, Survey and Nature Conservation (LUBW). The production site of the chemical manufacturer Solvay at Bad Wimpfen was identified as a point source discharging TFA into the River Neckar in quantities of 100 kg/day (12 kg/h at peak times). In this specific case, the substance is formed during the synthesis of fluorochemicals as a by-product to be separated.

Downstream in the Heidelberg/Mannheim area, drinking water gained from the Neckar catchment by riverbank filtration was polluted with TFA at more than 20 µg/L – significantly above the then permitted maximum (health-related indicator value) of 1 and 3 µg/L, respectively. Concentrations below this indicator value could not be obtained even by mixing the water with water from other sources. To guarantee the drinking water supply, a value applied as a precautionary measure of 30 µg/L was set for drinking water – which was, however, temporary and

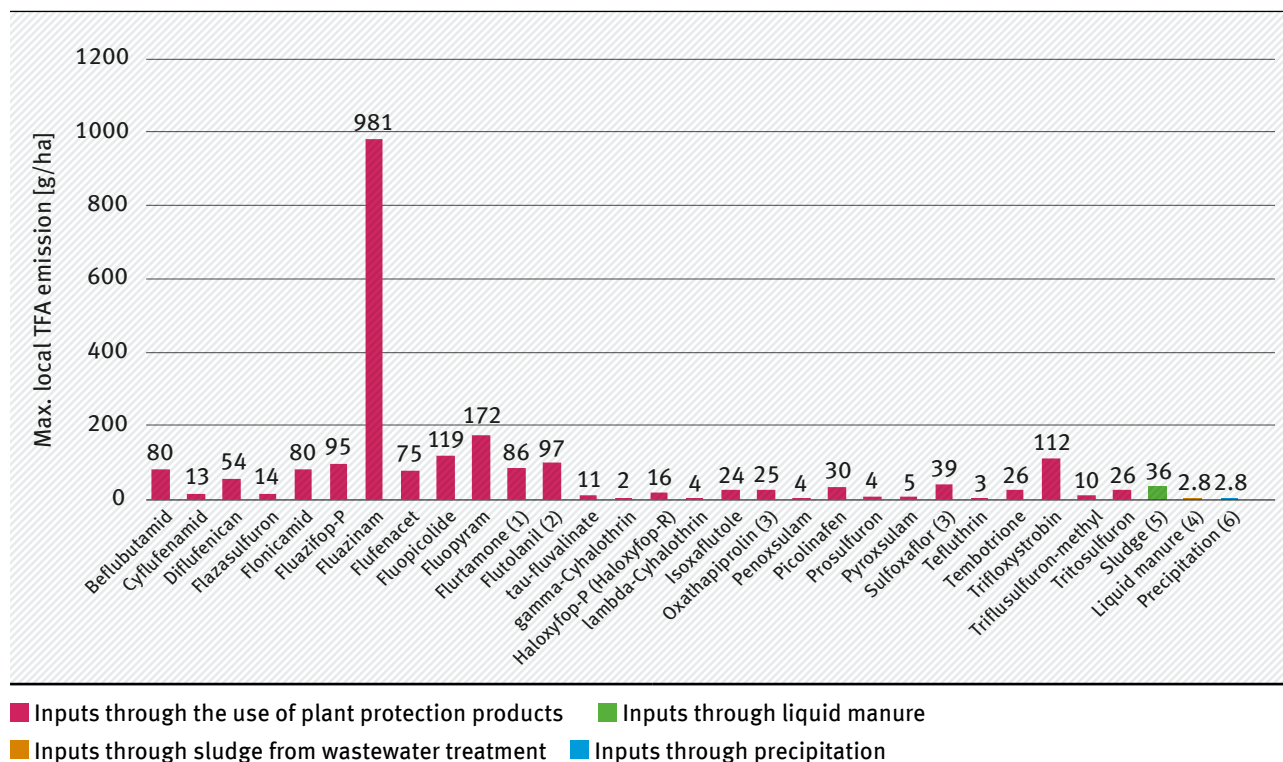
local in scope and accompanied by strict requirements to reduce TFA inputs (Infobox 5).

In this context, the emissions of TFA into the River Neckar were drastically reduced in the short term: Solvay identified one of its four plants as the main source of TFA and took it out of operation. Since late 2016, the other plants have been running at reduced capacity and no longer in parallel. By implementing these measures, the emission was reduced by 90% (Solvay, 2017; Heilbronner Stimme, 2016). Nevertheless, TFA concentrations in the river will only decrease in the medium term. Solvay commissioned an extensive study in recent years to investigate the chronic toxicity of TFA. On this basis, a new toxicological health-based guideline value for drinking water of 60 µg/L was derived and published as a recommendation by the German Environment Agency in May 2020 (UBA, 2020a; UBA, 2020b) (see Infobox 5).

It is not known at present how many other production sites in Germany emit TFA and might constitute a significant point source of TFA.

Figure 6

Comparison of estimated local TFA inputs through plant protection products,* liquid manure, sludge from wastewater treatment and precipitation



* Calculations on the basis of the quantities approved for use

TFA inputs from plant protection products were calculated directly from the maximum approved quantities of the active substances, which may be in the range between 10 and 2,000 g/ha. (1) This active substance is no longer approved at EU level (must be used up by 2020); (2) there are currently no products with this active substance authorised for use in Germany; (3) products containing this active substance are currently authorised but not marketed (no sales); (4) worst-case estimate calculated on the basis of individual measurements of TFA in liquid manure samples (Nöddler et al., 2019) – the value is not necessarily representative and should be verified by further measurements; (5) worst-case estimate calculated on the basis of modelling residues from human pharmaceuticals using the SimpleTreat model; (6) mean value from rainwater measurements during the 2019/2020 one-year measurement period in Behringer (2021); due to higher rates of TFA formation from new refrigerants and slightly increasing sales figures, a higher input is expected for the future. The input occurs across Germany.

Quelle: eigene Darstellung, Umweltbundesamt (Daten aus: BVL, 2021)

Office for Nature, the Environment and Consumer Protection of North Rhine-Westphalia (LANUV). The values detected were between 1.7 and 4.5 µg/L – which is within the range of the concentrations in the surface waters into which they discharge (LANUV, 2018). This may indicate that municipal wastewater treatment plants are not a major input pathway for TFA and that their impact on concentrations in rivers is rather small due to the dilution of treated wastewater in the receiving body of water. However, the LANUV data are compiled from individual samples and not from a time series, so it is not possible to generalise from them. Further tests with a larger number of samples would be welcome in order to obtain more definitive information on the spatial and temporal context of the TFA concentrations detected.

Further testing of municipal wastewater treatment plants as a potential input pathway is also important

with regard to the introduction of an oxidative fourth treatment stage. This may lead to a significant increase in the release of TFA from various fluorinated chemicals, simply because oxidation contributes to the accelerated formation of TFA (Scheurer et al., 2017).

3.2 Diffuse input

The diffuse input pathway of TFA through agriculture can be fed by plant protection products or fertilisers. Another diffuse input pathway is precipitation. In this section, we give quantitative estimates the maximum or probable TFA emissions via these input pathways.

Figure 6 shows the maximum emission of TFA per hectare of agricultural land. The basis used for plant protection products is their typical quantities and patterns of use in Germany. With no data from degradation studies available, a 100% rate of TFA formation from the precursor is assumed for

all substances – in analogy to the calculations in Chapter 2. In reality, this rate will depend not only on the properties of the active substance, but also on the soil types and local hydrological conditions. These factors are locally very heterogeneous and cannot be considered in this background papers. Figure 6 shows that, due to the large quantities used, fluazinam can play a particularly important part in TFA emissions through plant protection products locally. In comparison, local TFA emissions after use of flufenacet are in the medium range. However, flufenacet plays a much larger part across the board, as it is used on farmland all over Germany – while fluazinam is used much less widely. Thus, with respect to Germany as a whole, flufenacet remains the most important plant protection product for TFA inputs into the environment (see Chapter 2 and Figure 2).

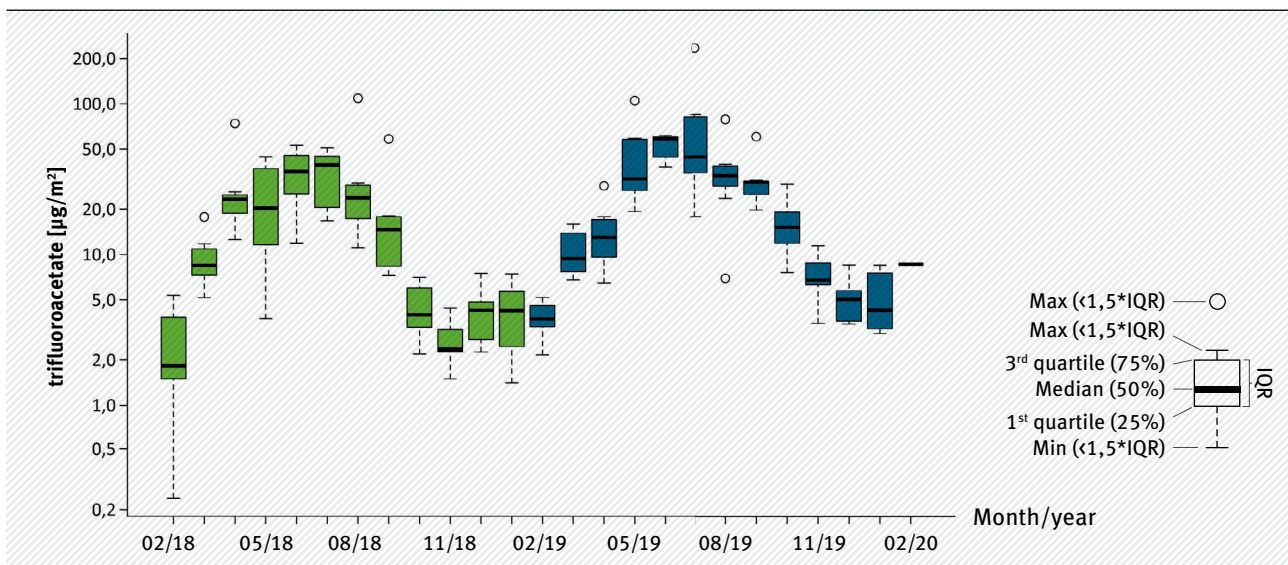
Besides plant protection products, Figure 6 contains the potential inputs through liquid manure and sludge from wastewater treatment as well as precipitation (more on this below). Liquid manure and sludge can contain TFA or its precursors, for instance via the use of pharmaceuticals and biocides (see Chapter 2). The calculation of the quantity of TFA input from liquid manure is based two data sources.

One of these consists of (not necessarily representative) individual measurements, which detected about 100 µg/L of TFA in liquid manure (Nödler et al., 2019). The other is the use of liquid manure on grassland, representing a maximum of the recommended applications of liquid manure (LWK Lu, 2014). The maximum TFA content in sludge from wastewater treatment is derived from model-based estimates by the German Environment Agency of residues of human pharmaceuticals in wastewater treatment plants and the maximum permitted quantity of sludge of 5 t/ha over a three-year period. The estimate assumes a complete degradation of the pharmaceuticals in the soil. This means that the quantities of TFA may be significantly overestimated, given that human pharmaceuticals are often very persistent. As regards potential inputs from the use of biocides, no such estimate was possible for lack of sales figures. For the reasons already stated, the proportion of the overall contamination of sludge by TFA as a substance itself or via its potential precursors within the scope of the EU REACH Regulation is not possible either.

TFA formed in the atmosphere, being highly soluble in water, can find its way into the water cycle through precipitation. Concentrations of TFA in precipitation

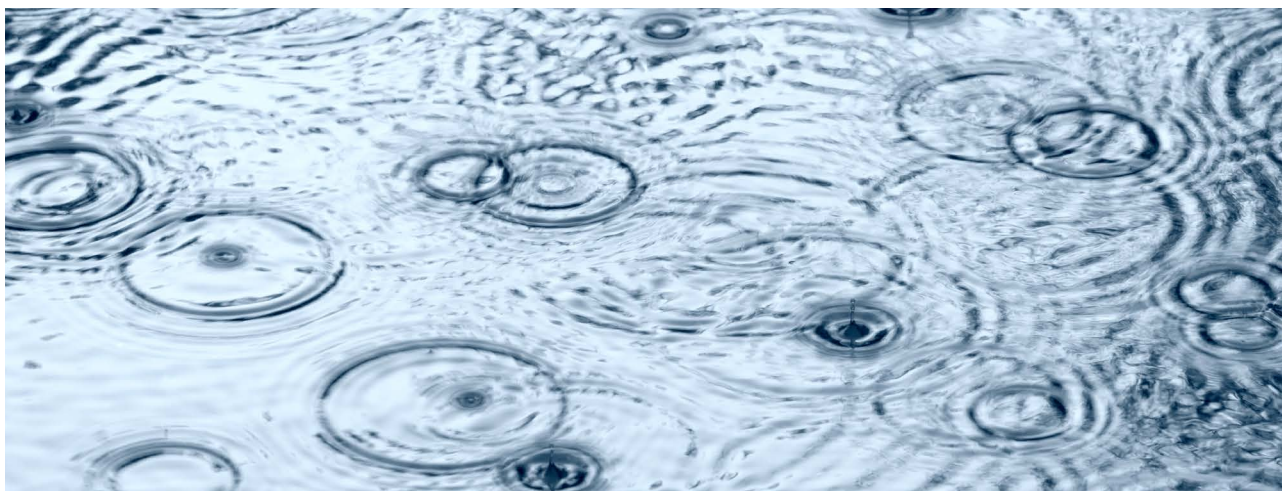
Figure 7

Monthly input of trifluoroacetate through precipitation in Germany between February 2018 (02/18) and February 2020 (02/20)



Monthly trifluoroacetate inputs through precipitation in Germany between February 2018 (02/18) and February 2020 (02/20). The box plots shown are based on the median values in the analysis of volume-equivalent composite monthly precipitation samples from seven monitoring stations of the German Meteorological Service across the country; only wet deposition is included. Data are grouped according to time (month and year). The Stuttgart station is not included for 02/18; in February 2020, measurements were only taken at the Stuttgart station. The y-axis is on a binary logarithmic scale. The two periods from February to January are shown in different colours. (IQR: interquartile range) (More details on the measurements in Behringer et al., 2021).

Source: Ökorecherche and TZW, 2021



were systematically measured for the first time in a 2-year nationwide measurement programme at eight monitoring stations of the German Meteorological Service in the period from early 2018 to early 2020 (Freeling et al., 2020; Behringer et al., 2021). Figure 7 shows a summary of the results. A comparison with measured values from several years ago shows a general increase of the TFA concentration in rainwater (Behringer et al., 2021). Local TFA input depends on the amount of precipitation and is subject to seasonal variations. In Germany, inputs are highest in the summer (Freeling et al., 2020; Behringer et al., 2021). The reason might be the higher solar radiation in summer leading to increased degradation of gases in the atmosphere. Another possibility being discussed is the increased emission of refrigerants from air conditioning in the summer. Future comparative measurements should therefore be carried out for at least a whole year.

From the concentrations in rainwater, it was possible to calculate the annual quantity of TFA input from the atmosphere in Germany. While inputs in the 1990s were in the range of 54 to 69 g/km² (measurement period: 1995/1996), inputs today are at least three to four times higher, at 190 g/km² (measurement period: 2018/2019) and 276 g/km² (measurement period: 2019/2020) (Behringer et al., 2021). This is equivalent to 1.9 g/ha and 2.8 g/ha, respectively. The total TFA input for Germany calculated on the basis of these data was approx. 67 t for the 2018/2019 measurement period (Freeling et al., 2020) and approx. 99 t for the 2019/2020 measurement period (Behringer et al., 2021). This significant increase can be explained, on the one hand, by the low amount of precipitation in 2018 and, on the other hand, by the increased use of

the refrigerant R-1234yf, which transforms to TFA at a rate of 100% and has been used in practically all new mobile air-conditioning systems in Europe since 2017 (see Chapter 2).

Figure 6 suggests that, at the local level, precipitation is relatively insignificant compared to other sources. This, however, only applies where the relevant land has indeed been treated with plant protection products, liquid manure or sludge from wastewater treatment plants – which applies to only part of the land area. Precipitation, on the other hand, falls in every part of the country throughout the year and thus affects all land, independent of the land use. The total quantities of TFA from refrigerants and blowing agents introduced across the country by precipitation will increase significantly, as documented in Chapter 2. However, where high TFA concentrations are measured in regions with intensive agricultural land use, plant protection products are the obvious cause.

The high potential for TFA input into waters from plant protection products is confirmed by modelling from the plant protection authorisation process. These models estimate concentrations to be expected in groundwater and surface water from the use of a product under unfavourable but realistic conditions. For flufenacet as an active substance, a reliable data source is available (EFSA, 2017a). According to this, following the use of products containing flufenacet (with a maximum applied quantity of 240 g/ha in cereal farming), the estimated input into groundwater is 27 µg/L, while the concentration in surface waters is between 0.3–0.6 µg/L. The models used for calculating the expected concentrations in the authorisation of plant protection products differ greatly, so the concentrations

are not directly comparable and do not directly represent contamination in the field. However, they do indicate that TFA inputs through agricultural use are emitted primarily via direct leaching into groundwater, and less by runoff into surface waters. This is plausible: as TFA is formed in several steps of degradation in the soil, it is less subject to surface runoff than to vertical leaching through the soil layers. The levels of TFA contamination measured in different surface waters and in groundwater support the conclusion that high levels of contamination in groundwater are likely to result from agriculture, especially the use of plant protection products (Chapter 4).

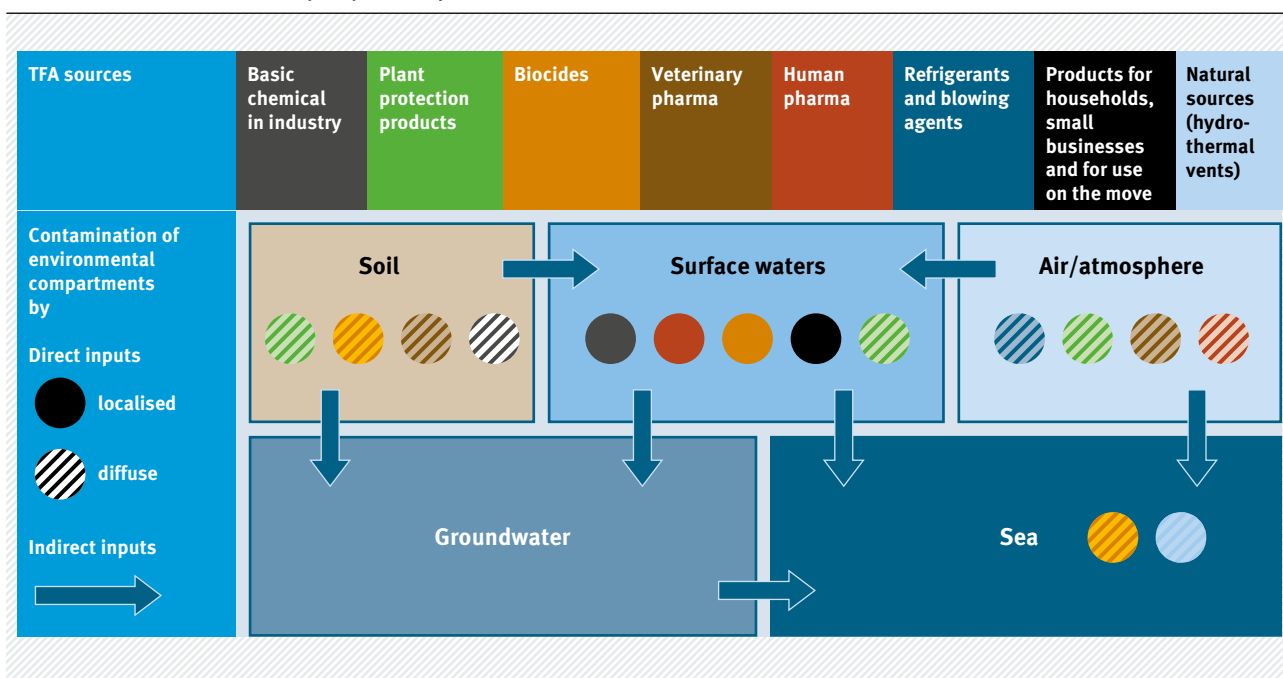
Further diffuse input pathways are found wherever products containing fluorinated chemicals for commercial users and consumers are used – within their intended range of application – in a widespread manner and in an open environment, i.e. in urban spaces along roads, in built-up areas, parks, landfill sites, etc.. Such inputs can also come from industrial and contaminated sites, or may occur as a result of accidents. The latter, however, do not form part of the “intended conditions of application” and, accordingly, are not considered in the evaluation processes of the different chemical legislations. As discussed in Chapter 2, such inputs are difficult to quantify and are likely to be relatively small.

Interactions of localised and diffuse inputs

Figure 8 provides a summary of the environmental compartments where TFA is introduced through localised and diffuse input pathways and shows the interactions of sources, input pathways and contamination (details in Chapter 4). It should be noted that the main input pathways are those through agricultural land, precipitation, industrial discharge and municipal wastewater treatment plants. It is apparent that surface waters, in particular, at the local level receive TFA predominantly via direct emissions from point sources. These are caused by e.g. biocides, human pharmaceuticals or chemical production sites. TFA in soil is largely the result of diffuse inputs, especially from plant protection products, but also from the application of e.g. biocides or veterinary pharmaceuticals in liquid manure. There are also diffuse inputs into the air, particularly through refrigerants and blowing agents, but also through e.g. plant protection products or anaesthetic gases. From these compartments, TFA is transported further, through indirect inputs, into groundwater and the sea. There are also some minor direct diffuse inputs into the sea, e.g. from anti-fouling products or hydrothermal vents.

Figure 8

Interactions of sources, input pathways and contamination



Source: own diagram, German Environment Agency

4 Contamination

Analyses of TFA in aqueous media have so far focussed primarily on drinking water, surface water and groundwater. Such analyses generally make use of liquid chromatography–mass spectrometry (LC–MS) techniques. To a smaller extent, gas chromatography and ion chromatography are also used, each in combination with mass spectrometry (Koch, 2018). At the time of writing, there is no standardised method for detecting TFA in water. Given the expected input quantities and problematic substance properties (see Chapter 1), monitoring of TFA concentrations is a relevant issue. In order to take account of this in future, for instance by statutory controls, the German Institute for Standardization (DIN) has initiated a project for standardising the analysis of di- and trifluoroacetic acid using LC–MS.

To capture precursor compounds of TFA, total oxidisable precursor (TOP) assay is now also being used (Houtz and Sedlak, 2021). Here, a specific oxidation reaction is used to convert polyfluorinated into perfluorinated substances (such as TFA) which are then detected using chromatography–mass spectrometry.

TFA is not captured by the sum parameter “adsorbable organic fluorine” (AOF). Due to its polarity, TFA is only adsorbed on activated carbon in very small quantities and thus escapes detection (DIN 38409-59).

Scheurer et al. (2017) describe a reliable and reproducible method for measuring TFA. Such a method having been lacking for a long time, it is only recently that TFA has been measured in the environment, and this is still not done across the board, but rather in a project-based manner, usually by water suppliers. The measured values reported below are thus not representative for Germany. For that to be the case, regular and extensive measurements in ground and surface water would be required – including of small surface waters and groundwater not used for drinking water production.

Since 2017, the federal states in Germany have in some cases carried out measurements in rivers and estuaries. Also since 2017, the German Environment Agency has recommended taking TFA into account in groundwater

monitoring by the federal states (UBA, 2019a). Several federal states and water suppliers have since included TFA in their measurement programmes or are planning to do so. Thus, we expect a better basis of data, at least for groundwater, in the coming years, providing a better overview of the distribution of TFA concentrations in German waters.

4.1 Marine environment

Very few measurements of TFA concentrations in the sea are available. These range from 0.01 µg/L in the Pacific to a maximum of 0.25 µg/L in the North Atlantic. TFA concentrations in the oceans cannot wholly be attributed to natural sources such as hydrothermal vents: anthropogenic input into the marine environment, e.g. due to atmospheric deposition or TFA-polluted rivers, is also relevant (see Chapters 2 and 3.2). Due to the persistence of TFA and the low level of evaporation of sea water, an accumulation of TFA in the marine environment may be assumed. Even low concentrations of TFA in rivers contribute to this accumulation in the case of continuous input (Nödler et al., 2019; Freeling et al., 2020).

Current measurements of TFA in the German waters of the North and Baltic Seas provide evidence for its wide distribution in the marine environment. In the Baltic Sea, in coastal waters of Mecklenburg-Western Pomerania in the north-east of Germany, TFA is mostly found in inshore waters with little water exchange: TFA concentrations were found in Saaler Bodden (mean value: 1.45 µg/L), Kleiner Jasmunder Bodden (mean value: 0.60 µg/L) and in the Szczecin Lagoon (mean value: 0.46 µg/L). In Wismar Bay, the Bay of Pomerania and the Warnow estuary, TFA concentrations were consistently below the limit of quantification of 0.3 µg/L³ (data provided by the State Agency for Environment, Nature Conservation and Geology, Mecklenburg-Vorpommern). TFA has also occasionally been measured in the North Sea. In 2018, Lower Saxony carried out a comprehensive state-wide survey of TFA contamination in surface waters (see Chapter 4.2) (Nödler et al., 2019). In addition, in May 2018, in parallel to the studies carried out as part of the Federal State Monitoring Programme

³ The limit of quantification (LOQ) varies according to the analytical method used; here, the LOQ is 0.3 µg/L.



(BLMP), 16 samples were taken in the North Sea by helicopter. Here, all the values were above the limit of quantification⁴ (median: 0.33 µg/L (n=16)) (Nödler et al., 2020). This level of concentration was confirmed by subsequent measurements in February 2020.

TFA primarily accumulates in marine waters with little water exchange and in estuaries of larger rivers. This is supported by the generally increased concentrations in the estuaries of the rivers Elbe, Weser and Ems (Nödler et al., 2020).

4.2 Rivers, lakes and estuaries

Rivers, lakes and estuaries are monitored by the competent environmental authorities, water suppliers and/or their corresponding water boards. So far, TFA is not routinely measured across all surface waters.

At present, there are analyses and reports of available measurements by the competent environmental authorities in Lower Saxony (Nödler et al., 2019) and North Rhine-Westphalia (LANUV, 2018) as well as by the International Commission for the Protection of the Rhine (ICPR, 2019). Almost all federal states have carried out measurements. The Elbe River Basin Community has included TFA in its co-ordinated monitoring programme for 2021.

In the majority of cases, samples and measurements are only taken once or twice a year. The water control station at Worms, on the Rhine, analysed daily mixed

water samples in 2017 and 2018 and weekly mixed water samples from 2019. In that period, maximum values ranging from 4.7 µg/L (2017) to 1.3 µg/L (2019) were measured. In 2018, in the River Elbe, a maximum of 1.8 µg/L (4 measurements) was detected at Schmilka (on the Upper Elbe, close to the border to the Czech Republic) and a maximum of 12.8 µg/L (12 measurements) was detected at Seemanshöft (located where the Elbe exits Hamburg harbour towards the North Sea; FIS FGG Elbe, 2020). In smaller surface waters in Lower Saxony and Mecklenburg-Western Pomerania, values of up to 7 and 8 µg/L, respectively, were measured in 2018 and 2019 (Nödler et al., 2019). In various surface water bodies in North Rhine-Westphalia, values above the limit of quantification – but still mostly below 3 µg/L – were frequently measured. In the Neckar region, measured values of up to 17 µg/L still occur. While the increased concentrations in the Neckar region can mostly be attributed to industrial product discharges (Infobox 2), in Lower Saxony and elsewhere, plant protection products are assumed to be the main source of TFA (LANUV, 2018; NLKWN, 2019).

These data are supplemented by measurements made by water suppliers as well as by their water boards and in local collaborations; these tend to take project-specific measurements, e.g. in investigating existing cases of contamination.

⁴ The limit of quantification (LOQ) varies according to the analytical method used; here, the LOQ is 0.05 µg/L.

On the basis of the possible input pathways listed in Chapter 3 and available measurements, a hierarchy of emission pathways into surface waters becomes apparent: Large industrial dischargers are of great significance locally. The share of discharges from municipal wastewater treatment plants remains to be established, but is likely to be of less significance locally. Where no such localised inputs exist, increased concentrations are highly likely to be attributable to agricultural activity, which is, after all, practised on about half the total territory of Germany. Inputs through precipitation lead to measurable but relatively low concentrations of TFA which affect all waters.

Given the paucity of data, however, it is not possible to trace locally increased TFA concentrations to specific sources and input pathways without specific investigation: local environmental conditions, particularities of land use, and the large number of potential – sometimes unquantifiable – sources and input pathways make it difficult to identify causes unequivocally. Yet, it is apparent even now that each of the pathways – localised discharges of treated wastewater, agriculture and precipitation – contributes in its own way to TFA concentrations in the environment and has a different effect on the concentration and dispersal of the inputs.

4.3 Groundwater

Only a few federal states currently test for TFA in groundwater bodies. Due to the importance of groundwater as a source of drinking water, some data from water suppliers and water boards are available, but not for the whole country.

Groundwater bodies in close hydrological connection with bodies of surface water are also strongly affected by the TFA content in the latter. On the River Neckar, near the industrial discharger mentioned in Infobox 2, more than 20 µg/L of TFA was detected in groundwater. Some bodies of groundwater in the Rhine and Elbe catchment areas showed corresponding peak concentrations of between 1 and 5 µg/L (IAWR, 2018; Steverkooperation, 2019).

However, some significantly higher concentrations have been detected in groundwater not connected to surface water. Concentrations of more than 3 µg/L are found particularly in regions with intensive agriculture. In the land of Saxony-Anhalt in Central Germany, values of 3.7–17 µg/L were measured at

29 sampling stations in agricultural areas; on three occasions, values were higher than 10 µg/L (unpublished data from a findings explanation process by the German Federal Office for Consumer Protection and Food Safety (BVL), 2018–2019). In Mecklenburg-Western Pomerania, a concentration > 3 µg/L was detected for 24% of a total of 181 groundwater sampling sites tested for TFA; in six places, it was > 10 µg/L (data provided by the Mecklenburg State Office for the Environment, Nature, and Geology, 2018–2019). In North Rhine-Westphalia, too, a TFA content > 3 µg/L was detected in several groundwater samples, with a maximum of 4.4 µg/L in a karst area with intensive agricultural use (LANUV, 2018).

In addition, the German Environment Agency has data from three drinking water catchment areas in Lower Saxony showing increased TFA concentrations. In southern Lower Saxony, 3.1–4.4 µg/L of TFA was detected in four wells. In central Lower Saxony, water suppliers found TFA concentrations around 10 µg/L at a front-end sampling site which is not connected to bodies of surface water. In a water protection area in northern Lower Saxony, TFA concentrations > 3 µg/L were found at 10% of the about 200 sampling sites; at three measuring points, concentrations were higher than 10 µg/L (unpublished data from a findings explanation process by the German Federal Office for Consumer Protection and Food Safety (BVL), 2018–2019).

For such groundwater bodies having little connection to surface water and showing increased levels of TFA, agriculture – in particular plant protection products – must be assumed to be the main source (see Figure 6). Long residence times of precursors in the soil can cause these compounds to degrade slowly, so that it may take years or decades after application of plant protection products until TFA is released and finds its way into groundwater.

Precipitation leaching through the soils into groundwater leads to inputs independent of local applications. This is reflected in a quantitatively relatively low but geographically widespread concentration affecting all bodies of groundwater fed by precipitation. Thus, shallow groundwater tends to be more polluted than deep groundwater. To date, shallow groundwater has been showing µg/L values in single digits, while levels below 0.5 µg/L are common in deep groundwater. However, TFA is persistent and mobile – it must be assumed that, with continuous inputs, it will eventually reach deeper aquifers as well.

4.4 Drinking water

So far, there are only sparse data from direct TFA measurements in drinking water. Nevertheless, TFA contamination in surface water and in groundwater is reflected in concentrations in drinking water, as TFA cannot easily be removed from raw water by the drinking water suppliers (see Chapter 5.3). Nearly 70% of drinking water in Germany is obtained from groundwater or spring water, the remaining 30% directly or indirectly from surface water (Statistisches Bundesamt, 2015). Therefore, increased levels of TFA are to be expected in drinking water in regions where high concentrations of TFA have already been found in the drinking water source (see Chapter 4.3).

A study by TZW tested 19 tap water samples from various places in Germany with different sources of drinking water and measured TFA concentrations ranging from < 0.05 to $2.5 \mu\text{g/L}$ (IAWR, 2018). The reason why TFA in drinking water has not been found in concentrations greater than $3 \mu\text{g/L}$ is that more strongly polluted raw waters are blended with water from different, less polluted sources to meet the legal requirements. Until recently, a health-related indicator value of $3 \mu\text{g/L}$ applied for TFA. That means that drinking water should not permanently be distributed if it contains TFA in concentrations greater than $3 \mu\text{g/L}$. Similar to a threshold value of the German Drinking Water Ordinance, that value may be temporarily exceeded if approved by the competent local health authority. Such approval, however, is linked to appropriate measures to reduce the concentration and to comply once again with the maximum value (Infobox 5).

An exception is the drinking water produced in the Neckar catchment near Heidelberg, with concentrations of more than $20 \mu\text{g/L}$ – a direct impact of the wastewater discharged (Ries and Morlock, 2017; Scheurer et al., 2017). The region on the Neckar was granted an exemption and a value of $30 \mu\text{g/L}$ was set as a precautionary measure. This, however, is strictly local in scope and temporary and comes with an obligation to carry out emission reduction measures at the local point of release – which are already underway in collaboration with the company discharging effluents containing increased concentrations of TFA (Infobox 2).

Meanwhile, as a result of further toxicological data, the health-related indicator value has been replaced by a health-based guide value of $60 \mu\text{g/L}$. This means that the previous value set as a precautionary measure no longer applies. However, it does not mean that TFA concentrations of up to $60 \mu\text{g/L}$ in drinking water are acceptable, only that they are not a cause of health concerns. The minimisation requirement according to Section 6 (3) of the Drinking Water Ordinance must still be complied with (UBA, 2020b) (see Infobox 5).

4.5 Soil

TFA, being extremely mobile, is barely retained in soils. As soon as TFA has been formed from precursors, therefore, it is swiftly washed out into groundwater or absorbed by plants along with soil water. No systematic data regarding TFA in soils are available to the German Environment Agency. So far, background contamination has not been determined. Sample analyses of soil material extracted at eight German Meteorological Service sites show TFA levels ranging from < 0.2 to $2 \mu\text{g/kg}$ dry weight (Behringer et al., 2021).

4.6 Biosphere

TFA can be absorbed by plants and, in principle, accumulate there. Boutonnet et al. (1999) showed the uptake of TFA via the xylem stream and its dispersal into the above-ground parts of the plant. TFA can accumulate in plants because, in gas exchange, some water is also released into the air, but less TFA (Boutonnet et al., 1999). Studies submitted in the approval process as part of active substance testing for the plant protection product flufenacet confirm that TFA is taken up into the plant through the root in significant quantities and transported to the upper parts of the plant (EFSA, 2017a). This process is particularly relevant on agricultural land, where TFA sources (e.g. degradation from plant protection products) meet fast-growing crops with high water consumption. There are indications that small quantities of TFA can also be taken up from the atmosphere directly via the leaf surface, e.g. through fog. An accumulation of TFA was observed in the needles of conifers and attributed to this process (Benesch et al., 2002; Solomon et al., 2016). A sample analysis of plant material gathered at a German Meteorological Service site in July 2019 shows a TFA content of 35 to $120 \mu\text{g/kg}$ (Behringer et al., 2021).



Scheurer and Nödler (2021) found TFA in beer and tea. They detected a mean TFA concentration of 6.1 $\mu\text{g}/\text{L}$ in beer and of 2.4 $\mu\text{g}/\text{L}$ in tea. Their studies also showed that the TFA concentrations found in beer are not attributable to the tap water used, but to its presence in the malt and thus to accumulation in plant components. With transpiration being the main cause of accumulation in the plant components, it may be assumed that TFA is mostly found in the leaves.

The EU Reference Laboratories for Residues of Pesticides found increased levels of TFA in various crops (EURL-SRM, 2017). This confirms the assumption that TFA is formed from precursors in plants, or is taken up directly from the soil, or both. The TFA cycle in the soil–plant zone and its influencing factors have not yet been examined in detail. Residues in the human body have not yet been recorded. TFA was not identified either by the German environmental study on health or in human samples in the environmental specimen bank.

5 Impact

5.1 Human health and ecosystems

Toxicological data

In 2019, the company Solvay (Infobox 2) made a study regarding the chronic toxicity of TFA in rats available to the German Environment Agency. In combination with already existing studies on genotoxicity, acute toxicity and subchronic toxicity, a health-based drinking water guide value was derived for TFA. The starting point was a study in which, when TFA was chronically administered to rats, no effects were observed up to a dose of 1.8 mg/kg body weight (no-observed-effect level, NOEL). When using a safety factor of 10 each for possible differences in sensitivity between rats and humans and within the human species, a tolerable daily intake (TDI) of 0.018 mg/kg body weight was derived for humans. Under standard conditions (70 kg body weight, 2 litres of drinking water consumption per day and an allocation of 10% of the TDI for drinking water), this results in a drinking water guide value of 60 µg/L (see UBA, 2020a). This replaces the health-related indicator value of 3.0 µg/L and the value set as a precautionary measure of 30 µg/L. This, however, does not mean that concentrations of up to 60 µg/L in drinking water are considered acceptable by the German Environment Agency in principle. On the contrary: in publishing the new drinking water guide value, the German Environment Agency recommends striving for a TFA concentration in drinking water of 10 µg/L or less. This is because, apart from the guide value, drinking water quality is also determined by hygienic considerations within the minimisation requirement (Section 6 (3) of the Drinking Water Ordinance) (UBA, 2020b).

Ecotoxicological data

The ecotoxicity of TFA has been tested on a number of aquatic and terrestrial species (see Table 1) and may be regarded as low. The most susceptible species found is the green alga *Raphidocelis subcapitata*, with an effective concentration (E_rC_{50}) of 192.48 mg/L. This end point is used for the risk assessment of aquatic organisms in the authorisation procedure for plant protection products. Using a safety factor of 10, this results in a regulatory acceptable concentration (RAC) of 19.25 mg/L.

For deriving a proposed environmental quality standard (EQS, see Infobox 5), several reliable studies of algae (*Raphidocelis subcapitata*) with the same end point (cell

division) were drawn upon to calculate an averaged chronic effective concentration ($E_rC_{10} = 1.04$ mg/L) (using the geometric mean). From this, using a safety factor of 50, a proposed EQS of 21 µg/L was derived for inland waters. For maritime waters, in the absence of marine test species, a proposed EQS of 2.1 µg/L was derived based on the aforementioned studies of algae, but using a safety factor of 500.

The toxicity of TFA for terrestrial plants can also be assessed as low. In their risk assessment, Boutonnet et al. (1999) give an EC_{50} of 5 mg/kg for mung beans and of 12 mg/kg for sunflowers/wheat following application of TFA to the soil.

On the basis of the available studies, TFA is not hazardous to health or harmful to ecosystems in the concentrations measured. However, these studies are insufficient for assessing specific risks of very persistent and very mobile substances within a precautionary and risk-oriented procedure.

5.2 Limits of the risk assessment and dealing with uncertainties

The available data on substance properties, information about input pathways and the risks to humans and the environment that may result from them, are almost entirely drawn from the registration and approval procedures of the various groups of chemicals. For a reliable exposure estimate, empirical data on degradation are required. For TFA, several studies on this have been submitted as part of the authorisation procedure for plant protection products – in soil, water, sediment and in different concentrations. In none of the studies was any degradation detected (EFSA, 2017a). However, the modelling programs used in the assessment of chemicals are not usually designed for persistent substances: by simulating only limited periods, they do not consider any long-term accumulation and thus tend to underestimate the concentrations to be expected in the environment in the long term. Nor do the studies on health and ecotoxicological assessments usually provided for the registration and approval of chemicals cover the special risks of very persistent substances. These are usually short-term studies and cannot account for (potential) long-term effects that may occur after several decades, affecting future generations. The effects of mixtures with TFA and other

Table 1

Summary of available (eco)toxicological indicators for TFA

Species	EC ₅₀ / E ₁ C ₅₀ / LC ₅₀	NOEC/ NOAEL
<i>Colinus virginianus</i>	> 2000 mg/kg bw/d	84 mg/kg bw/d
Rat	> 2000 mg/kg bw/d	98 mg/kg bw/d
<i>Brachydanio rerio</i>	> 1200 mg/L	300 mg/L
<i>Daphnia magna</i>	> 1200 mg/L	
<i>Raphidocelis subcapitata</i>	192.48 mg/L	
<i>Skeletonema costatum</i>	> 2400 mg/L	
<i>Chlorella vulgaris</i>	> 1200 mg/L	
<i>Chlamydomonas reinhardtii</i>	> 120 mg/L	
<i>Dunaliella tertiolecta</i>	> 124 mg/L	
<i>Euglena gracilis</i>	> 112 mg/L	
<i>Phaedactylum tricornutum</i>	> 117 mg/L	
<i>Microcystis aeruginosa</i>	> 117 mg/L	
<i>Scenedesmus subspicatus</i>	> 120 mg/L	
<i>Lemna gibba</i>	1990 mg/L	
<i>Myriophyllum sibiricum</i>	357 mg/L	
<i>Myriophyllum spicatum</i>	312.9 mg/L	
<i>Eisenia fetida</i>		320 mg/kg dw soil
<i>Folsomia candida</i>		≥ 100 mg/kg dw soil
<i>Hypoaspis aculeifer</i>		≥ 100 mg/kg dw soil

bw/d – body weight per day
dw soil – dry weight soil

Source: data from the EU active substance assessment for flufenacet (EFSA, 2017a) and the publication by Boutonnet et al. (1999)

substances or their behaviour under different environmental conditions and media are also not considered by these tests.

This, however, would be advisable, particularly for very persistent substances such as TFA. Given its persistence, mobility in the water cycle and the impossibility of reversing existing contamination, TFA will persist for a long time and spread far in the environment. Thus, in practice, it will come into contact with other substances and various environmental media. An adequate risk assessment would therefore have to cover much longer timescales and much greater spatial scales than those used by standard methods. Probability-based approaches show that even very

rare risks become more probable the longer it takes for a substance to degrade, since the period of time during which a substance remains in the environment is greatly increased (Cousins et al., 2019). For TFA, this period is practically indefinite: the risk increases accordingly and is left to future generations. These are not mere theoretical considerations: there are many examples of risks that had been overlooked and later became apparent in practice, often decades after use (Infobox 3).

The examples in Infobox 3 show that regulating persistent substances is not overly conservative, but reasonable according to the principle of precaution. In 2018, the European Court of Justice decided that

the precautionary principle (Infobox 4) must also be applied in cases where there is uncertainty over the existence of risks. In the Court's view, measures must be taken before the risk becomes visible and quantifiable. In considering such measures, health, safety and the environment should be given preference over economic interests (ECJ, 2018).

In its Agenda 2030 (2015), the United Nations agreed to take concrete responsibility for the next generations and to implement sustainable, environmentally sound development. Sustainable Development Goal (SDG) No. 12.4 explicitly aims to reduce the emission of chemicals – irrespective of their toxicological properties – into air, water and soils in order to minimise adverse effects on the environment and

INFOBOX 3: Historical examples of risks that were overlooked

The **plant protection product tolylfluanid**, now banned, forms a mobile degradation product that is introduced into groundwater in relatively high concentrations, but for which no (eco)toxicological effects were shown. However, in ozonation – a common process in drinking water treatment – this degradation product is transformed into the carcinogenic substance dimethylnitrosamine (NDMA). This was not detected during the authorisation process for plant protection products and later only noticed by chance at the waterworks (Schmidt and Brauch, 2008). In response, testing the behaviour of all relevant substances used in drinking water treatment was included in the approval process for pesticidal agents as a mandatory data requirement.

From the 1940s, the **insecticide dichlorodiphenyltrichloroethane (DDT)** was frequently used because of its high efficacy and relatively low health and environmental risks. However, in the 1970s, it was discovered that DDT and its degradation product dichlorodiphenyldichloroethylene (DDE), accumulate in the food chain due to their persistence, chemical stability and high solubility in fat. It also disrupts the reproductive behaviour and the structure of the eggshells of birds: thinner shells broke prematurely, leading to fewer viable offspring being raised. Furthermore, DDT is suspected of interfering with the endocrine system and of being a carcinogen, whereupon it was banned in many industrialised countries. It is part of the “dirty dozen”, the first 12 particularly persistent and hazardous chemicals banned worldwide by the 2001 Stockholm Convention. However, it continues to be detected in various environmental media, e.g. in the fat tissue of polar bears or in European soils used for agriculture (Nuijten et al., 2016; Silva et al., 2019).

Neonicotinoids are insecticide agents that have been used for many years in e.g. seed protectants. In recent years the seed dust and its dispersal in the air was found to be highly toxic for bees, endangering their populations (Cousins et al., 2019). Bees, however, are essential for agricultural production as pollinators.

Chlorofluorocarbons (CFCs) were used from the 1930s as propellants, refrigerants or solvents, showing relatively low toxicity. Only after CFCs had been used extensively for about 40 years, it became apparent that they deplete the ozone layer and are extremely effective greenhouse gases, remaining in the atmosphere for up to 100 years. Then, under the Montreal Protocol on Substances that Deplete the Ozone Layer, worldwide restrictions on and bans of the use of CFCs in certain applications were introduced for the protection of the ozone layer (Cousins et al., 2019; UBA, 2017b; also see Infobox 1).

Polychlorinated biphenyls (PCBs) were being produced from 1929 and used in transformers and capacitors and as softeners in grouting. Similarly to DDT, they have a high chemical stability and are also noted for the non-inflammability. PCBs, too, are persistent and bio-accumulative. Due to improper waste recycling and by diffuse inputs, they were able to spread widely in the environment and also accumulate in human fat tissue. They have even been detected in the Antarctic (Risebrough et al., 1976). PCBs are suspected of damaging the immune system, disrupting the endocrine system and of causing cancer. Along with DDT, they were banned worldwide in 2001 under the Stockholm Convention, but they are still found in the environment (Cousins et al., 2019).

It is currently impossible to predict what consequences the accumulation and spatial dispersal of very mobile and very persistent TFA may have.

health. This is particularly relevant to persistent substances like TFA which, once discharged, remain in the environment for many decades and cannot be removed. Today's use of persistent substances will become the burden of future generations.

To address these specific risks of highly persistent substances in the environment, a study by the European Commission calls for the establishment of a single criterion based on the persistence of substances in assessing chemicals (COM, 2017), which in itself

should trigger further regulatory action. TFA is particularly critical in this regard, as it is not only extremely persistent, but also spreads widely through the water cycle (e.g. UBA, 2017a), is continuously reintroduced globally (see Chapter 2) and is already present in water bodies in high concentrations (see Chapter 4). It is therefore reasonable to apply the precautionary principle to this substance, even though – or precisely because – it has so far not been a problem in (eco)toxicological terms.

INFOBOX 4: The precautionary principle at national, European, and international levels

The idea of the precautionary principle is to avoid environmental damage from the outset, rather than repairing it after the fact at great cost, if possible at all. Accordingly, in case of an incomplete knowledge base, the risk must be avoided or greatly reduced. There are numerous examples of damage occurring that had not been foreseen (Infobox 3), providing historical evidence for the necessity of the precautionary principle. In Germany, it is one of the main principles of environmental law; in the EU, it is an important operational principle in environmental policy; and it is an international guideline, especially in the discourse on sustainability:

National level: The precautionary principle is explicitly mentioned in Article 34 (1) of the Unification Treaty as a commitment by legislators; it is thus applicable federal law. Furthermore, the precautionary principle is enshrined in Article 20a of the Basic Law. That article instructs the state to protect the natural foundation of life for future generations, which may require not only defence against hazards, but also precaution.

European level: The precautionary principle is set out in Article 191 of the Treaty on the Functioning of the European Union (TFEU). In its 2000 communication on

the applicability of the precautionary principle, the European Commission stresses the importance of the precautionary principle as a key element of EU policy for risk prevention.

International level: Participants of the 1992 United Nations Conference on Environment and Development committed to applying the precautionary principle for the protection of the environment: “In the face of threats of irreversible environmental damage, lack of full scientific understanding should not be an excuse for postponing actions which are justified in their own right. The precautionary approach could provide a basis for policies relating to complex systems that are not yet fully understood and whose consequences of disturbances cannot yet be predicted” (Chapter 35 of Agenda 21). This commitment was confirmed in 2015 in Agenda 2030. In addition, the precautionary principle is enshrined in several international conventions, such as the UN Framework Convention on Climate Change and the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic.

(modified from UBA, n.d. b)

5.3 Water supply

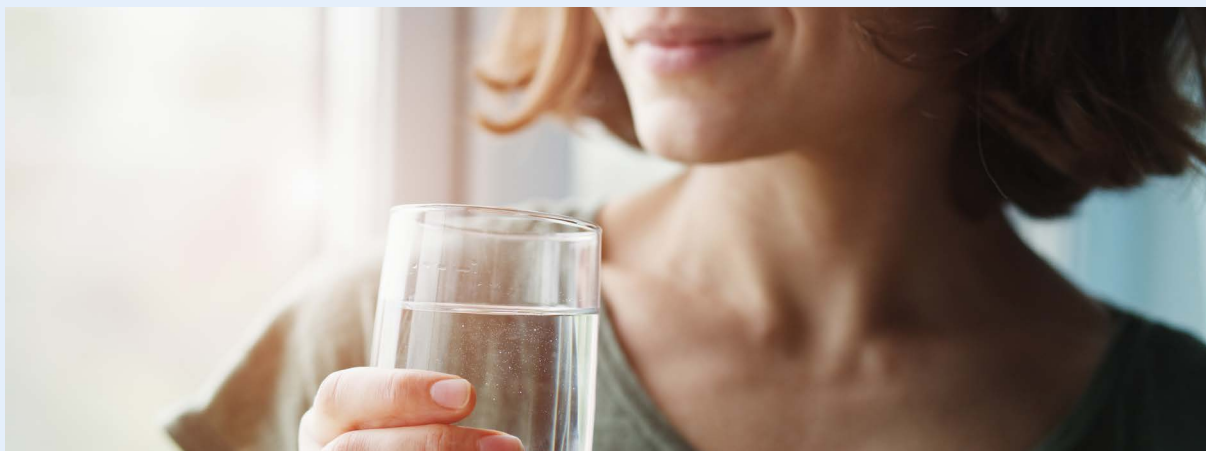
Drinking water supply carries a specific risk in connection with TFA. Being highly soluble in water and spreading along the water cycle, TFA will sooner or later find its way into drinking water sources. Even now, increased concentrations can be found, and the health reference values applicable in Germany have not always been complied with (see Chapter 4 and Infobox 5). No practicable and economical method exists for removing TFA from water, once the substance is released into the environment. Only by means of reverse osmosis is this technically possible, but with regard to drinking water supply, this is not practicable in economical and quantitative terms – nor socially desirable (IAWR, 2018; Scheurer et al., 2017). In some cases, raw waters of different provenance needed to be blended in order to adhere to the health reference value of 3 µg/L that applied in Germany until recently – in the face of a drier climate and increasing demand for water, this is not a sustainable solution. There are certain limits that apply to drinking water, drinking water sources and water bodies (Infobox 5). In addition, a minimisation requirement applies in Germany, according to which water should be free from synthetic chemicals as far as possible. The amended Drinking Water Ordinance makes provision for considering the entire drinking water chain – from the catchment areas of water bodies right up to the tap – in complying with the minimisation requirement. For TFA, given its properties, the only practical method is to reduce its input in the catchment area.

German citizens are particularly sensitive about water purity: drinking water should be free from synthetic substances, even if these are not currently deemed hazardous to health. Water suppliers are therefore keen to meet this expectation, which causes conflict locally with agriculture and other applications from which TFA can be introduced. Mineral water producers, in particular, depend on

purity at the source, as their water must not contain any measurable traces of chemicals. According to the Mineral Waters Ordinance, waters are no longer deemed pure if they contain an anthropogenic trace substance at more than 0.05 µg/L – which is considered an indication of other economic activities having too great an impact in the catchment area. Furthermore, these waters must not be treated or blended with other waters. Some wells are already contaminated with the degradation products of plant protection products to a greater extent than permitted, threatening their closure due to organic trace substances (Ökotest, 2021; Ökotest, 2014; Stuttgarter Zeitung, 2013; Manager Magazin, 2012; Spiegel, 2014). Both regular drinking water suppliers and mineral water producers depend on TFA inputs remaining as low as possible.

The situation with regard to TFA is set to remain uncertain, particularly for drinking water supply from groundwater, the main source of drinking water in Germany (Statistisches Bundesamt, 2015). The path from the emission of TFA into the environment to its input into groundwater may take several years or decades. Measures taken now may not bring about any improvement for a number of years. It seems reasonable to assume that conflicts will intensify with inputs from diffuse sources showing an upward trend (see Chapters 2 and 3). Unlike in major rivers, which transport TFA into the sea, TFA can accumulate in groundwater. However, measures designed only for areas of drinking water production will not be sustainable. This is because of bodies of groundwater not yet used for drinking water production may gain in importance in the future and start being used as a source of drinking water – particularly if the climate becomes more arid.

INFOBOX 5: Different thresholds and limits for TFA



Legally controlled substances are usually subject to consistent threshold values. For example, in the Drinking Water Ordinance, active substances in pesticidal and biocidal products and/or their relevant transformation products are regulated with a threshold value of 0.1 µg/L. The same value applies for assessing the chemical quality of water bodies in accordance with the Groundwater Ordinance and the authorisation of plant protection products under substance law. There is often no such consistency for substances that are not legally controlled, as administrative rules and conventions may vary widely between areas – as in the case of TFA.

Drinking water

There are or have been various limits for TFA that can be used for assessing already contaminated water. These limits are intended, above all, for the competent health authorities which have to assess the quality of drinking water and confirm its harmlessness to health:

- ▶ **Health-related indicator value:** this is a precaution-based limit which varies according to the available toxicological data and includes a large safety factor. For degradation products of plant protection products with no known (eco)toxicological effects, so-called non-relevant metabolites, it is 1 or 3 µg/L, depending on available studies. For TFA, the health-related indicator value was 3 µg/L until May 2020, when it was replaced by the drinking water guide value (UBA, 2020; UBA, 2020a).

- ▶ **Drinking water guide value:** this value is derived separately for each substance on the basis of its hazardousness. In the case of TFA, the value is 60 µg/L, derived from a chronic study. It replaces the significantly lower health-related indicator value, as it is based on a better database and thus eliminates some uncertainties (UBA, 2020; UBA, 2020a). According to the current state of knowledge, drinking water contaminated by TFA are of no concern to human health up to 60 µg/L. If that value is exceeded, suitable measures must be taken to return to a compliant value. However, this value should not be taken as a target for inputs or as a requirement for drinking water quality (for more details, see UBA, 2020b).
- ▶ **Value applied as a precautionary measure:** unlike the health-related indicator value and the guide value, this limit is local in scope and temporary. Furthermore, its applicability is linked to specific measures to reduce inputs (UBA, 2008). A value of 30 µg/L was temporarily set as a precautionary measure in the River Neckar region (Infobox 2).

In addition, the Drinking Water Ordinance, with its minimisation requirement, stipulates that contamination of drinking water must be kept as low as possible. The amended European Drinking Water Directive (Directive (EU) 2020/2184) stipulates that all Member States are to set a limit for non-relevant metabolites such as TFA in order to be able to manage their inputs. Thus, non-relevant metabolites – including TFA – can in future be legally controlled for the first time by the Drinking Water Ordinance.



Surface water and groundwater

In assessing the chemical quality of surface and groundwater, the following thresholds apply, which are derived individually for each substance and agreed at the national level together with the German federal states as the competent authorities for assessing chemical water quality:

- ▶ Environmental quality standard (EQS): this applies to bodies of surface water; the legal basis is EU Directive 2008/105/EC and the national Surface Water Ordinance. TFA is not controlled by an EQS in either. The German Environment Agency proposes an EQS for TFA of 21 µg/L for surface water bodies and, derived from this, of 2.1 µg/L for maritime waters, based on ecotoxicological data (ETOX, 2020) (see Chapter 5.1).
- ▶ Neither the EU Groundwater Directive (2006/118/EC – as amended by 2014/80/EU) nor the German Groundwater Ordinance so far contains any thresholds for TFA. However, point 2.4 of Annex 4 to the Groundwater Ordinance requires the monitoring of the bodies of groundwater concerned for metabolites not relevant under plant protection law, which include TFA.
- ▶ De minimis thresholds (DMTs): these apply to inputs into groundwater; they have not yet been set for TFA. DMTs are based on existing limits, EQSs or ecotoxicological thresholds (LAWA, 2016).

Management of inputs

The different legislative processes permitting the introduction of chemicals on the market currently only make provision for one threshold in the area of plant protection products – in the form of a general threshold of 10 µg/L in groundwater for the group of substances of non-relevant metabolites, which includes TFA (see Chapter 6.1). The discharge of treated wastewater is subject to permits issued locally, which may take account of TFA at the discretion of the issuing authority. However, this rarely happens in practice (see Chapter 3.1).

Thresholds/limits and sustainability

Thresholds and limits provide a pragmatic guide for classifying TFA contamination in surface waters, groundwater and drinking water. It is not, however, sustainable to assess and control persistent substances such as TFA by only using such values. TFA does not degrade and therefore accumulates in waters where it is continuously introduced. This means that, over time, the EQS of 21 µg/L proposed for surface water and the toxicological drinking water guide value of 60 µg/L may be exceeded. Such exceedances cannot then be reversed, as TFA cannot be removed from water by economical means in quantitative terms. In order to protect surface waters, groundwater and drinking water in the long term, the use of TFA and its precursors in areas with a high environmental exposure should be greatly reduced and replaced wherever possible, irrespective of thresholds and limits (see Chapter 7).

We currently recommend not exceeding 10 µg/L in surface waters and groundwater in all cases. This value is consistent with the provisions of plant protection law and for drinking water hygiene. Due to the specific properties of TFA, measures to ensure compliance with the 10 µg/L threshold must already be taken if significantly lower concentrations are found.

6 Measures

6.1 Statutory restrictions

Registration of chemicals

Chemicals produced and used in the EU must be registered under the EU Chemicals Regulation (REACH). There are exemptions for active substances in plant protection products and biocides and the active ingredients of veterinary and human pharmaceuticals. REACH registration requires a comprehensive exposure and risk assessment by the registrants in cases where the substance meets at least one of the criteria stated in Art. 14 (4) of the Regulation or if there are further indications of dangerous properties as listed in the Technical Guidance Documents on REACH. On the one hand, this applies to substances classified under Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regulation). On the other hand, it also covers chemicals that are persistent, bio-accumulative and toxic (PBT), or very persistent and very bio-accumulative (vPvB) – and others where specific concerns exist. Such an assessment includes all the steps in the life cycle of a substance, from its manufacture up to its appropriate disposal. All relevant exposure pathways in connection with these steps must be assessed: of the substance itself through exhaust air and wastewater and into soil (direct exposure), indirect and direct discharges into surface waters, and emissions into the environment as a result of maintenance and purification processes.

In the risk assessment, the registrant must provide evidence that the intended use will not pose an unacceptable risk to human health or the environment. In the case of substances for which no appropriate thresholds can be derived (here: PBT and vPvB substances or those with endocrine effects on organisms in the environment), the minimisation requirement applies for inputs into the environment (see Infobox 5). In both cases, registrants must define technical and/or organisational measures for appropriately reducing inputs into the environment. The legislation does not provide for an obligatory validation of the risk assessments in registrations by the authorities at the superordinate level. Rather, implementation of the proposed measures to minimise risk must be verified by the competent local supervisory authority for each individual case.

TFA meets neither the PBT nor the vPvB criteria, but is classified, among other things, as Aquatic Chronic 3 (H412). This classification is mainly based on gaps in the data and does not reflect a specific known risk to aquatic organisms going beyond the risk thresholds set out in Chapter 5.1 (Table 1). The exposure assessment carried out by registrants need only consider their own applications of TFA and its intended uses in their own supply chain. The calculations which have to be provided are typically made only on the basis of generic assumptions applicable to the entire EU area – a localisation to individual member states or even specific local emission sources is therefore not possible. The results of the exposure and risk assessments, which require information containing business secrets relevant to competitors, are not made public. There is no obligatory overall assessment process by the authorities in which all inputs from all applications by all registrants are aggregated. The release of TFA from degradation processes of precursors is not considered either.

As already mentioned, TFA is considered to be very persistent and very mobile (vPvM) in the environment. This criterion has not yet been officially included in the REACH Regulation and is based on a proposal by the German Environment Agency for protecting the water cycle, in particular drinking water sources (UBA, 2017a). According to this recommendation, vPvM substances pose a particular problem to drinking water sources: not only do they hardly degrade under environmental conditions, but they are also generally highly soluble in water, hardly adsorb on the soil matrix and, due to these properties, they cannot easily be removed from the water. However, analytical methods for vPvM substances are frequently complex, which makes them difficult to monitor and any findings not necessarily representative. In addition, the high persistence (vP) means that any uncertainties from the approval or authorisation procedures in various areas under chemicals law and as yet unknown residual risks are of greater significance, with the substance circulating through various ecosystems for many decades and centuries (UBA, 2017a; Cousins et al., 2019).

The vPvM criterion and the areas of risk linked to it wholly apply to TFA (see Chapters 5.2 and 5.3). Due to its specific properties being precisely not of a toxicological nature, no safe concentration in the form of a single threshold value can be derived. Therefore, the German Environment Agency recommends that registrants, as part of their responsibility for PMT and/or vPvM substances such as TFA, carry out an extensive exposure and risk assessment and implement local minimisation strategies (UBA, 2017a). This could then also extend into other regulatory areas.

Use of chemicals

As already mentioned, under REACH, it is incumbent on registrants to define the conditions for the safe use of TFA. According to current knowledge, registrants' assessments do not suggest that each intended use of TFA as a substance leads to unacceptable risks to human health or the environment. No official restriction of the manufacture and use of TFA has been defined so far.

In the absence of empirical data, TFA has not yet appeared as a relevant degradation product in the areas of biocides and pharmaceuticals and is therefore not explicitly controlled in those areas. For plant protection products, the formation of TFA has been proven directly for individual active substances, which is why it is subject to control as a plant protection product metabolite under the EU Plant Protection Regulation (EC) No 1107/2009. In the relevant processes, no (eco) toxicological risks have been identified for TFA so far, and thus it is a so-called non-relevant metabolite for which a general threshold value of 10 µg/L applies to inputs into groundwater (SANCO 221/2000). However, the formation of TFA has so far only been documented for the active substances flurtamone and flufenacet. Flurtamone is no longer approved, and the restriction of TFA in flufenacet has been prevented in court and by the authorities (Infobox 6). No empirical data are available for the many other active substances that can form TFA; hence, no restrictions can be imposed in the approval procedure for these substances.

As with TFA as a basic chemical, registration under REACH is also obligatory for the individual refrigerants and blowing agents on the market where more than 1 t/a of an individual substance is manufactured in the EU or imported into the EU. Independently of

this, further legal requirements may exist for refrigerants and blowing agents. For instance, the manufacture and use of substances from the group of CFCs and HCFCs, which damage the ozone layer, is already banned under Regulation (EC) No 1005/2009. Due to their long life, they will remain in the atmosphere for many decades still. Furthermore, the use and placing on the market of partially fluorinated hydrocarbons (HFCs), which are highly effective greenhouse gases, has been regulated in the EU since 2006. These substances have established themselves as substitutes for CFCs and HCFCs, but may release TFA. With the coming into force of Regulation (EU) No 517/2014 (EU F-gas Regulation) on fluorinated greenhouse gases, the quantity of HFC available on the market is being gradually reduced from 2015 to a fifth of the original quantity by 2030.

Furthermore, additional bans on use and placing on the market have been put in place, with refrigerants and/or blowing agents with a short half-life and thus a limited global warming potential being preferred. However, in weighing the risks of these refrigerants and blowing agents, the increased potential for the formation of potentially persistent transformation products, a displacement of the inputs into different environmental compartments and the effects on these that may result from this – as seen with the example of TFA – are not given the same weight as the global warming potential of the source substances. Internationally, the production and use of HFCs has also been restricted since 2019 by the Kigali revision of the Montreal Protocol. Under the EU F-gas Regulation, manufacturers, importers and exporters of fluorinated greenhouse gases and those placing products with fluorinated gases on the market must report to the European Commission. Some halogenated gases among HCFCs, HFCs, the newer unsaturated HFCs and HCFCs and halogenated ethers, form TFA in degradation processes in the atmosphere (Infobox 1 and Behringer et al., 2021). The example of TFA-forming refrigerants and blowing agents shows how focusing on one particular good to be protected affects the assessment of acceptable risks, and reveals the importance of a holistic assessment of chemicals.

Discharge of industrial wastewater

The discharge of wastewater from industrial plants is regulated at the national level in the German Ordinance concerning Requirements for the Discharge of Wastewater (Wastewater Ordinance), with sector-specific requirements given in its individual annexes. Each of these contains minimal requirements on the basis of which local or regional water boards are to decide on permits for discharge. TFA is not explicitly

regulated here but is to be considered, if at all, on a case-by-case basis where the substance is already a known issue locally. Another difficulty is that TFA and its precursors are used in different sectors. The example of Solvay showed the high and lasting impact of localised industrial inputs and the key role that may be played by discharge permits (Infobox 2). There is thus a significant need for improvement in this area.

INFOBOX 6: TFA from plant protection products: regulatory obstacles in protecting groundwater

Flufenacet, a frequently used plant protection products, forms TFA in large quantities. In 2017, data were made available to the German Environment Agency providing evidence of this and showing that the application of flufenacet causes major inputs of TFA into groundwater (EFSA, 2017). For many products using flufenacet as an active substance, the expected inputs of TFA into groundwater exceed the regulatory threshold for non-relevant metabolites of 10 µg/L. In order to keep inputs below this threshold, the amount and times in which the product is applied must be restricted. Several companies that had applied for authorisations took legal action against this restriction, arguing that these incriminating data were not applicable on formal grounds. In one case in September 2020, the competent administrative court ruled in favour of the applicant and declared the restriction unlawful for a specific product: according to the ruling, Germany had to follow other EU states in authorising the product without restrictions. Furthermore, the court ruled that TFA was a subject that had to be addressed at the European level in the active-substance procedure. Since then, the Federal Office for Consumer Protection and Food Safety (BVL) – the competent authority for issuing authorisations in Germany – has withdrawn the restrictions for all other products containing flufenacet, even though the court had only issued a ruling in respect of a single product and the conditions of its use are not transferable to all other cases.

Regarding the applicability of the data, reference is made to the ongoing active-substance procedure for flufenacet at the EU level. Once the procedure is completed, the data would be published and their

application would be mandatory. The procedure had almost been completed when it was extended by another three years in order to test for endocrine activity. This testing for endocrine effects does not affect the calculated concentrations of TFA in groundwater or their assessment, but does delay the formal completion of the procedure. Accordingly, many product applications are currently being assessed on the knowledge basis of 2004, when the previous active substance approval was completed. At that time, however, it was not known that flufenacet forms TFA, nor that it can harm birds and aquatic organisms – another new finding only resulting from the 2017 data. It is expected that products will not be re-assessed according to this new knowledge until 2024/2025 – nearly 20 years after the end of the last active substance approval. However, even the 2004 procedure had already identified questionable substance properties which justify classifying flufenacet as a candidate for substitution: according to the EU Plant Protection Products Regulation (EC) No 1107/2009, such substances should again be subject to a new active substance approval after only seven years.

There is no convention according to which incriminating data can only be used after the formal completion of active substance approval. The parties involved disagree about when known and validated data represent the state of the art in science and technology which is the basis for assessing plant protection products. This question, which pertains to European law, should be settled by the European Court of Justice, which is responsible for establishing a binding interpretation of European law.

Quality of surface waters, groundwater and drinking water

TFA inputs or concentrations are not explicitly regulated by law in the national Ordinances on Drinking Water, Groundwater or Surface Water. However, some administrative standards and policies containing limits do exist (Infobox 5).

Other objectives independent of limits are to minimise substance inputs into waters, to keep the exposure of aquatic ecosystems to any contaminants as low as

possible, and to keep drinking water sources as free from anthropogenic substances as possible (Infobox 7). The aspiration behind these objectives, which also seeks to take account of consumers' desire for pure water, is known internationally as the ALARA principle: as low as reasonably achievable. According to this principle, substance inputs into waters from economic activity should be kept as low as possible, even if no acute or chronic risk has been established.

INFOBOX 7: Principles for minimising substance inputs into waters

Minimisation requirement

“Concentrations of chemical substances capable of contaminating drinking water or adversely affecting its quality shall be kept as low as it is feasible with reasonable effort in accordance with generally accepted good engineering practice, taking account of individual cases” (Sect. 6 (3) of the German Drinking Water Ordinance).

Avoiding deterioration

“Member States shall ensure the necessary protection for the bodies of water identified with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water” (Art. 7 (3) of the EU Water Framework Directive, WFD). The “avoiding deterioration” principle applies to all components and substances listed in the status definitions of the WFD. Given that TFA is (so far) not regulated in the WFD daughter directives on EQSs or the national ordinances implementing the WFD, the “avoiding deterioration” principle is not applicable. The same applies to the “preventing deterioration” principle according to point (a) of Art. 1 (2) of the Marine Strategy Framework Directive (MSFD).

Principle of concern

“Substances may only be stored or deposited adjacent to a body of surface water where there is no concern about any adverse effect on water quality or water drainage. The same shall apply to the transport of liquids and gases through pipelines” (Sect. 32 (2) of the German Water Resources Act)

“Permission for introducing and discharging substances into groundwater may only be issued where there is no concern about any adverse effect on water quality.” (Sentence 1 of Sect. 48 (1) of the Water Resources Act)

“Substances may only be stored or deposited where there is no concern about any adverse effect on the quality of groundwater. The same shall apply to the transport of liquids and gases through pipelines” (Sect. 48 (2) of the Water Resources Act)

“Facilities for storing, bottling, manufacturing and treating water-polluting substances and facilities for using water-polluting substances in the areas of commercial activity and public institutions must be designed, established, maintained, operated and decommissioned in such manner that there is no concern about any adverse effect on the quality of waters” (Sect. 62 (1) of the Water Resources Act)

Sustainable water management

Sustainable water management in accordance with Sect. 5, 6, 48, 57 of the German Water Resources Act not only requires protecting waters to ensure their current and future use, but also the maintenance and improvement of the functioning and viability of the waters as part of the ecosystem.

6.2 Political strategies and collaborative approaches

Along with the administrative standards and objectives independent of limits mentioned in Chapter 6.1, there are various political strategies and collaborative approaches for protecting waters by means of overarching policies.

At the EU level, these include the Zero Pollution Strategy, the Farm-to-Fork Strategy, sustainability strategies and others agreed for implementing the Green Deal (COM, 2019). TFA is not considered explicitly by these overarching strategies, but is implicitly included in their scope.

The National Action Plan for Sustainable Plant Protection (NAP) is an instrument implementing European Directive 2009/128/EC, for which the German Federal Ministry for Food and Agriculture (BMEL) is responsible. The objective of the NAP is to reduce the inputs of non-relevant metabolites such as TFA to below the health reference value (BMEL, 2013). The Trace Substances Dialogue initiated by the Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection (BMUV), which includes many stakeholders from industry, administration and civil society, also has the objective of monitoring and reducing anthropogenic substance inputs from all sources (BMUV, n.d.). The German Environment Agency has recommended including TFA in these considerations.

Some German federal states have also become active in this field. At a regional level in North Rhine-Westphalia, the “Pure Ruhr” policy seeks to minimise the presence of all kinds of micropollutants – including those not relevant (eco)toxicologically – and aims to avoid inputs above the health reference value (MULNV NRW, 2014). Other federal states have at least had their awareness raised and have initiated first steps towards limiting substance inputs, such as by declarations of intent from Schleswig-Holstein. A statement from the state parliament says: “The protection of this resource (editor’s note: drinking water) should be given a high priority. All available options should be pursued for reducing the use of plant protection products as far as possible and to avoid contaminating the environment” (SH, 2013). Similar aspirations are voiced by North Rhine-Westphalia, where a press release from the State Ministry for the Environment says: “On the basis of the risk assessments by the German Environment

Agency in collaboration with water suppliers, the North Rhine-Westphalia Ministry for the Environment will initiate necessary measures for further protecting the drinking water supply in 2017.” TFA, in particular, is a much discussed topic there. The press release quotes the former minister, Mr Rimmel, as follows: “From a precautionary perspective, TFA inputs should be significantly reduced and measures for minimising them should be taken. With the sources in North Rhine-Westphalia not definitively identified, we must and shall carry out further analyses and research to definitively identify the input sources of TFA. Discharges into the Rhine, directly or indirectly, must cease. The use of TFA-forming preparations and plant protection products in drinking water areas must be put under scrutiny everywhere” (MULNV NRW, 2016).

In addition, there are trans-regional collaborations and agreements espousing the protection of rivers, frequently with the aim of establishing uniformly high standards for major rivers. For instance, the Rhine 2040 Strategy of the International Commission for the Protection of the Rhine (ICPR) aims to reduce inputs of substances from industry and agriculture by 30% by 2040, compared to the period from 2016–2018 (ICPR, 2020). In a European River Memorandum (ERM), water suppliers along all major central European rivers recently published an action plan including a target value for anthropogenic, non-natural trace substances that have no known effects on biological systems but are not easily degradable microbially (ERM, 2020). This target value of 1 µg/L is intended particularly for substances such as TFA: substances with a good basis of toxicological data for which there are no known specific (eco)toxicological risks and which are persistent in the environment. The memorandum states: “For non-natural organic substances that have been sufficiently assessed toxicologically and classified as non-hazardous, a limit of no more than 1 µg/L is justified.” The motivation behind this is to ensure drinking water production with close to natural treatment in the long term and to apply a precaution-based approach to this (ERM, 2020).

Although the subject of TFA is considered important by many political actors and those in practice, what is missing is an overarching strategy and action plans for minimising TFA inputs that do justice to the multiplicity of sources and the differences in input pathways – and the different responsibilities and levels of authorities associated with this.

First steps towards reducing TFA inputs into the environment have already been initiated. The Federal Republic of Germany, together with four other states (the Netherlands, Denmark, Sweden, Norway) is preparing a restriction proposal under REACH for regulating the manufacture and application of the large group of PFAS. Due to their specific properties, PFAS – whose working definition of chemical structures covered by the upcoming restriction proposal would at present also cover TFA – are a group of substances of particular environmental concern (see Chapter 2). By means of an extensive restriction, the plan is to regulate both the manufacture and the application of PFAS so as to keep inputs into the environment of this group of substances as low as possible in the future. Applications of importance to society where PFAS emissions can be minimised by other appropriate measures would be exempted from the restriction. PFAS include, among other things, the fluorinated refrigerants already mentioned which, like other representatives of the

PFAS group of substances, can potentially degrade into TFA. It is currently being investigated to what extent fluorinated refrigerants and the manufacture and application of TFA-forming plant protection products, pharmaceuticals and biocides can be addressed via the REACH restriction.

In addition, the German Environment Agency is preparing a report analysing possible regulatory measures, the objective being to prepare a plan of action and to initiate regulatory measures where appropriate. But even without an overarching strategy, political actors and authorities should create a binding legal framework for all groups of substances, so as to improve and, wherever possible, standardise the control of substances such as TFA – both for substance inputs into the environment and for protecting waters, and thus also regulating the discharge of wastewater.

INFOBOX 8: Local co-operation for the protection of drinking water: River Stever Co-operation

For 30 years, stakeholders in water management, agriculture and public authorities have been working on reconciling drinking water protection with agricultural activity locally. The River Stever Co-operation brings together the North Rhine-Westphalia Chamber of Agriculture (Coesfeld/Recklinghausen district office) and the water suppliers Gelsenwasser AG, Stadtwerke Coesfeld GmbH, Stadtwerke Dülmen GmbH and Gemeindewerke Nottuln, which co-operate with trade, agricultural industry and district and state authorities. The aim here is to minimise the use of plant protection products and associated risks. For instance, farmers receive subsidies for using fewer plant protection products and combining these with e.g. mechanical weed eradication.

For the past three-and-a-half years, the topic of TFA has also been on the River Stever Co-operation's agenda. Working jointly with agrochemical companies, TFA is measured across the entire catchment area, and TFA sources and input pathways are being identified. According to the current state of the research, the relatively high concentrations of TFA in surface waters can be attributed to the application of plant protection products – primarily to those having flufenacet as the active substance. This can be seen, e.g. from input peaks at times when flufenacet is typically being applied. Here, an upward trend is discernible, which may however be linked to the aridity of recent years, leading to less dilution. The sources and precise input pathways are to be investigated in yet more detail in the near future, so that effective measures for reducing TFA inputs can be developed (Steverkooperation, 2019).

6.3 Local co-operations

An important source of TFA is agriculture, which routinely comes into conflicts with drinking water production. To reconcile agricultural activity with drinking water production locally, local co-operations have been established in some regions, principally between agriculture and water management. These collaborate in investigating causes of contamination, co-ordinate their activities and, ideally, come up with viable solutions taking account of concerns on both sides. Such co-operations are found particularly in regions that have well-drained soils and registering high substance inputs from agriculture. An important prerequisite is sufficient local availability of time, funding and expertise, and a mutual willingness to co-operate. One example regarding TFA is the River Stever Co-operation, supported by the plant protection product manufacturer Bayer (see Infobox 8). By their own accounts, however, such local co-operations need a reliable regulatory framework. For example, the fact that TFA inputs from plant protection products are not sufficiently regulated is a major challenge for acceptance and willingness to co-operate on the part of the agricultural sector. The different thresholds and requirements for drinking water (see Infoboxes 5 and 7) create uncertainty and differing viewpoints as to what should be the frame of reference locally.

Beyond the national plant protection product authorisation process, there are other instruments providing acute assistance for drinking water production areas where particularly high plant protection product residues have been measured in water. Evidence of several exceedances of a threshold of 3 µg/L by a non-relevant metabolite allows a water supplier to apply for application rule NG301, which makes provision for a five-year ban of the base substance in the drinking water production area concerned (see Infobox 9). In principle, this obligation is also applicable to TFA – a substance with many sources – if there is plausible evidence of agriculture being the decisive source locally. It is also possible to apply for a finding clearance procedure if the concentration exceeds 10 µg/L in groundwater. This procedure requires the authorised company to investigate the causes of substance input locally. On that basis, future inputs can be prevented – either at the local level, by adapting

INFOBOX 9: Information and contacts regarding NG301 and the finding clearance procedure

The point of contact for application rule NG301 and the findings explanation process in plant protection product control is the Federal Office for Consumer Protection and Food Safety (BVL). Public authorities and water suppliers can make reports there. Further information and reporting documents can be found at:

NG301: www.bvl.bund.de/ng301

Findings explanation process: www.bvl.bund.de/fundaufklaerung

activities, or at the level of the granted authorisation, e.g. by stipulating additional application rules, or – in extreme cases – by revoking the authorisation for all of Germany (see Infobox 9). These options are valuable as acute responses to existing high concentrations, but they do not replace the principle of precautionary action: to prevent increased concentrations > 3 µg/L or > 10 µg/L, much earlier action is required to reduce TFA inputs – due to their delayed impact, particularly in groundwater.

7 Outlook

TFA inputs are diverse and high. They carry risks and potential conflicts between the parties involved and their interests, as we have shown in this paper with the examples of fluorinated refrigerants and the impact on drinking water supply (see Infoboxes 1, 8, and Chapter 5.4).

On the other hand, fluorochemicals containing a C-CF₃ group fulfil many important functions and cannot always be replaced by available alternatives in the short term. However, all interested parties are called upon to support actions for minimising TFA inputs into the environment by taking a nuanced, knowledge-based and, where necessary, pragmatic approach, and to contribute to a successful outcome by their own actions. The German Environment Agency, too, will continue to take part and offer support within its remit.

The main areas of action include:

Closing gaps in the data

The emission pathway of TFA, from the source all the way to the water cycle, should be sufficiently known and monitored. There are gaps in the data here on various levels. The number of fluorochemicals that might form TFA due to their molecular structure and the areas of application of these substances has not yet been recorded in full. We pursue a pragmatic approach in this regard, beginning by looking more closely at the four most relevant input pathways and analysing the chemicals associated with them:

1. Atmospheric inputs: fluorinated gases such as refrigerants and blowing agents are responsible for more than half the total quantity of TFA.
2. Inputs through agriculture: here, it has been demonstrated that plant protection products play a major part, but liquid manure and sludge from wastewater treatment may also have a – currently unknown – share.
3. Inputs from wastewater from industrial facilities: large quantities of TFA or its precursors are able to reach rivers via this pathway. Only a few isolated examples of this are known so far, which do not allow conclusions to be drawn as to its importance compared to other pathways. This needs to be looked at more closely.
4. Inputs through the wastewater system: a great mishmash of potential TFA-forming substances arrives at municipal wastewater treatment plants, where they can degrade to TFA: pharmaceuticals, biocides, fluorochemicals for domestic use, etc. The part played in TFA contamination by wastewater treatment is largely unknown, but we do not currently assume it to be large.

In addition, the state of contamination should be better investigated by including TFA in water and soil monitoring programmes of the federal states in Germany and in measurements of raw water by default. To that end, analytical methods and regulatory conditions must be put in place – the work in progress at DIN has taken the first steps (Chapter 4). TFA is already included in the “Recommendation list for monitoring plant protection product metabolites in German groundwater” (UBA, 2019a) and is being tested for regularly by more and more federal states.

Besides water, the impact of TFA in soils should also be investigated to determine whether measures under the German Soil Protection Ordinance must be taken. The soil–groundwater and soil–crop pathways should be looked at and the determination of precautionary values should be considered.

Consistent regulation

Knowing which input pathways are mainly responsible for which kinds of contamination is a crucial basis for driving effective regulation and minimisation. At the same time, a pragmatic approach is essential, because sources and input pathways are so complex that it will not be possible to attribute each specific contamination to a definitive source in the short term.

TFA is a “forever chemical”: it will not disappear and will continue to accumulate unless inputs are reduced. Based on available knowledge, it is already clear that the input of such persistent substances as TFA must be reduced. Once the substances have found their way into the environment it is difficult to remove them. Therefore, closing gaps in our knowledge and devising concrete actions should run in parallel.

Such actions include improving the regulation of TFA by authorities in all relevant areas. This can be driven forwards on the basis of current knowledge. As knowledge increases, these efforts can be adjusted dynamically where necessary. An initiative by individual EU member states (including Germany) is preparing a comprehensive restriction proposal for the PFAS group of substances under the REACH Regulation. As things currently stand, TFA and precursors that degrade into TFA would also be covered by this restriction proposal. It is now being investigated to what extent the manufacture and application of TFA-forming plant protection products, pharmaceuticals and biocides can also be addressed by the REACH restriction along with fluorinated refrigerants. Subsequently, the European Commission will decide, together with member states, on EU-wide implementation of this restriction proposal. Further options for action by the authorities in the different areas must follow and are being examined in a report.

In view of the risks and conflicts, waiting for a knowledge base containing no gaps would be unreasonable. The following should apply to the future regulation of substances: whenever a risk assessment is to be carried out for fluorinated chemicals, TFA should be considered as well. Whenever a permit for discharge is issued to a company from the chemical industry, possible TFA precursors and concentrations should be ascertained and the possibility of controlling them through the level of fees should be considered. Regulation and administrative options should be used at all levels and be made consistent – EU, Germany, Land, local authority. This requires the identification and co-operation of key persons, institutions and disseminators, including from associations and universities.

Effective minimisation

Classic statutory regulation of substances and media is urgently required. But that in itself will not be sufficient to reduce TFA inputs to a low level in the short term. Manufacturers, distributors and users of TFA or its precursors should already now examine its use critically as a precaution: Can the quantity of the substance used or the release into the environment be reduced? Is the use essential? Are more environmentally sustainable substances or methods available? How can these be supported? The German Environment Agency is currently examining what framework is necessary for this.

A political minimisation strategy including relevant stakeholders would be beneficial and desirable. This could include the following components for efficiently avoiding TFA emissions:

- ▶ **Substitution:** Where chemicals or non-chemical methods exist that can serve as a substitute for TFA-forming substances and cause less harm to the environment, this should be done and may receive support from the authorities. It should be noted that the substitutes should not cause new environmental problems (“regrettable substitution”), as seen in the case of refrigerants (Info-box 1).
- ▶ **Essential use:** The concept of “essential use” is being discussed in the context of the EU chemicals strategy for sustainability (CSS). It is intended to make it easier to implement controls and bans of hazardous compounds in non-essential use. Socio-economic analysis could be omitted for particularly critical substances, which could be banned irrespective of available alternatives and socio-economic consequences. This is discussed by Cousins et al. (2019) for PFAS. It is, however, unlikely that the use of TFA and its precursors, i.e. refrigerants, pharmaceuticals, etc., may be regarded as non-essential generally.
- ▶ **Reduction as early as possible in the emission chain:** Since TFA cannot be removed from waters, emissions of the substance or its precursors into the environment should be avoided as early as possible in the emission chain, in the following order of priority: (1) no use or less use of fluorinated chemicals (substitution, phase-out); (2) adjustments to the pattern of use

(measures for minimising risk in sale and use);
 (3) adjustments to the disposal process (sensitive disposal of products containing fluorochemicals);
 (4) wastewater treatment (e.g. using reverse osmosis in large industrial facilities).

► **Restriction of manufacture, sale and use:**

In the course of preparing the PFAS restriction proposal under REACH, a restriction on the use of TFA and its precursors in plant protection products, refrigerants, biocides and pharmaceuticals within this proposal is also being discussed. Subsequently, the European Commission will decide, together with member states, on EU-wide implementation of this restriction proposal. Depending on the definitions, this would be an effective measure to avoid TFA emissions at the source.

In these considerations, polluters (production, trade) should be held more accountable, e.g. by developing substitutes, setting up reverse-osmosis facilities, paying for consequential damage. The state is under the obligation to implement binding standards and to provide financial incentives for substitutes and other alternatives.

According to current knowledge, the main TFA emitters are refrigerants and plant protection products. These should be looked at as a matter of priority:

► **Refrigerants:** To date, European legislation has only led to a reduction in fluorinated gases with a high global warming potential. However, an unintended consequence of such legislation is that diffuse TFA inputs will continue to increase, particularly from refrigerants used in mobile air-conditioning systems. The reason for this is that while the main substitute HFC-1234yf is less damaging to the climate, it forms five times as much TFA, and in a shorter period of time, than HFC-134a. A change to halogen-free alternatives must therefore continue to be supported in all areas of application of halogenated gases. This necessitates not only supporting the development and introduction of robust technical solutions for the various areas of use, but also promoting professional training in the refrigeration sector regarding the handling of halogen-free refrigerants, which may be inflammable or have higher operating pressures. Promoting professional qualification will ensure that such units can be installed and maintained

properly. Funding programmes such as the German Ordinance on the Promotion of Refrigeration and Air Conditioning Systems (BAFA, 2020) must be continued and expanded. In all other funding programmes, it would also be useful if funds were no longer made available for developments, installations or applications that cause emissions of halogenated substances. Halogen-free technologies must consistently be demanded in calls for tenders, particularly in public-sector procurement. Campaigns providing information free of charge are necessary and important for the networking of stakeholders and should be supported and continued. Competitions such as Deutscher Kältepreis (German Refrigeration Prize, <https://www.co2online.de/ueber-uns/kampagnen-projekte/deutscher-kaeltepreis/>) can make new technologies known to the public and should be continued.

► **Plant protection products:** Fluorinated plant protection products have properties that also benefit the environment. With the C-CF₃ group facilitating access through the roots, the same effect will be obtained with less of the active substance. The use of active substances such as flufenacet can be reduced but is difficult to substitute for, since they are very effective against certain weeds. Before substituting a plant protection product for another, the possibility of a “regrettable substitution” should be studied carefully, as plant protection products are generally ecotoxic per se, with inherent environmental risks. For that reason, European regulations and strategies, among other things, aim for altogether more environmentally compatible plant protection, i.e. the overall use of plant protection products and the dependency on chemical plant protection products are to be reduced. In its 5-point programme for sustainable plant protection, the German Environment Agency has made proposals for this (UBA, 2016). For the specific case of TFA, a possible approach might be to work out, in conjunction with the chambers of agriculture, which fluorinated plant protection products can be replaced by non-chemical methods, considering innovative and practicable alternatives. Supplementary research should be publicly funded. Support measures for farmers for implementing the new methods and mitigating possible additional risks would also be useful. To that end, besides easily accessible advice, it will be necessary to design the EU’s Common

Agricultural Policy (CAP) in an environmentally compatible way, providing funding for sustainable and sensible measures (UBA, 2021).

Supporting local co-operations

In some areas, TFA contamination is already very high, leading to acute conflicts and an urgent need for action – for instance, in some water protection areas where there is agricultural activity. In such locations, it is not feasible to wait for consistent regulation and a political framework strategy for TFA minimisation. What is useful and worthy of support is co-operation schemes in which agriculture and water management sector representatives already co-operate effectively and wish to become active (Chapter 6.3). Knowledge of substance properties is available at the German Environment Agency. We would like to share our knowledge effectively and are working on specific support for local stakeholders, considering the following aspects (this list is incomplete):

- ▶ **Input pathways:** Is there a wastewater treatment facility in the catchment area of the drinking water wells? Is there intensive agriculture? The German Environment Agency is planning to provide an overview of potential input sources, which might be in the form of an interactive map.
- ▶ **Exact sources:** Which plant protection products are being used? Is a particular crop cultivated often that comes with particular plant protection product applications? The German Environment Agency is working on a nuanced review and possible quantification of TFA inputs from different plant protection products and their areas of application. A paper on this is in preparation.
- ▶ **Contamination:** How high are TFA concentrations in different places, and do they fluctuate widely? Local knowledge on this topic is usually very good, but it must be reconciled with the potential sources. Here, the available knowledge at the German Environment Agency and the aforementioned publications can provide valuable support.

Conclusion

TFA contamination is high, is expected to continue to increase, and already leads to risks and conflict. Interested parties report a need for action, many stakeholders acknowledge the problem and some political actors express a will to enact change. The German Environment Agency is examining possible regulation measures. However, more effort will be needed to reduce TFA inputs into the environment appropriately, especially in the short term, and so to reduce the risks associated with such a persistent and mobile substance. A first step has been taken with the current (as of June 2022) restriction proposal under REACH being prepared in co-operation between several EU member states for restricting the manufacture and use of substances covered by the structural definition of PFAS. However, it is not yet clear whether active substances of plant protection products and biocides and active ingredients of pharmaceuticals, which are relevant causes of TFA being found in the environment, will be covered by this restriction.

What is missing is a joint overall strategy to guide stakeholders in their relevant areas and to initiate improvements. This should include, among other things, the consistent regulation of substances, subsidies for alternative products and methods, support for research and development, water law, and raising awareness among companies and citizens. With this paper, we have contributed a technical basis for such a strategy and given ideas and starting points for the sustainable protection of natural and drinking waters from a persistent, mobile substance with many sources.

In view of the risks and conflicts, waiting for an overall strategy would, however, be unreasonable. We therefore call on all stakeholders even now to contribute to reducing the input of TFA into the environment. In this paper, we have shown approaches and areas of action; possible official measures within the remit of the German Environment Agency are in progress.

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