TEXTE
167/2023

Final report

Trifluoroacetate (TFA): Laying the foundations for effective mitigation – Spatial analysis of the input pathways into the water cycle

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Abstract: Trifluoroacetate (TFA): Laying the foundations for effective mitigation - Spatial analysis of the input pathways into the water cycle

Trifluoroacetate (TFA; CF_3COO^-) is a very persistent and very mobile substance that can accumulate in certain environmental compartments. Commonly applied water treatment processes are incapable to remove TFA. Therefore, TFA poses a challenge for water protection in general and the protection of drinking water resources in particular. Although the currently known acute toxicity of TFA is rather low, inputs of TFA to water bodies should be avoided whenever possible.

The origin of TFA in the environment has long been a controversial topic: The detection of TFA in pre-industrial water samples of studies conducted in the late 1990s to the early 2000s suggest that TFA is also naturally occurring. However, to date, research has not provided adequate scientific evidence to support this hypothesis. In contrast, there is mounting evidence from recent studies that large amounts of TFA are released into the environment by various anthropogenic sources and that the concentrations of TFA in certain environmental compartments have considerably increased over the last decades. However, due to the large number of possible sources and precursors, for which often only insufficient information is available, it is difficult to attribute TFA pollution to specific origins.

In this project, TFA pollution and its sources in Germany were spatially and quantitatively analysed to assess the contributions of the various possible input pathways and to derive a basis for coordinated, effective, and consistent mitigation measures.

During the project, it became clear that there is a lack of reliable data concerning both environmental TFA concentrations and TFA emissions. Therefore, the project results are subject to some uncertainty. It can be deduced, however, that significant widespread diffuse emissions of TFA are mainly caused by the usage of pesticides and volatile TFA-precursors (e.g., certain refrigerants), while industrial plants can cause local hotspots of TFA contamination.

The following mitigation strategies were discussed at a workshop:

- Mandate for policy-makers and authorities to intensify their efforts to include TFA and other very persistent and very mobile substances in regulatory frameworks both at EU and national level - especially if these substances also cause toxic effects in humans or in the environment even at low concentrations.
- Strengthening of existing approaches to reduce the contamination of the aquatic environment by pesticides, e.g., established programs to investigate the cause of pesticide contamination in water protection areas in cooperation with pesticide producers.
- Continuation and expansion of the monitoring programs by responsible national or regional authorities and other actors in order to identify causes and trends and, if necessary, to be able to initiate and assess concrete mitigation measures.

Information on TFA and selected project results were prepared in the form of an interactive map (https://gis.uba.de/maps/TFA-sources-and-contamination) and a Story Map for the interested public and can be accessed online (https://storymaps.arcgis.com/stories/4b8f21e2b1c049f28d317ba64cdb4bf7).

Kurzbeschreibung: Trifluoracetat (TFA): Grundlagen für eine effektive Minimierung schaffen – Räumliche Analyse der Eintragspfade in den Wasserkreislauf

Trifluoracetat (TFA; CF_3COO^-) ist ein sehr persistenter und sehr mobiler Stoff, der sich in bestimmten Umweltkompartimenten anreichern kann. Mit herkömmlichen Wasseraufbereitungsmethoden ist TFA nicht zu entfernen. Daher stellt TFA eine Herausforderung für den Gewässerschutz im Allgemeinen und den Schutz von Trinkwasserressourcen im Speziellen dar. Obwohl nach bisherigem Kenntnisstand die akute Toxizität von TFA gering ist, sollten Einträge von TFA in Gewässer daher möglichst vermieden werden.

Die Herkunft von TFA in der Umwelt ist seit langem ein kontrovers diskutiertes Thema: Der Nachweis von TFA in vorindustriellen Wasserproben in Studien, die Ende der 1990er bis Anfang der 2000er Jahre durchgeführt wurden, deutet darauf hin, dass TFA in geringem Umfang auch auf natürliche Weise entstehen kann. Bislang hat die Forschung jedoch keine ausreichenden wissen-schaftlichen Beweise für diese Hypothese erbracht. Im Gegensatz dazu haben beispielsweise Eis-bohrkerne aus der Arktis und archivierte Biota-Proben aus Deutschland bewiesen, dass zumin-dest die überwiegende Menge an TFA in der nicht-marinen Umwelt auf anthropogene Quellen zurückzuführen ist. Aufgrund der Vielzahl möglicher Quellen und Vorläufersubstanzen, zu denen häufig nur unzureichende Informationen vorliegen, ist es jedoch oft schwierig, TFA-Belastungen auf eine bestimmte Eintragsquelle zurückzuführen.

In diesem Projekt wurden deutschlandweit TFA-Belastungen sowie deren Quellen räumlich und mengenmäßig analysiert, um so den Beitrag der verschiedenen, möglichen Eintragspfade abzuschätzen. Auf diese Weise wurde eine fachlich fundierte Basis für koordinierte, effektive und konsistente Minderungsmaßnahmen abgeleitet.

Im Projektverlauf bestätigte sich, dass die Datenlage – sowohl die TFA-Belastungen als auch die TFA-Emissionen betreffend – mangelhaft ist, wodurch teilweise Unsicherheiten bei den Projektergebnissen nicht ausgeräumt werden können. Es kann davon ausgegangen werden, dass flächenhaft bedeutende Einträge vor allem durch die Anwendung von Pflanzenschutzmitteln und leichtflüchtigen TFA-Vorläufersubstanzen (z. B. Kältemittel) erfolgen, während Industriebetriebe teilweise lokal sehr hohe Belastungen verursachen.

Minimierungsstrategien, die unter anderem im Rahmen eines Workshops diskutiert wurden, um-fassen:

- Auftrag an Politik und Behörden, sich verstärkt für die Aufnahme von TFA und anderen sehr persistenten und sehr mobilen Substanzen in rechtliche Regelwerke, sowohl auf nationaler wie auch auf EU-Ebene, einzusetzen – insbesondere, wenn diese Stoffe zudem noch toxische Effekte beim Menschen oder Umweltorganismen bereits bei niedrigen Konzentrationen hervorrufen.
- Stärkung bestehender Ansätze zur Minimierung von Belastungen durch Pflanzenschutzmit-tel, wie z. B. der Fundaufklärung mit Unterstützung der Hersteller,
- Weiterführung und Ausweitung der Monitoringprogramme auf Länderebene, um Ursachen und Trends zu erkennen und ggf. konkrete Maßnahmen einleiten und überprüfen zu können.

Informationen zu TFA sowie ausgewählte Projektergebnisse wurden in Form einer interaktiven Karte (https://gis.uba.de/maps/TFA-Herkunft-und-Belastungen) sowie einer StoryMap für die interessierte Öffentlichkeit aufbereitet und online zur Verfügung gestellt (https://storymaps.arcgis.com/stories/2fb9cd41ab0e4f2f88bc86e2ec81f24d).

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List of abbreviations

Abbreviation	Meaning
ATKIS	Official Topographic Cartographic Information System
Basic-DLM	Digital base landscape model
BfG	Federal Institute of Hydrology
BfR	Federal Institute for Risk Assessment
BMUV	Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection
BVL	Federal Office for Consumer Protection and Food Safety
CCAC	Climate and Clean Air Coalition
DCD	Dicyandiamide
DW	Dry weight
EFSA	European Food Safety Authority
E-PRTR Regulation	European Regulation for the establishment of a European Pollutant Register for the implementation of the PRTR Protocol
EU	European Union
CFC	Chlorofluorocarbons
GIS	Geographic information system
GIZ	German Agency for International Cooperation
GWB	Groundwater bodies according to WFD
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
IEC	International Electrotechnical Commission
IVA	Agricultural Industry Association
JKI	Julius Kühn Institute
LAWA	Federal Government/Federal States Working Group on Water
LAWA-AG	LAWA Committee on Groundwater and Water Supply
LAWA-AO	LAWA Committee on Surface and Coastal Waters
LANUV	State Office for Nature, the Environment and Consumer Protection of North Rhine-Westphalia
LU	Livestock units
nrM	Non-relevant metabolite (of active substances in pesticides)

Abbreviation	Meaning
ORC	Organic Rankine cycle (plants for generating electricity from low-temperature heat, such as geothermal or waste heat)
PAPA	Panel Pesticides Applications
PFAS	Per- and polyfluorinated alkyl substances
PFC	Perfluorocarbon
PPP	Plant Protection Products
PRTR	Pollutant Release and Transfer Register
REACH	Regulation on the Registration, Evaluation, Authorisation and Restriction of Chemicals; Regulation EC (No.) 1907/2006
rM	Relevant metabolite (of active substances in pesticides)
ROS	Regression on order statistics
RRP	REACH regulated fluorinated chemicals, refrigerants and pharmaceuticals
SAIO	Statistics on Agricultural Input and Output
SMS	Substance from multiple sources
SUR	Sustainable use regulation on pesticides 2022/0196 (draft regulation of the Ordinary legislative procedure, 2022/0196 (COD))
SVHC	Substance of Very High Concern
SW	Surface water
SWAT	Soil & Water Assessment Tool
TFA	Trifluoroacetate
TGD	Technical guidance document
TZW	TZW: DVGW-Technologiezentrum Wasser (German Water Centre)
UBA	German Environment Agency
uHCFC	Unsaturated hydrofluorochlorocarbon
uHFC	Unsaturated hydrofluorocarbon
EQS	Environmental quality standard
VO	Ordinance
WFD	Directive 2000/60/EC establishing a framework for Community action in the field of water policy - *Water Framework Directive*
WP	Work package
WSC	Water supply company
WWO	Waste Water Ordinance

1 Introduction and Background

The origin of trifluoroacetate (TFA; CF_3COO^-) in the environment has long been a controversial issue. The detection of TFA in pre-industrial water samples collected in the late 1990s to the early 2000s suggest that TFA is also naturally occurring (Frank et al. 2002; Scott et al. 2005). Joudan et al. (2021) critically evaluated the results from earlier monitoring studies and argued that there is insufficient evidence to support the paradigm of natural sources of TFA. In contrast, there is increasing evidence from recent studies that large amounts of TFA are released into the environment by multiple anthropogenic sources and that the concentrations of TFA in certain environmental compartments have considerably increased over the last years and decades.

TFA is an important starting reagent for the synthesis of numerous fluorinated substances, as it can be used to incorporate trifluoromethyl groups ($-CF_3$) into complex molecules (Solomon et al. 2016). TFA is for example used in the production of pharmaceuticals and agrochemicals, finds application in the peptide synthesis, and is used as a solvent and catalyst in polymerisation and condensation reactions. Trifluoroacetic acid (EC No. 200-929-3) is currently registered under Article 10 of the REACH Regulation (REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals) with a tonnage band of 100-1,000 t/a (as of July 2023), plus lower tonnages of the anhydride and various salts.

There are currently just under ten million known synthetic substances with at least one CF_3-moiety in their molecular structure (CAS 2021) and many of these substances enter the environment in the course of their intended use or due to losses during manufacture and transport. Compounds containing at least one carbon-bound trifluoromethyl moiety ($C-CF_3$) are potential pre-cursors TFA. This is due to the exceptionally high (bio)chemical stability of the $C-CF_3$-moiety, which results in the release of TFA as a quasi-terminal degradation product in the environment (Scheurer et al. 2017; Solomon et al. 2016; Tisler et al. 2019). As important TFA sources, fluorinated gases and certain pesticides have been strongly in the public discussion so far.

Furthermore, TFA can be formed during the thermolysis of fluoropolymers, such as polytetrafluoroethylene (Ellis et al. 2001; Cui et al. 2019). Therefore, it can be assumed that the thermolysis of fluorinated polymers in high-temperature industrial and domestic applications (waste incineration, combustion engines, furnaces, etc.) is a potential source of TFA in precipitation, especially in urban regions. For example, environmental modelling showed that approx. 21 ng/L of TFA in precipitation in the city of Toronto was attributed to the thermolysis of fluoropolymer products (Ellis et al. 2001).

Due to its strong tendency to deprotonation, trifluoroacetic acid is present in the aquatic environment almost exclusively in the form of its anion TFA. As a result of its high mobility, high stability and its various potential sources, TFA is found ubiquitously in the aquatic system in Germany. TFA has already been detected in various compartments of the water cycle, with concentrations commonly in the high ng/L- to µg/L-range.

In addition to its high mobility and persistence in the environment and during water treatment, the numerous and complex emission pathways of TFA raise concerns among water suppliers and authorities. TFA has recently been referred to as a "substance of multiple sources" (SMS) (Nödler and Scheurer 2019). However, the individual contributions of the different TFA sources on a temporal and spatial basis are still largely unknown. This knowledge gap poses a problem for the calibration and validation of environmental models, the establishment of mass balances or for the identification of temporal trends in time-series for decision making processes, if

regulatory actions are needed. For this reason, the compilation of monitoring data for TFA is essential.

The study by Scheurer et al. (2017) showed that industrial sites can be a dominant source of TFA to surface waters and groundwaters (pot. main input pathway industry; Sect. 5.1). During a screening of tap and surface waters in Southwest Germany in 2016/17, exceptionally high TFA levels were detected in the Neckar River. An industrial site, specialised in the production and processing of TFA, was identified as the source of contamination and had a significant impact on surface and ground waters downstream. The high TFA concentrations in the Neckar led to a significant increase in the TFA concentration of the Rhine River after its confluence with the Neckar River near the city of Mannheim. This is astonishing, considering the fact that the average discharge of the Rhine at the confluence is approx. nine times greater than the that of the Neckar River.

The work of Scheurer et al. (2017) also found that, in the case of TFA, the sampling of surface waters must be carried out with a sufficiently high temporal resolution (e.g., volume-equivalent 7-day composite samples) to obtain a representative picture of the chemical pollution of a surface water. This is due to the fact that the discharge of TFA into receiving waters by industrial enterprises is not constant, but rather discontinuous. In the case of river systems with a high discharge in Germany (Rhine, Danube, Elbe, Weser, Oder), discrete sampling with lower temporal resolution (e.g., monthly grab sampling) may be sufficient to show general differences in the average TFA concentration/load of these rivers. When comparing concentration values, however, the hydrological conditions (i.e., the discharge) at the time of sampling should always be taken into account in order to be able to consider for the physical effect of dilution, as streamflow usually explains a substantial part of the variance of the concentration of a solute in a surface water.

The most discussed anthropogenic source of TFA is the formation of TFA in the atmosphere through photodegradation of certain hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and unsaturated hydrofluorocarbons (uHFC)and unsaturated hydro-chlorofluorocarbons , uHCFC). These substances were introduced as substitutes for ozone-depleting chlorofluorocarbons (CFCs) and find application mainly used as refrigerants, gaseous fire extinguishing agents and foam-blowing agents (potential main input pathway precipitation, Sect. 5.4). In the troposphere, these compounds can react with hydroxyl and chlorine radicals and thus be converted to trifluoroacetyl chloride (CF_3COCl) or trifluoroacetyl fluoride (CF_3COF), which in turn rapidly hydrolyse to TFA in the presence of atmospheric moisture (Behringer et al. 2021). Due to its low Henry's Law constant and high solubility in water, TFA is primarily scavenged from the atmosphere by wet deposition (Bowden et al. 1996). According to current knowledge, precipitation is one of the most important diffuse input pathways of TFA to the non-marine environment.

The study by Freeling et al. (2020a) showed that, at least, for the situation in Germany, the TFA concentration in precipitation depends more on the sampling date than on the sampling location. It can therefore be assumed that TFA inputs via the precipitation pathway do not lead to spatial hotspots of TFA contamination in water bodies. Rather, it can be assumed that the wet deposition of TFA leads to a background TFA concentration of approx. 0.3-0.4 µg/L TFA in surface waters in Germany, as this corresponds to the current mean precipitation-weighted (i.e., volume-weighted) TFA concentration in precipitation in Germany (Freeling et al. 2020a). Conversely, TFA concentrations in surface waters >1 µg/L indicate the existence of further TFA sources in the catchment area. It should be noted that a certain dilution of the TFA concentration of surface waters is to be expected through mixing with lower contaminated groundwater, whereby the degree of dilution depends on the TFA concentration of the groundwater as well as

the runoff formation and thus the relative composition of the components of runoff. Freeling et al. (2020a) derived a current annual TFA input via wet deposition of just under 100 tons for the total area of Germany.

In order to obtain a first state-wide overview of the pollution of surface waters in the German federal state of Lower Saxony with TFA, Nödler et al. (2019) carried out TFA measurements in spring (May) and autumn (November) in parallel with the quarterly monitoring of the river basin-specific and priority pollutants. The sampling included all sampling sites that were used to establish the pollution inventory according to the European Water Framework Directive (WFD) in Lower Saxony. This procedure had the advantage that the results obtained for TFA could be placed in the context of the general pollution situation according to the WFD. In the samples taken in May (n = 51), TFA levels of 0.23-3.0 µg/L were detected (median: 0.92 µg/L). Similar levels (0.16 - 5.7 µg/L; median: 0.86 µg/L) were detected in the samples taken in November (n = 55). The areas of Cloppenburg, Hannover-Hildesheim and Meppen could be identified as TFA pollution hotspots. The areas of Meppen and Cloppenburg are intensively used for agriculture. With a concentration of 3 µg/L TFA, the highest measured value was detected in May 2018 in the Vechte (Samern, county of Grafschaft Bentheim). This sample also had the second highest sum concentration of 70 pesticides, among them representatives with C-CF_3-substructure such as flufenacet and diflufenican (Nödler et al. 2019).

When it comes to agrochemicals, around 40% of all fluorine containing pesticides currently on the market contain a C-CF_3-moiety (global view; Ogawa et al. 2020). Consequently, a large number of active substances must be considered as potential TFA precursors (main input pathway agriculture, Section 5.3). Analyses of cattle and pig slurry as well as of fermentation residues by TZW (TZW: DVGW-Technologiezentrum Wasser) show that these matrices can also be considered to be potential TFA sources due to their use as agricultural fertilisers (TFA content in the samples: approx. 100 µg/L; unpublished data). An estimated mass of 20 t TFA per year is introduced via the application of liquid manure in Germany, assuming an average concentration of 100 µg/L TFA and an annual liquid manure volume of 200 million tons (Füßler 2011).

Based on the domestic sales of all active substances of plant protection products (PPP) containing one or more C-CF_3-groups in Germany in the years 2016 to 2018 (BVL 2021) and assuming a molar TFA yield of 100 % (i.e. worst-case scenario), a theoretical formation potential of approx. 500 t TFA per year can be derived when these compounds break down in the environment and release TFA as a quasi-terminal degradation product (UBA 2021b). Preliminary monitoring data from Lower Saxony and roughly calculated potential TFA releases as a result of PPP and liquid manure application indicate that intensive agricultural activity can lead to elevated TFA levels in the surface waters of such areas. An analysis of the correlation between TFA concentration in water bodies and land use could help to clarify the relevance of this input pathway.

The contribution of municipal wastewater treatment plants to the TFA budget in water bodies is currently still difficult to quantify (potential main input pathway of municipal wastewater treatment plants, section 5.2). It can be assumed that the TFA concentration in wastewater is primarily determined by the TFA concentration of the local raw water resource(s) used for drinking water production. Since plant (EURL-SRM 2017; Scheurer and Nödler 2021) and presumably also animal foods contain TFA, a TFA input from human excreta is likely. Municipal wastewater treatment plants should therefore be considered as potential point sources of TFA. A comparison of the TFA concentrations in the effluent of wastewater treatment plants with the respective receiving waters could provide vital information on the contribution of municipal wastewater treatment plants to the total TFA load of surface waters. Since some of the currently

used active pharmaceutical ingredients do also contain trifluoromethyl groups, a biological or abiotic release of TFA during wastewater treatment and in the environment (after the discharge of the treated wastewater) is also possible.

The methods developed in this project for testing spatial correlations between TFA input pathways and loads can also be applied to other trace substances. This is particularly relevant for the aforementioned SMS substances, which originate from a variety of sources that may be regulated differently due to competing responsibilities. For a targeted and rapid implementation of regulatory measures to reduce inputs of SMS substances, their most significant sources must be identified. In recent years, TZW has identified numerous substances from industry and agricultural practices that can be detected in the aquatic system and for which this issue exists. These include, for example, the nitrification inhibitor dicyandiamide (DCD), which is also used in the production of pressboard to bind outgassing formaldehyde (Scheurer et al. 2016). The same holds true for 1H-1,2,4-triazole, which is used as a nitrification inhibitor, but it also has other potential entry pathways. As such, the compound is used as an industrial chemical and can also be formed through the degradation of azole fungicides (Scheurer et al. 2016). Sulfamic acid, which has already been detected in the mg/L range in municipal wastewater in Germany, is used as a building block for chemical synthesis, but is also applied directly as an acidic cleaning agent intended for industrial and house-holds applications. In addition, the compound can be formed in wastewater treatment plants upon the biodegradation of the artificial sweeteners acesulfame and cyclamate (Freeling et al. 2020b).

For many of these SMS substances, however, the individual contributions of all potential sources on a temporal and spatial basis are largely unknown.

2 Objective

The aim of the project is to compile and evaluate reliable findings and data on the sources and the occurrence of TFA in various environmental media on a spatial and quantitative basis. The project is based on a publication by the German Environment Agency (UBA 2021b) which is supplemented by our own research in order to systematically identify data gaps and to derive recommendations for action. The goal is to obtain an overall picture of the pollution of the aquatic system in Germany with TFA, to characterise relevant input pathways and to identify knowledge and data gaps.

The existing knowledge and the existing knowledge deficits are brought together and processed in a targeted manner. The central element is a geographic information system (GIS) that collects and combines the baseline data in suitable layers and enables evaluation and cartographic visualisation. This visualised representation provides the basis to identify priority fields of action for targeted TFA mitigation and enables the analysis of different areas of TFA release. Finally, the results are presented to the public in a comprehensible way and are made available in the form of an ArcGIS Story Map and an interactive map in the form of a web application.

The goal of the project is to align and compare the TFA concentrations measured in surface and ground waters in Germany with the relevant input pathways for TFA to identify and to elucidate pollution hotspots. In this context, not only relevant TFA sources are to be considered, but also the boundary conditions that potentially have an impact on the TFA pollution, such as precipitation, land use or physiographic factors. This approach can help to initiate an effective and technically sound TFA reduction strategy under the involvement of the relevant stakeholders and aids to identify the levels at which administrative action for regulation must begin. Hence, the aim of the project is to identify stakeholders who, have an interest in reducing the inputs of TFA and its precursors and/or who are responsible for the emissions of these substances. Another goal is to identify missing interfaces between authorities and to recognise potentially existing deficits in the monitoring of processes and substances as well as the elucidation of shortcomings in regulatory procedures.

By achieving the objectives outlined, a foundation will be created for the initiation of processes to reduce the medium to long-term input of TFA into the environment.

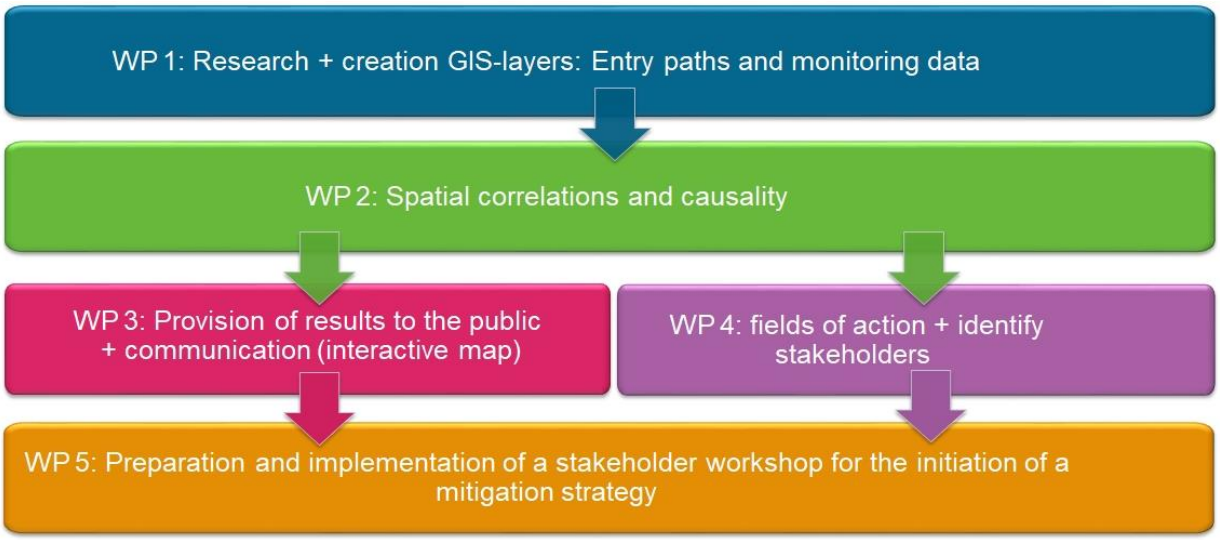
3 Methods and Project Approach

The project was divided into several work packages (see Figure 1).

The aim of work package (WP) 1 was to collect and to prepare the available data on the occurrence of TFA in various environmental compartments and to compile the available knowledge on possible TFA emissions and emission sources. Within the framework of the project, GIS layers were created and handed over to the German Environment Agency (UBA). WP 2 combines the results of WP 1 and evaluates possible input pathways for TFA, considering the spatial correlations and causalities as well as the sales and emission quantities of TFA and its precursors.

Within the framework of WP 3, the results were made available to the public utilising an ArcGIS Story Map[1] and an interactive map[2]. In WP 4, fields of action and stakeholders were identified. Finally, a stakeholder workshop was held in WP 5 to initiate a mitigation strategy.

Figure 1: Work packages



Source: own illustration, TZW.

[1] https://gis.uba.de/maps/Trifluoracetate

[2] https://gis.uba.de/maps/TFA-sources-and-contamination

4 Environmental Concentrations of TFA in Water Bodies

4.1 Data Basis

4.1.1 Surface waters and hydrological units

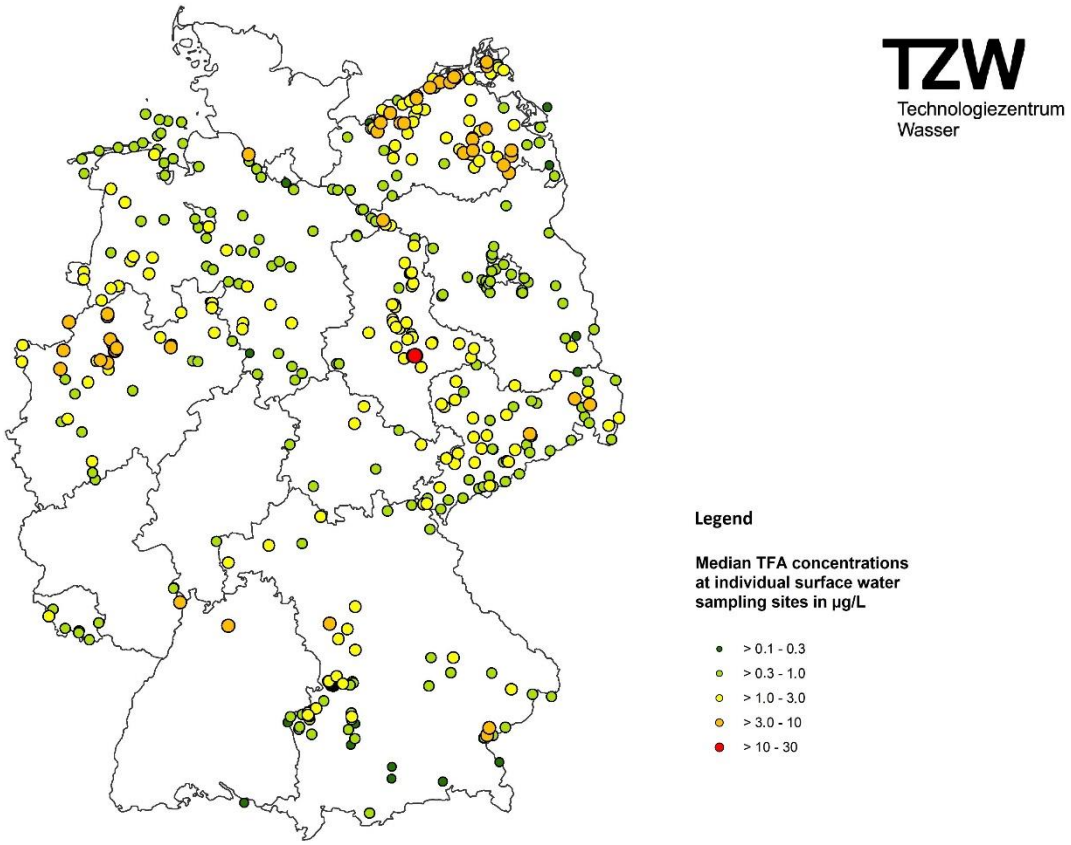
The surface waters in Germany are summarised in Layer A. In addition to the polygon data from the ATKIS-Basic-DLM (official topographic cartographic information system digital base landscape model) provided by the client, open data from the BfG Geo-Portal (BfG 2021) were used. These data are available as continuous line features. The ATKIS polygon data, on the other hand, only represent larger water bodies, and some stream segments are missing.

For the following evaluations and visualisations, geodatasets (geometries) of hydrological and administrative units (sub-basins according to the Water Framework Directive; groundwater bodies; municipal boundaries, county boundaries, and state boundaries) were also included (see Figure 4 and Figure 7).

4.1.2 TFA data from surface water monitoring

The client provided TFA concentration data of surface waters (origin: Federal Government/Federal States Working Group on Water (LAWA)) for 13 federal states. This monitoring data covered the years 2016 to 2021, whereby some federal states provided time series over several years for numerous monitoring sites, while values from other federal states were only available for a single year or only for a few monitoring sites. The median TFA concentration for each sampling points are shown in Figure 2. In addition, surface water monitoring data were provided by four water supply companies (WSC) for the project following a request from UBA and TZW. For confidentiality reasons, the data from WSC cannot be presented in full detail but are used for the calculation of summary statistics for TFA for the sub-catchments. Hence, Figure 2 only depicts the results of the LAWA monitoring.

Figure 2: Results of the TFA surface water monitoring from LAWA-AO.

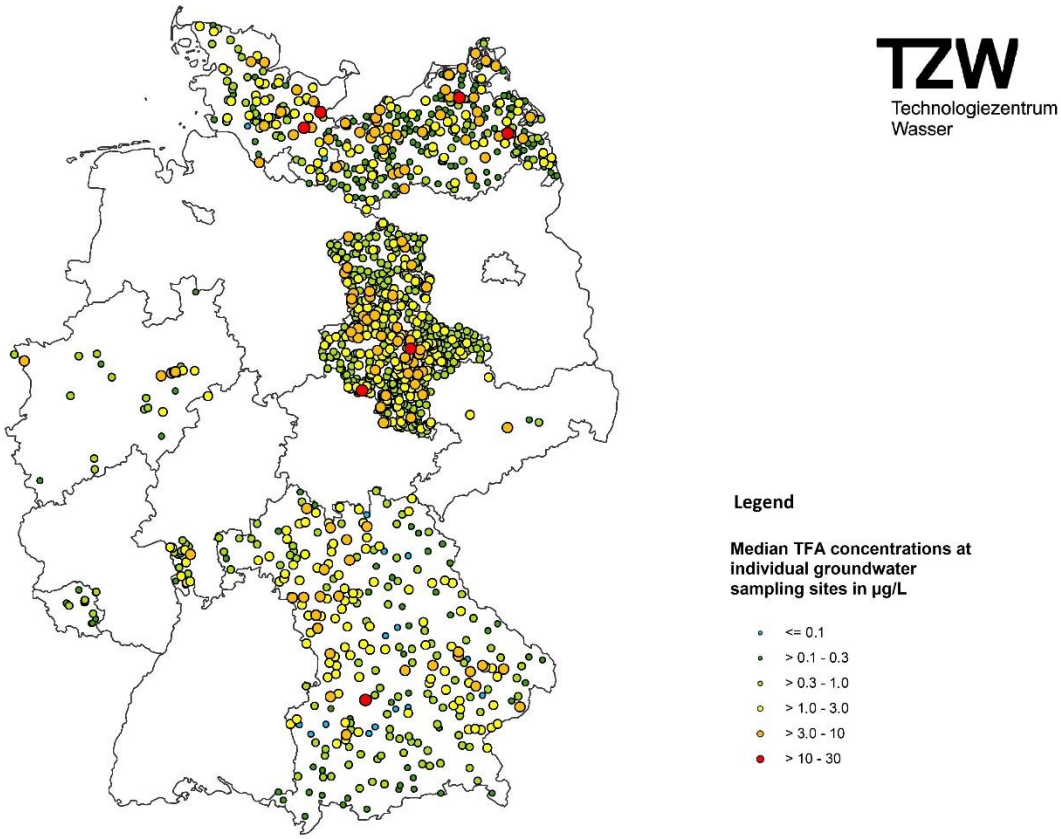


Source: own illustration, TZW.

4.1.2.1 TFA data from groundwater monitoring

The client provided TFA concentration data of groundwaters (origin: LAWA) for eight federal states. This monitoring data covered the years 2017 to 2020. For some of the German federal states, the entire period is covered by the data set and most monitoring sites were sampled and analysed for TFA on multiple occasions. In other federal states, only individual data points are available for a few monitoring sites. In addition to the data by LAWA, measurement data for groundwater (and raw water used for drinking water production) were available, which were provided by ten WSC following a request from UBA and TZW. Data from the groundwater database "Wasserversorgung Baden-Württemberg" were also used. Publication of the WSC data is only possible in anonymised form or with their explicit consent. Therefore, Figure 3 only shows the results of the LAWA monitoring.

Figure 3: TFA groundwater monitoring data from LAWA-AG.



Source: own illustration, TZW.

4.2 Methods and Results

For the evaluation and better visualisation of TFA levels in surface waters and groundwaters in Germany, all individual values were spatially aggregated. The assignment of the TFA concentration values to groundwater bodies or river catchments also made it possible to anonymise the concentration data provided by water suppliers and other institutions for the study, since each point information (i.e., georeferenced surface or groundwater monitoring site) was converted into an area-based information (i.e., river catchment or groundwater body). For each groundwater body and for each river catchment for which at least one numerical TFA concentration value was available, the following statistical parameters (i.e., summary statistics) were derived: arithmetic mean, median, maximum and standard deviation of the TFA concentration.

The data sets of TFA concentration in surface water and groundwater in this work contained left-censored data points. Left-censored observations, sometimes referred to as “non-detects” or “less than” values (e.g., <25 ng/L), are concentrations that are known only to be somewhere between zero and the limit of quantification (LOQ). A commonly used method in environmental chemistry, to deal with values below the LOQ, is to substitute a fraction of the LOQ for each censored value, or to exclude them from the analysis. However, research has shown that this approach produces poor estimates of statistics, such as means, correlation coefficients, regression slopes, or hypothesis tests and can obscure trends or other patterns in the data, which can lead to misinterpretation (Helsel 2006). In the here presented study, regression on order statistics (ROS) was used for a more robust estimate of mean and median values (Helsel

2011). ROS is a so-called imputation procedure in which the censored data points (i.e., values below the LOQ) are filled up based on a probability plot of the uncensored data points (i.e., values above the LOQ), thus avoiding arbitrary substitution or deletion of censored data (Helsel 2005). Only when the application of the ROS procedure was not possible, due to a too large relative number of censored data points, numerical values below the LOQ were substituted by the quotient of the LOQ and the square root of the number 2. After deriving the median concentration of each groundwater and surface water monitoring site, the mean value of the median concentrations of all monitoring sites located within the same water body (i.e., groundwater body or river catchment) was calculated. Since the environmental concentrations of TFA follow a right-skewed distribution, the median is the better measure of central tendency in comparison to the arithmetic mean. The two-tiered aggregation of the data (1st tier: aggregation of the individual values at the level of individual monitoring sites; 2nd tier: aggregation at the level of groundwater bodies or river catchments) ensured that monitoring sites for which a large number of data points were available did not contribute disproportionately to the arithmetic mean at the level of the groundwater bodies or river catchments. In addition to the average median TFA concentration, the maximum TFA concentration was determined for each groundwater body and river catchment, respectively. It should be mentioned that, as a result of the spatial aggregation of TFA concentrations at the level of groundwater bodies or river catchments, small-scale differences in concentrations (e.g., elevated TFA levels in a surface water downstream of an industrial point source) can become indiscernible.

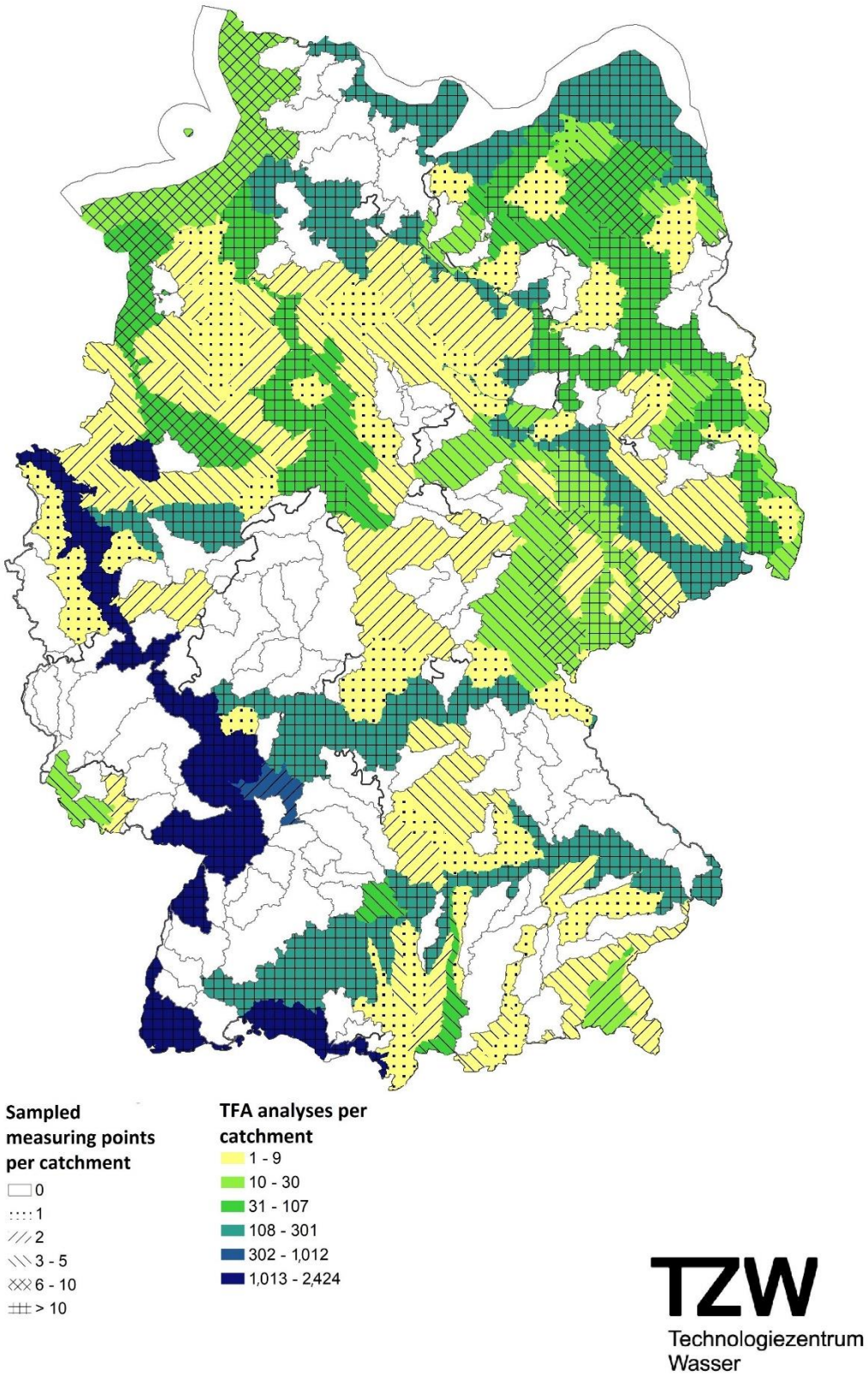
4.2.1 Surface water

The aggregation of the TFA concentrations in surface waters (n=7684 individual values) was carried out on the basis of the river catchments located within Germany with an area of at least 500 km^2, which are presented in Figure 4 (n=216) (Hydrologischer Atlas von Deutschland/BfG 2003). In total, aggregated TFA concentrations were derived for 108 of the 216 river catchments. On average, approx. 71 individual values were available for each of the 108 river catchments (median: 6 individual values) (see Figure 4). Figure 4 shows the average median TFA concentrations of the river catchments in Germany. Analogously, Figure 6 shows the maximum TFA concentrations of the river catchments.

4.2.2 Groundwater

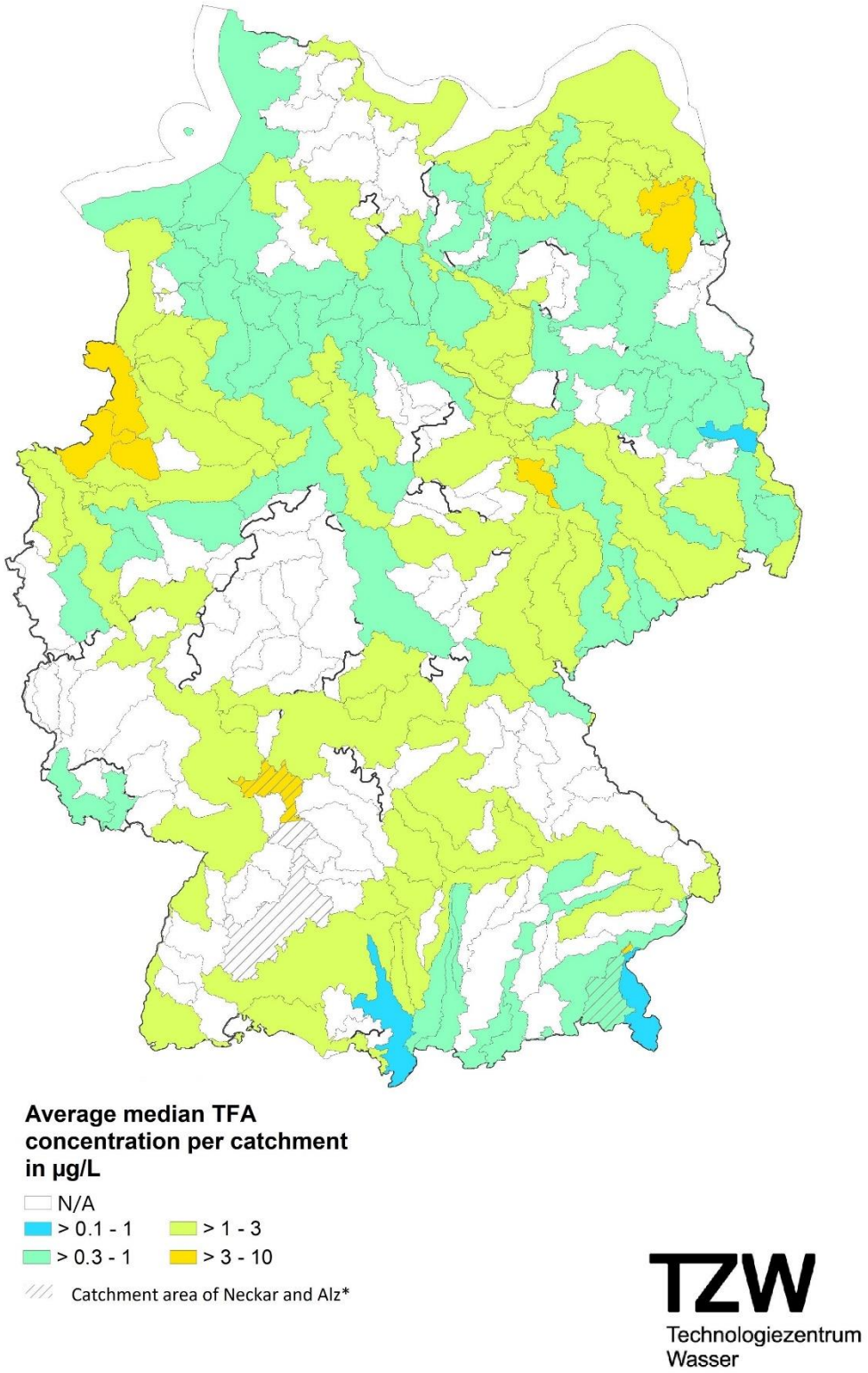
TFA levels in groundwater (n=8401 individual values) were aggregated on the basis of Germany's groundwater bodies (n=1177) as they are defined under the European Water Framework Directive (EU-WFD). In total, aggregated TFA concentrations were derived for 414 of the 1177 groundwater bodies. On average, approx. 20 individual values were available for each groundwater body (median: 4 individual values) (see Figure 7). Figure 8 shows the average median TFA concentrations of WFD groundwater bodies in Germany. Analogously, Figure 9 shows the maximum TFA concentrations of the WFD groundwater bodies.

Figure 4: Location of river catchments areas within Germany with a size of at least 500 km² with information on the number of sampled monitoring sites



Source: own illustration, TZW.

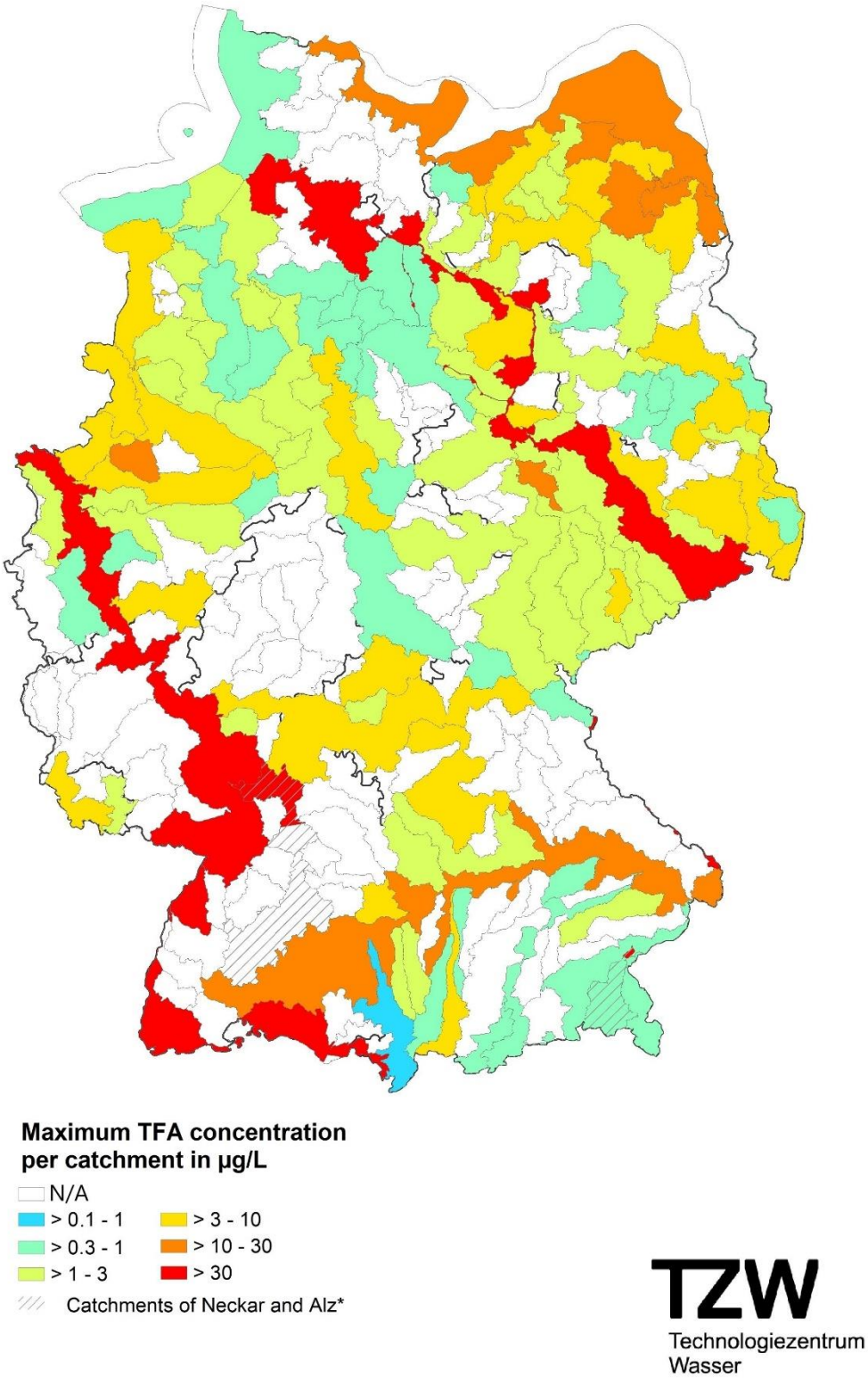
Figure 5: Average median TFA concentrations in river catchments with an area > 500 km² in Germany



*In the catchments of the Neckar and Alz rivers, the concentrations in the upper and lower areas differ greatly due to point discharges. The catchment areas were therefore subdivided.

Source: own illustration, TZW; EZG geometries: Hydrological Atlas (BfG 2003).

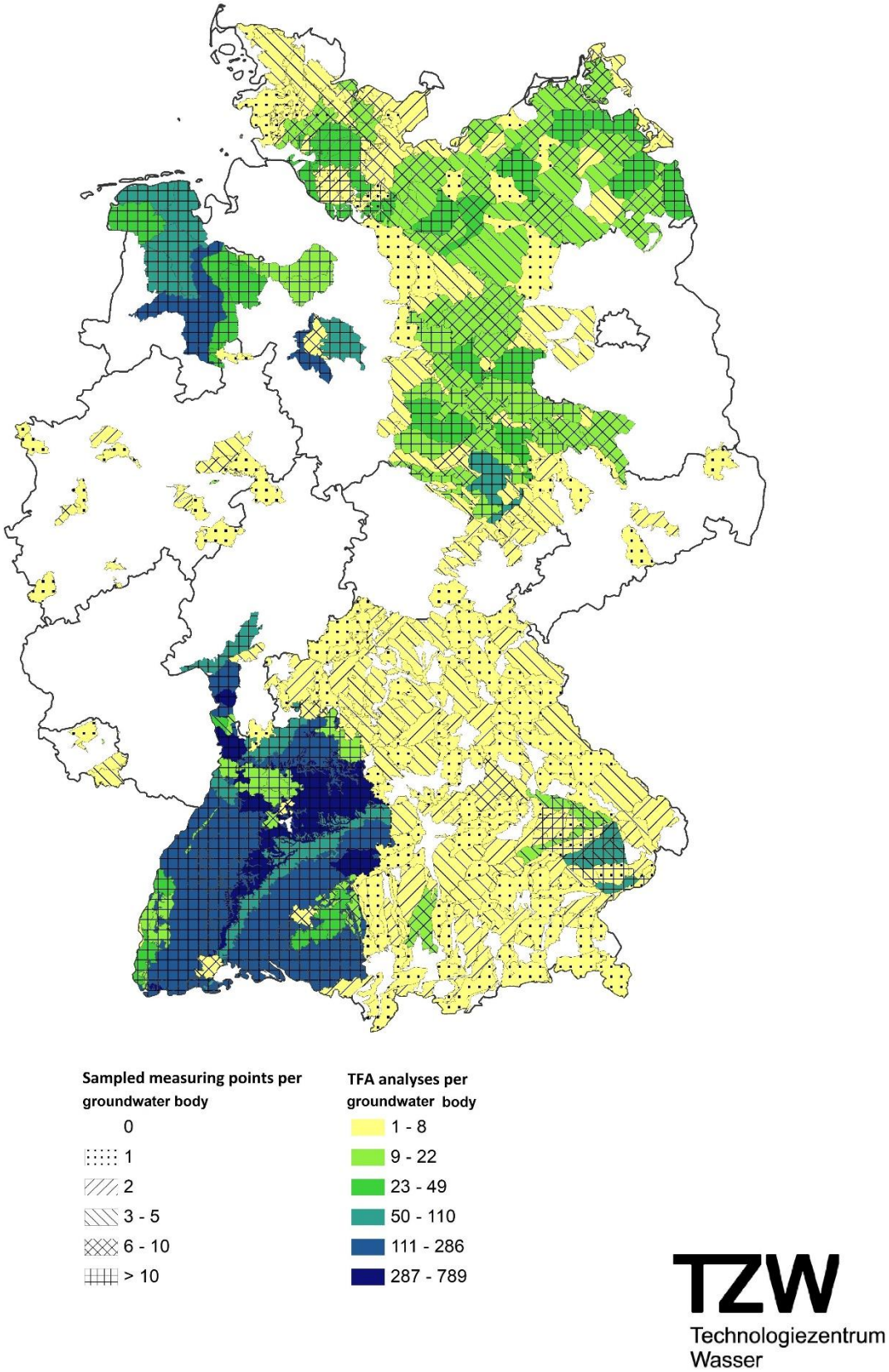
Figure 6: Maximum TFA concentrations in river catchments with an area >500 km² in Germany.



*In the catchments of the Neckar and Alz rivers, the concentrations in the upper and lower areas differ greatly due to point discharges. The catchment areas were therefore subdivided.

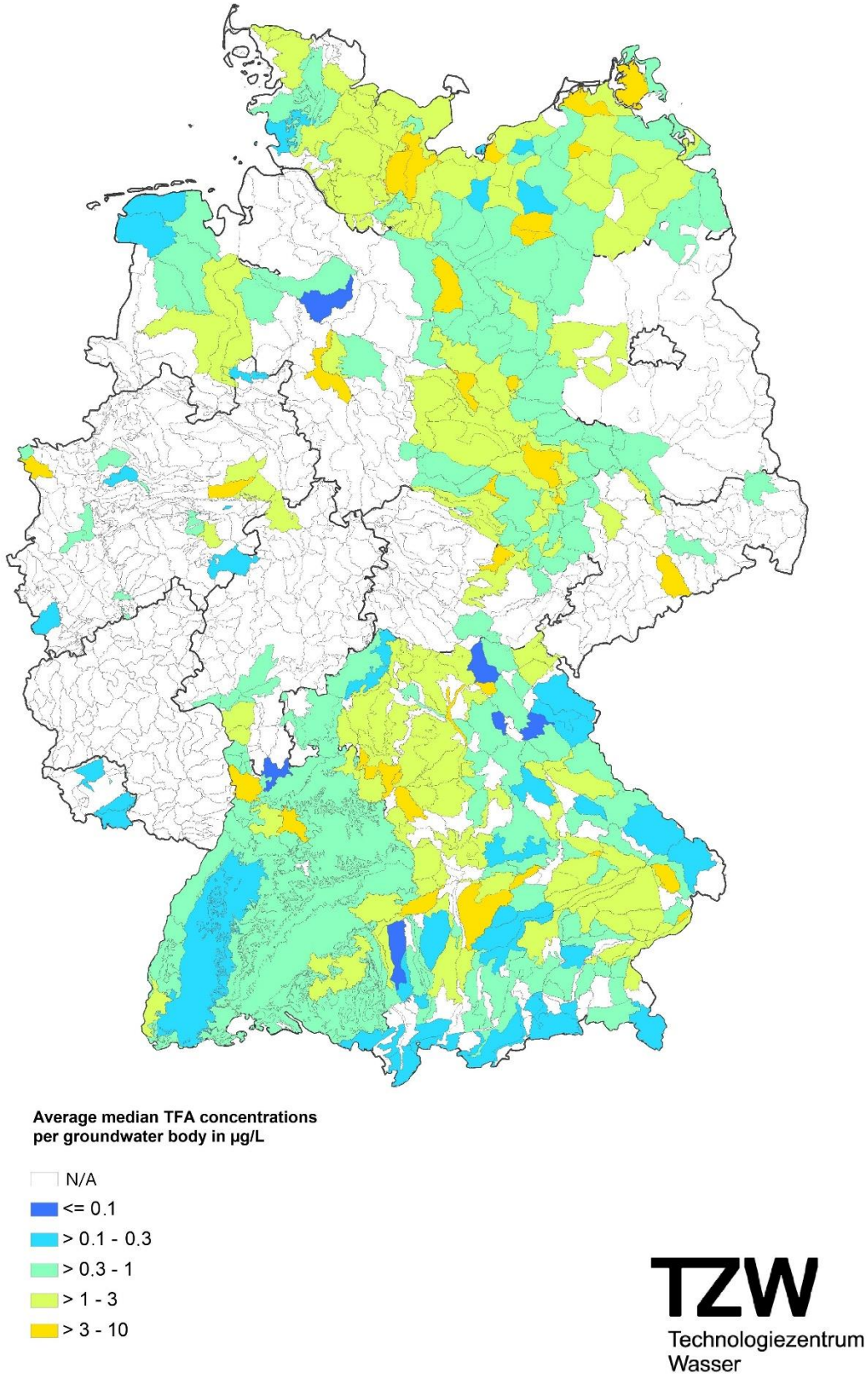
Source: own illustration, TZW; EZG geometries: Hydrological Atlas (BfG 2003).

Figure 7: Location of WFD groundwater bodies (GWB) in Germany with information on the number of sampled monitoring sites.



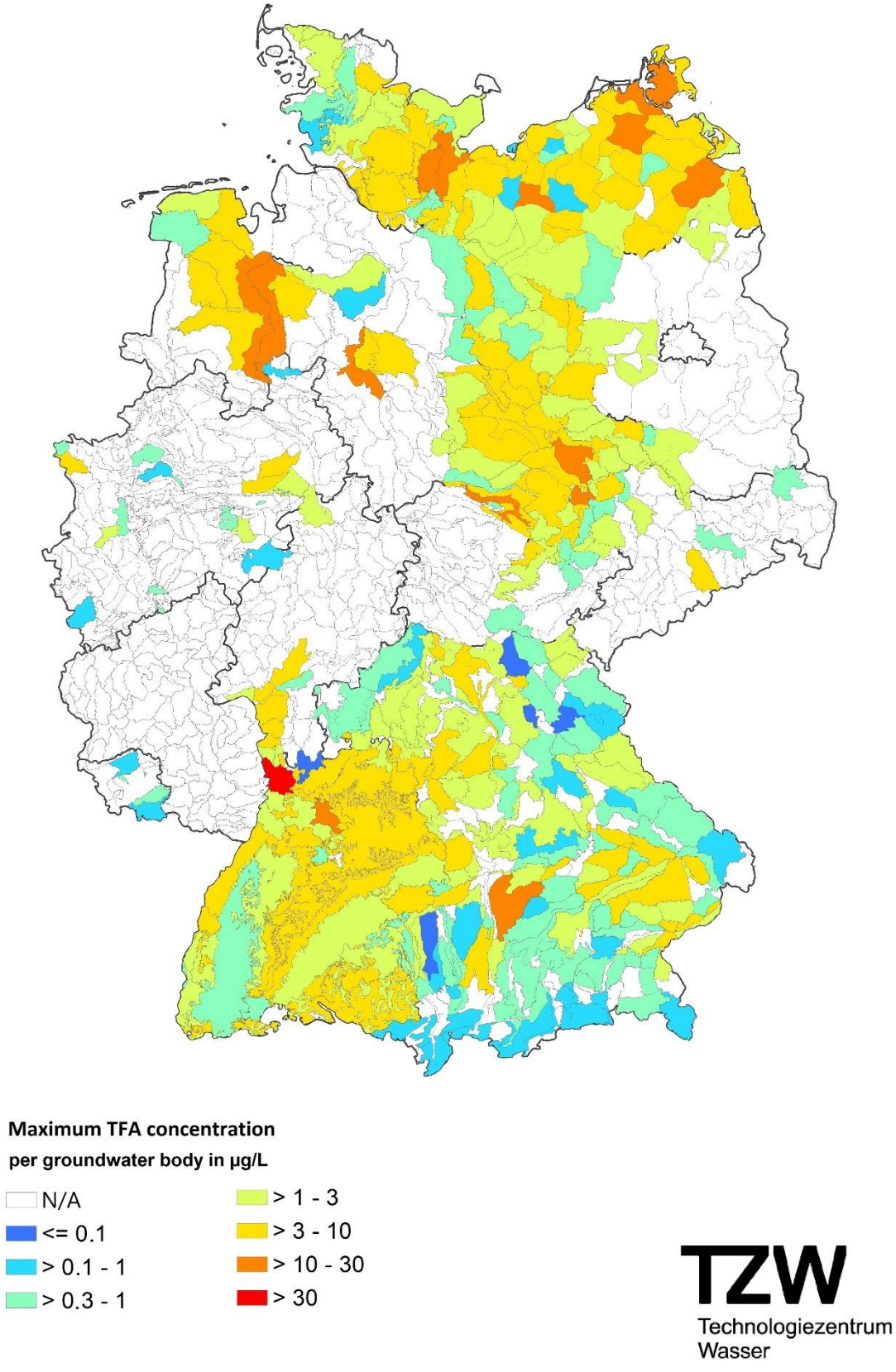
Source: own illustration, TZW; geometries of groundwater bodies: BfG geoportal (BfG 2021).

Figure 8: Average median TFA-concentrations in WFD groundwater bodies in Germany.



Source: own illustration, TZW; geometries of groundwater bodies: BfG geoportal (BfG 2021).

Figure 9: Maximum TFA levels in WFD groundwater bodies in Germany.



Source: own illustration, TZW; geometries of groundwater bodies: BfG geoportal (BfG 2021).

5 Analysis of TFA Sources and Input Pathways

5.1 Industry

5.1.1 Data basis

Information on industrial plants in Germany that emit TFA directly, or indirectly via sewage treatment plants into the aquatic environment was not available. Therefore, no statements can be made on the relevance of the industrial input pathway for the TFA concentration/load in surface waters and groundwaters in Germany and on the location of TFA-emitting plants. According to the European Pollutant Release and Transfer Register Regulation (E-PRTR Regulation, see UBA (2022)) on the establishment of a European Pollutant Release and Transfer Register, certain businesses are required to report specified information on emissions and wastes to their respective national authority for inclusion in the European register. It is conceivable that industrial plants in Germany that have reported the release of fluorides into the environmental compartment water and that are active in the field of chemical production are also potential emitters of TFA into flowing waters. Industrial plants for which these criteria apply are listed in Table 1 (UBA 2022). It should be noted that the E-PRTR Regulation does not give any information about the identity of fluorinated chemicals produced and/or processed at the facility. Hence, it is not possible to draw any conclusions from the available information if TFA or potential precursors of TFA are released to the aquatic system by these companies.

Table 1: Industrial facilities in Germany that release fluorides into the environmental compartment water according to the E-PRTR Regulation and are active in chemical synthesis. The data apply to the reporting year 2019 (UBA 2022).

Company	Location	River catchment area	Activity according to E-PRTR Regulation	Annual fluoride load released into water (as total F) in kg/a
Wacker Chemie AG, Burghausen plant	84489 Burghausen	Danube	Chemical plants for the industrial production of basic organic chemicals	15900
BASF Schwarzheide GmbH	01987 Schwarzheide	Elbe/ Labe	Production of oxygenated hydrocarbons	6400
Remediation operations Wismut GmbH	01824 Königstein	Elbe/ Labe	Production of oxygenated hydrocarbons	4330
INOVYN Germany GmbH	47495 Rheinberg	Rhine	Chemical plants for the industrial production of basic organic chemicals	3830
Solvay Chemicals GmbH	47495 Rheinberg	Rhine	Chemical plants for the industrial production of inorganic basic chemicals	13100
Basell Polyolefine GmbH	50389 Wesseling	Rhine	Chemical plants for the industrial production of basic organic chemicals	6890

Company	Location	River catchment area	Activity according to E-PRTR Regulation	Annual fluoride load released into water (as total F) in kg/a
Evonik Operations GmbH	45772 Marl	Rhine	Chemical plants for the industrial production of basic organic chemicals	6860
Solvay Fluor GmbH	74206 Bad Wimpfen	Rhine	Chemical plants for the industrial production of inorganic basic chemicals	55700
BASF SE	67063 Ludwigshafen on the Rhine	Rhine	Production of oxygenated KW	23200
Honeywell Specialty Chemicals	30926 Seelze	Weser	Production of salts	23100

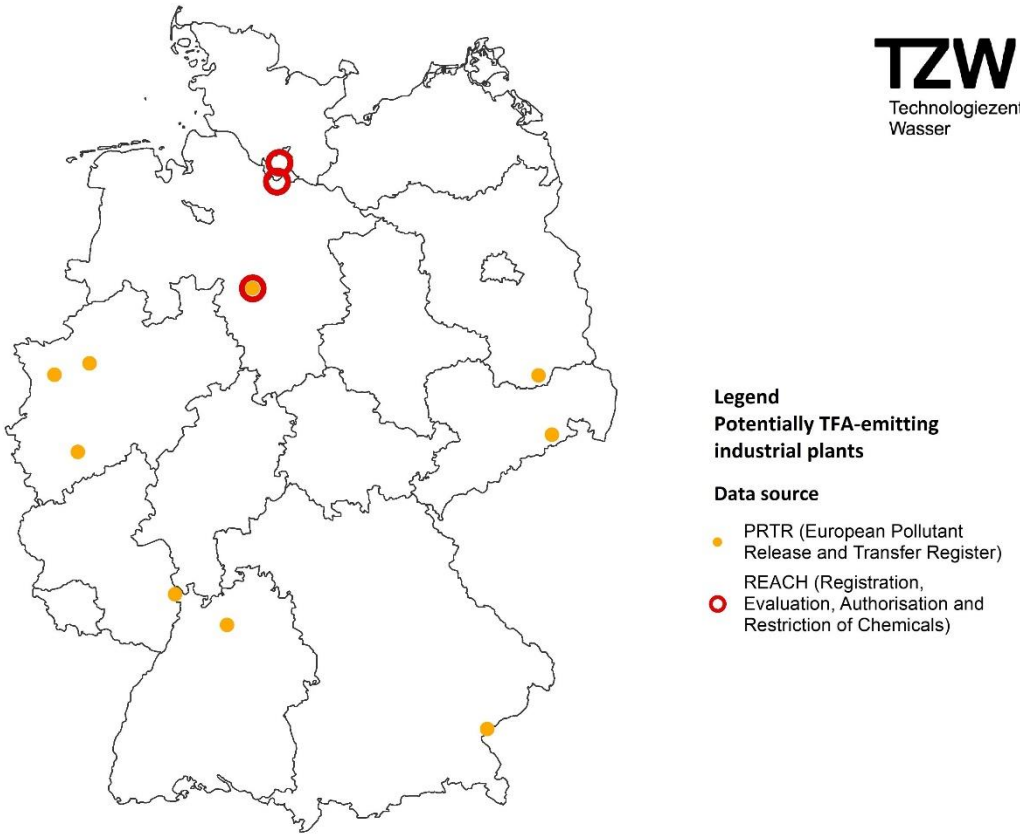
Substance-specific information on chemicals regulated under REACH can be found on the homepage of the European Chemicals Agency (ECHA). Trifluoroacetic acid (CAS number: 76-05-1; EC number: 200-929-3) is registered under REACH with a tonnage band[3] of 100 t/a to 1,000 t/a (ECHA 2022). Only the companies with registrations according to article 10 of the REACH Regulation were considered (https://echa.europa.eu/registration-dossier/-/registered-dossier/5203/1/2). Four out of seven active registrants in the European Union for TFA are located within Germany (Table 2). Whether and to what extent the companies listed in Table 1 and Table 2 actually emit TFA into the aquatic environment cannot be answered here. The locations of the of potentially TFA-emitting industrial plants in Germany are shown in Figure 10.

[3] Sum of the amount of TFA produced in the European Economic Area and the amount of TFA imported into it.

Table 2: Active registrants (as of March 2022) for trifluoroacetic acid (CAS number: 76-05-1; EC number: 200-929-3) in the European Union under the REACH Regulation (ECHA 2022). Only companies with registrations according to Art. 10 of the REACH Regulation are considered.

Company	Location	Country
ACETO GmbH	22085 Hamburg	Germany
Chr. Olesen ChemPharm GmbH	21218 Seevetal	Germany
Honeywell Specialty Chemicals Seelze GmbH	30926 Seelze	Germany
Solvay Fluor GmbH	30173 Hanover	Germany
BASF Agri Production SAS	69130 Écully	France
RHODIA OPERATIONS	93300 Aubervilliers	France
Global Product Compliance (Europe) AB	22363 Lund	Sweden

Figure 10: Location of potentially TFA-emitting industrial plants in Germany.



Source: TZW; data basis: UBA (2022), ECHA (2022).

5.1.2 TFA Inputs from the Industry

TFA can be introduced directly (i.e., as a primary source) into water bodies via industrial manufacturing processes. TFA is an important building block in the production of numerous fluorinated organic substances, as it can be used to incorporate trifluoromethyl groups (-CF_3) into complex molecules. The addition of a CF_3-moiety can significantly enhance the biological

activity of molecules by promoting electrostatic interactions with biological targets, increasing metabolic stability and improving cell membrane permeability and bioavailability (Tong et al. 2019). Since numerous pesticides and pharmaceuticals are equipped with at least one carbon-bonded trifluoromethyl group (C-CF_3), it is conceivable that TFA is also introduced into the aquatic environment by manufacturing plants of these substances.

Industrial fluorochemical plants that produce and/or process trifluoroacetic acid and its derivatives are potentially of great quantitative relevance for the discharge of TFA into the aquatic system. A prominent example for this are the high concentrations of TFA in the Rhine river downstream of the mouth of the Neckar river and in the groundwater near the city of Heidelberg in 2016 and 2017, which were caused by an industrial plant which discharged TFA into the Neckar river (Scheurer et al. 2017). The monitoring started by TZW in 2016 demonstrated that industrial discharges can significantly influence the TFA levels of downstream water bodies (surface waters and groundwater), even if they are located at great distances from the emitting industrial facility. For example, TFA levels above 100 µg/L were detected in the Neckar in 2016. Despite the low water flow of the Neckar compared to the Rhine (the average discharge of the Rhine at the Neckar confluence is about 9-times higher than the that of the Neckar River), the high levels in the Neckar led to a strong increase in the Rhine downstream of the mouth of the Neckar near Mannheim. While the TFA content at Basel and Karlsruhe (upstream the confluence) was just above 0.4 µg/L, 1.1 µg/L were detected in the Rhine at Mainz (downstream the confluence).

Similar results were obtained in the Alz catchment in Bavaria, Germany (sampling: 2016/2017), in which TFA concentrations increased approx. 40-fold from the upper Alz River (<0.5 µg/L) to downstream a fluorochemical plant (up to 22 µg/L) (Scheurer et al. 2017).

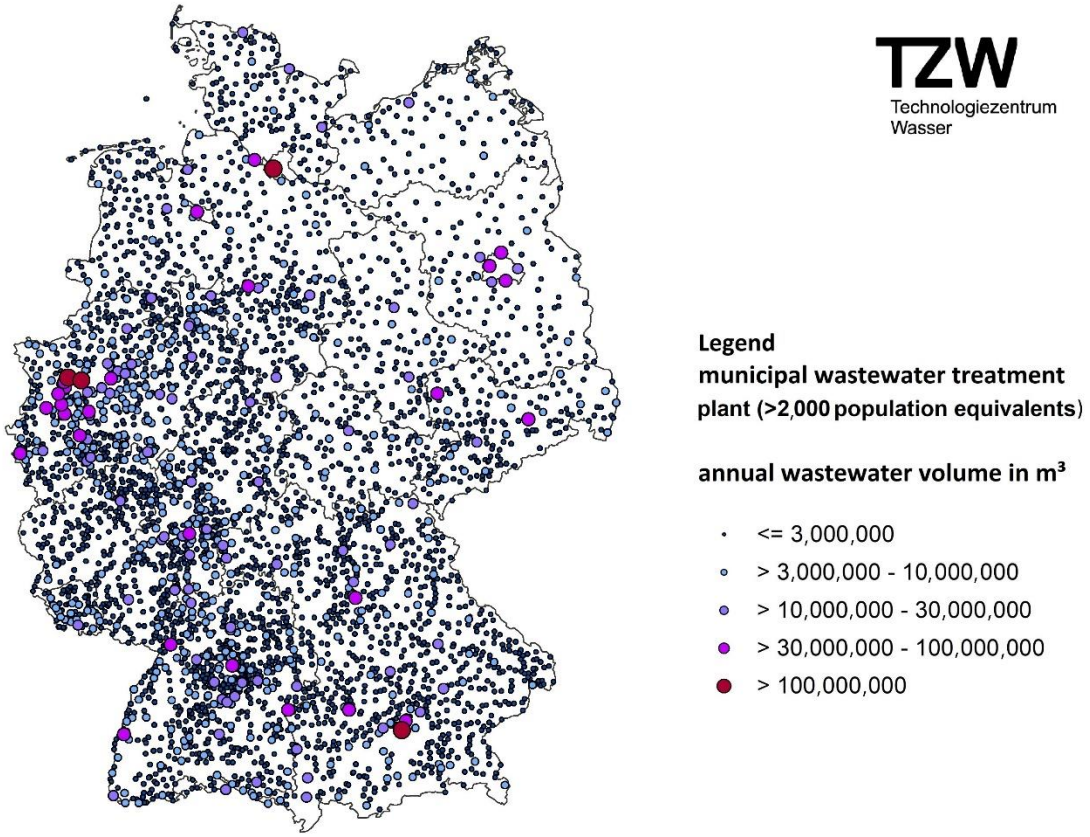
5.2 Municipal Wastewater Treatment Plants

5.2.1 Data basis

The ATKIS Basic-DLM data was complemented by data from *Thru.de*[4] , which was also provided by the UBA. The ATKIS data source contains more objects, as wastewater treatment plants with population equivalents < 2000 are also included. The *Thru.de* dataset, on the other hand, also contains information on population equivalents and treatment processes of the individual municipal wastewater treatment plants. Figure 11 shows the *Thru.de* data classified by wastewater volume (reporting year: 2018).

[4] *Thru.de* is an internet portal of the UBA and provides data on how many pollutants German industrial companies release into the environment and how much waste they dispose of outside their operations.

Figure 11: Location of the municipal wastewater treatment plants with > 2000 population equivalents (p.e.). The representation provides information on the annual wastewater volume of each wastewater treatment plant. Reporting year: 2018.



Source: own illustration, TZW, based on data from Thru.de.

5.2.2 TFA inputs from municipal wastewater treatment plants

Municipal wastewater treatment plants are a source of TFA into the aquatic environment. This can be explained by the presence of TFA precursors such as pharmaceuticals or biocides as well as the transformation products of these substance in the wastewater and the fact that TFA is not removed during wastewater treatment. Research has shown that wastewater and wastewater-influenced waterbodies can bear a TFA formation potential through biotic (Scheurer et al. 2017) or abiotic (e.g. ozonation (Scheurer et al. 2017) and photodegradation (Tisler et al. 2019)) degradation. Due to the comparatively high stability of many TFA precursors found in wastewater, it can be assumed that their residence times in flowing waters (defined as the time span between the discharge of the precursor substance into the receiving water body and its discharge/entry into the ocean) are too short in Germany to be completely degraded/converted to TFA.

At this point, we would like to briefly discuss the possible consequences of the increasing use of processes for advanced wastewater treatment in wastewater treatment plants (i.e. quaternary treatment). Scheurer et al. (2017) showed that precursor substances in wastewater can be biologically and oxidatively degraded to TFA. The oxidative degradation of precursor substances as a result of ozonation could therefore lead to a release of TFA during wastewater treatment. When activated carbon is used, on the other hand, TFA precursors are potentially adsorbed and thus the TFA formation potential of the wastewater tends to be reduced by the use of activated carbon filters. However, due to the high background concentrations of TFA in municipal

wastewater, it is so far unclear whether typical loads of potential precursors in wastewater contribute significantly to the TFA balance of a wastewater treatment plant. It has to be noted that TFA itself cannot be removed by commonly applied water treatment processes (Scheurer et al. 2017).

The analysis of the effluents of several municipal wastewater treatment plants in the German federal state of North Rhine-Westphalia by the State Office for Nature, the Environment and Consumer Protection of North Rhine-Westphalia (LANUV) showed similar TFA levels in comparison to surface waters in the same state. This is a further indication that municipal wastewater treatment plants are not a main input pathway for TFA and that their influence on concentrations in surface waters is rather low.

It can be assumed that the TFA concentration of treated wastewater is mainly determined by the concentration in the drinking water of the households connected to the respective sewage system. In order to quantify the contribution of wastewater treatment plants to the TFA concentrations of surface waters, monitoring of the TFA concentrations or loads in the effluent of wastewater treatment plants and in the receiving water body prior to the wastewater discharge is required.

5.2.2.1 Biocides

Biocides are chemicals or microorganisms used in the non-agricultural sector to control pests (such as rodents, insects, fungi, microbes), including disinfectants, rat poisons or wood preservatives. Currently (as of November 2021), 68 biocidal active substances are authorised in Germany, five of which have at least one C-CF_3-substructure in their molecule (BAuA 2021). Sales volumes for biocidal products in Germany are not published (as of December 2022). A quantitative estimation of potential TFA inputs from biocides and a spatial analysis between input and TFA contamination was therefore not carried out. However, it can be assumed that the contribution of biocides to the TFA balance plays a minor role due to the small number of potential precursor substances.

5.2.2.2 Human and veterinary medicinal products

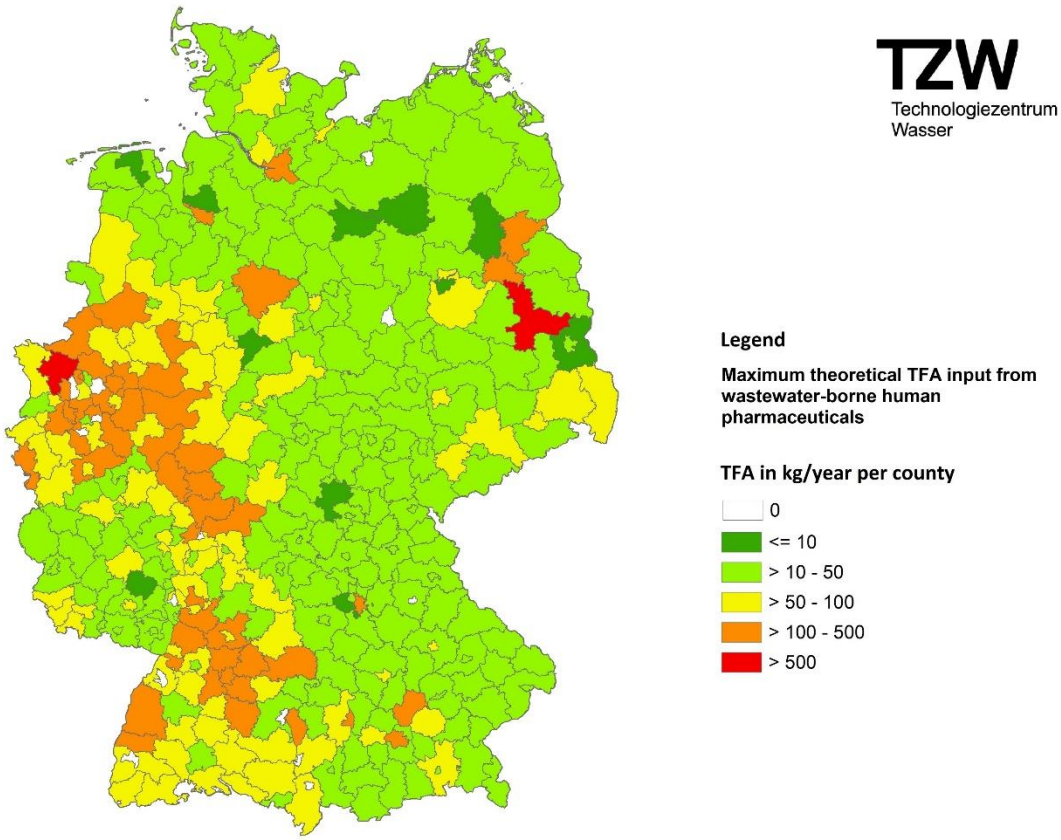
A search in the online database DrugBank revealed that 408 active pharmaceutical ingredients contain at least one C-CF_3-moiety (DrugBank 2021). 39 of these active pharmaceutical ingredients are currently approved in Germany (UBA 2021b). From the annual consumption data of the active substances (data basis: IQVIA, unpublished) and under the conservative assumption of a molar TFA yield of 100 %, a theoretical release of 29 t/a TFA from the degradation of human medicinal products can be derived for Germany for the year 2020 (UBA 2021b).

The gaseous inhalation anaesthetics isoflurane, sevoflurane and desflurane account for almost a quarter of the theoretically formed TFA quantities from human pharmaceuticals. Their main input is not via the wastewater pathway, but via emissions into the atmosphere, where TFA is formed from these precursor substances by oxidative degradation processes and can be released into the environment as a result of atmospheric deposition. In Germany, approx. 180 t of these substances are used annually, of which 176 t are emitted into the atmosphere (long-term average for the years 2011 to 2018; ZSE 2020). Taking into account the substance-specific TFA formation rates, a maximum of approx. 7 t/a of TFA are produced (Behringer et al. 2021). Because of the long half-lives of the three inhalation anaesthetics in the atmosphere (multiple years) and the fact that they are transported over great distances and are rather well-mixed in

the atmosphere, it is not possible to quantify the release of TFA from the atmospheric degradation of inhalation anaesthetics in Germany.

Assuming an annual municipal wastewater volume in Germany of 9.6 billion m^3 (UBA 2021a) and a TFA input of 22 t/a from the degradation of wastewater-borne human pharmaceuticals, the mean TFA concentration in wastewater is approx. 2.3 µg/L. By combining the total theoretical release of TFA through the degradation of human pharmaceuticals, with data on the annual wastewater volume of individual wastewater treatment plants in Germany and assuming that there are no spatial differences in the consumption of pharmaceuticals in Germany, the annual TFA release per wastewater treatment plant was estimated. Subsequently, the inputs were aggregated at the county-level in order to ensure comparability with other TFA input paths (Figure 12). The inputs were attributed to the county in which the wastewater treatment plant is located. As mentioned above, due to the persistence of many of pharmaceuticals, a complete transformation to TFA during wastewater treatment or during river transport is unlikely. Figure 12 therefore is representing a worst-case scenario.

Figure 12: Maximum theoretical TFA input from wastewater-borne human pharmaceuticals per county.



Source: own illustration, TZW.

There are seven veterinary pharmaceuticals with at least one C-CF_3-substructure which are currently approved in Germany. These are the analgesic flunixin and its meglumine salt, the inhalation anaesthetic isoflurane and the antiparasitics fipronil, fluralaner, pyriprole and esafoxolaner (UBA 2021b). As only the quantities of antimicrobial agents are publicly available in Germany, the theoretical input of TFA from the degradation of other veterinary medicinal

products cannot be quantified at present. Hence, no spatial analysis of the TFA input and contamination can be carried out for veterinary pharmaceuticals at the moment.

5.3 Agriculture

5.3.1 Data basis

To analyse the influence of agriculture on TFA loads in aquatic ecosystems in Germany, data from the 2016 agricultural structural survey of the statistical offices of the Federation and the Federal States were used (Statistical Offices of the Federation and the Federal States 2021b). These were available in tabular form and were linked to the geometries of the urban districts and counties in order to be able to display and use them in the GIS (see for example Figure 13). In addition, ATKIS data on agriculture was used. The ATKIS data distinguishes between arable land, orchards, hops, asparagus, vineyards and fruit plantations.

5.3.2 Methods and results

5.3.2.1 Liquid manure

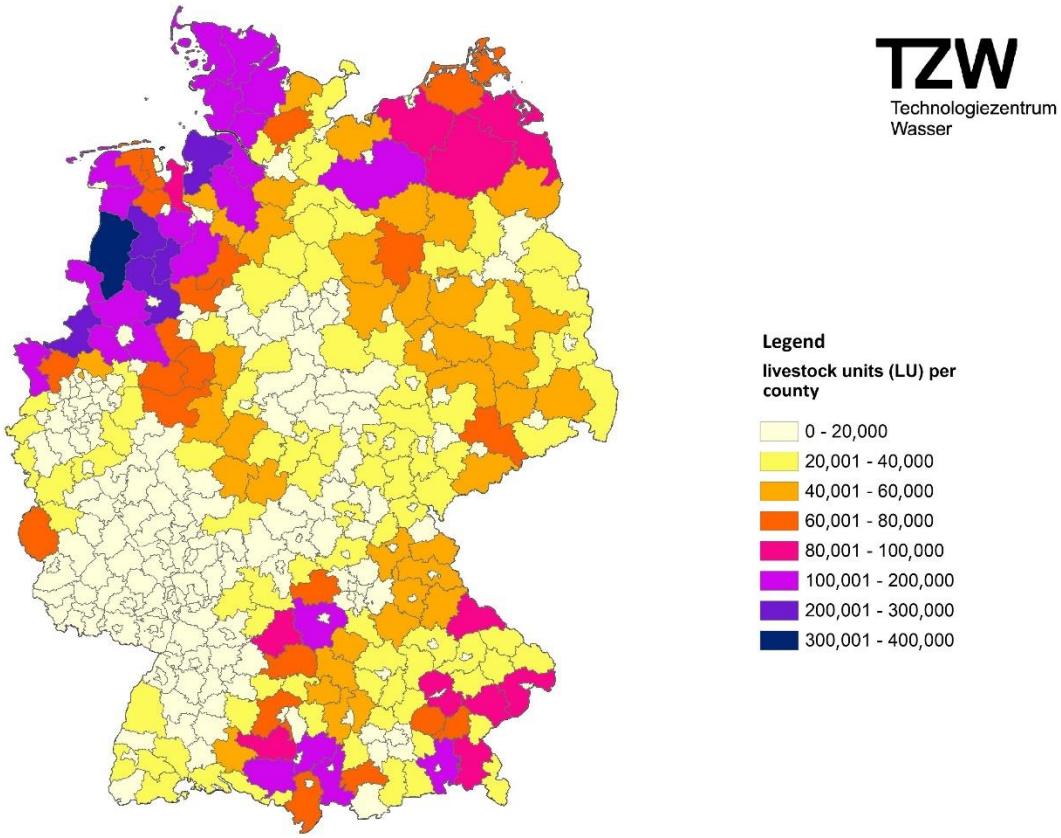
Due to the high bioavailability of TFA, its significant residence time in biota, its phytoaccumulation (Freeling et al. 2022a) as well as its occurrence in precipitation (Freeling et al. 2020a) it is not surprising that TFA has already been detected in terrestrial plants. For example, for wheat roots it was shown that TFA can be readily taken up and translocated into straw, leaves and grains due to its high-water solubility and small molecular size. The uptake of TFA by wheat is mainly an energy-dependent, active process. It is believed that TFA can also be taken up by the plant through passive transport processes (especially anion channels), i.e. without mediating carrier proteins (Zhang et al. 2019).

Of more than 1,600 food samples of plant origin, TFA was detected in almost every sample (EURL-SRM 2017). In herbs and leafy vegetables, a mean concentration of 50 µg/kg to 100 µg/kg was determined. Sacher et al. (2019) showed through comparative analyses of plants from background and highly contaminated sites, where per- and polyfluorinated alkyl substances (PFAS) containing paper fibres had been mixed with compost and applied to agricultural land, that TFA can be detected in all plant samples regardless of their origin. In contrast, other short-chain perfluorinated compounds were only found in plant samples that came from contaminated sites. The highest TFA levels were detected in leafy matrices with a maximum concentration of approx. 500 µg/kg dry weight detected in maize leaves from an uncontaminated site.

Preliminary investigations by the TZW indicate that TFA is present in two- to three-digit µg/L concentrations in liquid manure and digestate, although this information so far only refers to the analysis of three environmental samples (pig slurry, cattle slurry, biogas digestate). The TFA present in the excreta of farm animals is probably primarily due to the ingestion of plant-based animal feedstuff because of the high TFA levels detected in plant matrices. Assuming a mean TFA concentration in liquid manure of 100 µg/L and an annually applied liquid manure volume of approx. 190 million m^3 (Federal Statistical Office 2020) a resulting TFA input of approx. 19 t/a can be assumed in Germany. Since information on the annual volume of liquid manure applied (sum of pig slurry, cattle slurry, manure from other origins and biogas digestate) was only available at the federal state level (Federal Statistical Office 2020) the livestock population in livestock units (LU) was used as a quantitative measure for the application of manure in Germany, as this information was available for all German counties in Germany. The raw data for this came from the agricultural structure survey of the year 2016 (Statistical Offices of the Federation and the Federal States 2021b). Especially in the federal states of Schleswig-Holstein,

Lower Saxony, Mecklenburg-Western Pomerania, North Rhine-Westphalia, Baden-Württemberg and Bavaria there are many counties which have very high livestock numbers (> 80,000 LU) (Figure 13).

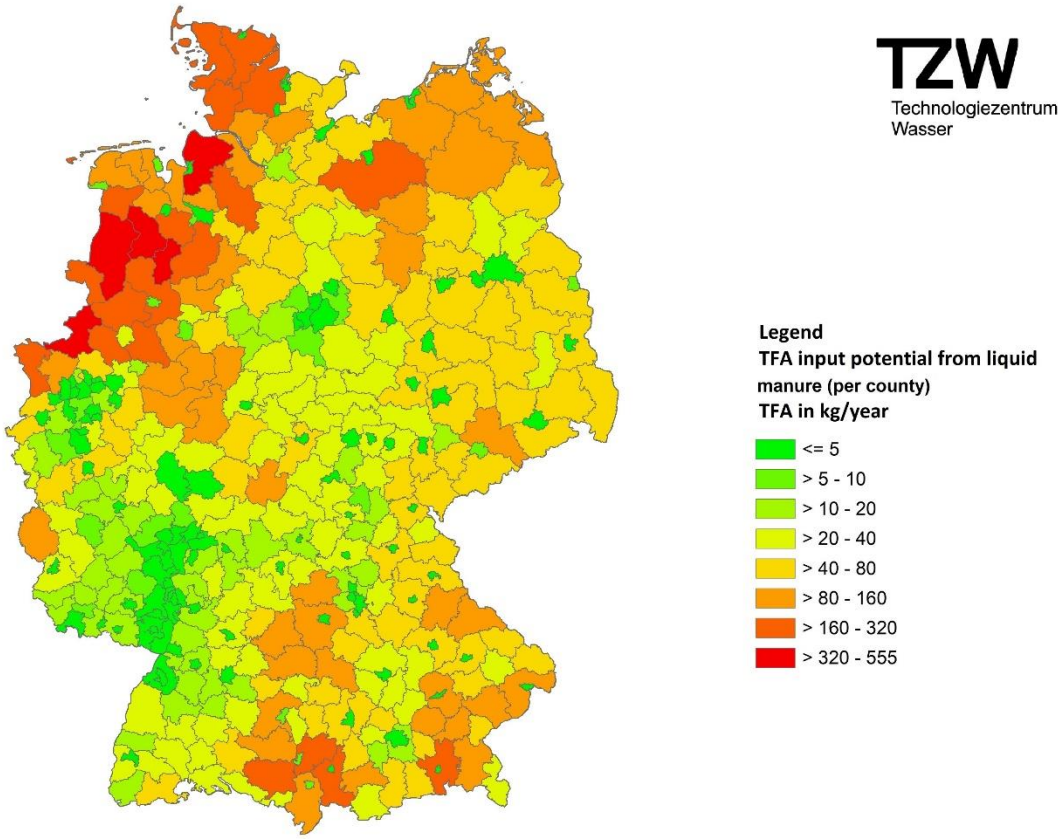
Figure 13: Livestock population in livestock units (LU) for German counties.



Source: own presentation, TZW; based on data from the 2016 agricultural structure survey/agricultural census (Statistical Offices of the Federation and the Federal States 2021b).

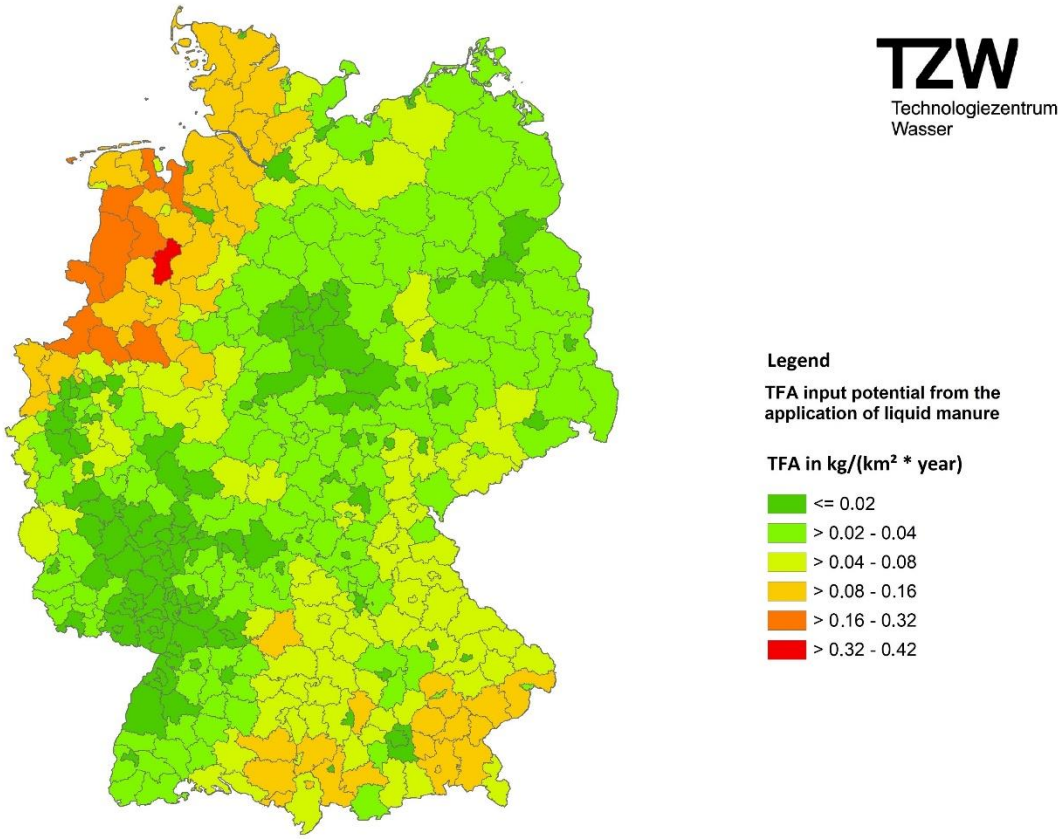
The high linear correlation ($r=0.99$; $p<0.001$) between the annually applied volume of liquid manure and the livestock population in LU at the federal state level indicates that the livestock population can be used as a proxy for the applied volume of liquid manure. From the volume of liquid manure, which was estimated on the basis of the livestock density and assuming a mean TFA concentration in liquid manure of 100 µg/L, the resulting mass of TFA was determined for each administrative. The absolute masses are shown in Figure 14. In Figure 15 the masses have been standardised by area to take account of the different sizes of the counties. In regions with high livestock numbers, an increased input of TFA into the environment can be expected as a result of the application of liquid manure. However, it should be mentioned that the applied amount of liquid manure is only a rough indicator for the amount of TFA discharged into water bodies from this source. It is likely that TFA (similar to the plant nutrients present in liquid manure) is kept to a certain extent in a cycle (soil → soil water → plant → animal feed → farm fertiliser), which means that only a part of the mass of TFA introduced by the application of liquid manure is emitted into the aquatic system.

Figure 14: Absolute TFA input potential from the application of liquid manure for the counties in Germany.



Source: own illustration, TZW.

Figure 15: Relative (i.e. area-normalized) TFA input potential from the application of liquid manure for the counties in Germany.



Source: own illustration, TZW.

5.3.2.2 Plant Protection Products

24 active substances currently approved in Germany that are used in PPP contain at least one carbon-bonded trifluoromethyl moiety. As about 50 % of Germany's land area is used for agriculture, it can be assumed that PPP are used extensively. Therefore, the application of PPP represents a significant potential source of TFA in the environment. Based on the average annual domestic sales of all C-CF_3-containing acitve substances in PPP in Germany for the years 2016-2019 (BVL 2021) and assuming a molar TFA yield of 100 % (i.e. worst-case scenario), this results in a theoretical formation potential for PPP of approx. 521 t TFA per year in Germany. It should be noted that at this time (November 2022) the active substances flupyrsulfuron-methyl, flurtamine, haloxyfop-P and picoxystrobin are no longer approved in the EU.

In order to carry out a spatial analysis of the inputs of TFA from the degradation of PPP in Germany for a specific time period, spatially differentiated information on PPP application is required. As this information was not available, data (spatial resolution: counties) on the cultivated area of various field crops from the 2016 agricultural structure survey in Germany (Statistical Offices of the Federation and the Federal States 2021a) were merged with estimated values from the Julius Kühn Institute (JKI) on the average amount of active ingredient applied per PPP and field crop (JKI 2021). Only PPP with at least one C-CF_3-substructure in their molecule were taken into account. The figures on the quantities of active substances applied annually are the result of an extrapolation for Germany based on the PAPA surveys (PAPA: Panel Pesticides Applications) and quantities only exist for the crops winter wheat, winter barley,

winter oilseed rape, potatoes, maize, sugar beet, hops, apple and wine. Table 3 shows all active substances that were used for the evaluation, as well as the field crops for which the substances are used.

Table 3: Considered active substances that are potential precursors for TFA and for which PPP containing the active substances were authorized in Germany in at least one year of the observation period (2016-2019).

The "x" indicates the crops in which an active ingredient is used.

Active substances of PPP	Winter wheat	Winter oilseed rape	Winter barley	Sugar-beet	Apple	Hops	Potato	Maize	Wine
Beflubutamid	x		x						
Cyflufenamide	x		x		x				x
Diflufenican	x		x		x				
Flazasulfuron									x
Flonicamide	x	x		x	x	x	x		
Fluazifop-P		x		x		x	x		
Fluazinam							x		
Flufenacet	x		x				x	x	
Fluopicolide						x	x		x
Fluopyram	x	x	x		x				x
Flupyrsulfuron-methyl	x								
Flurtamone	x		x						
gamma-cyhalothrin	x	x	x						
Haloxyfop-P (Haloxyfop-R)		x		x					
Isoxaflutol								x	
lambda-cyhalothrin	x	x	x	x	x	x	x	x	x
Metaflumizone							x		
Oxathiapiproline							x		x
Penoxsulam	x		x						
Picolinafen	x		x						
Picoxystrobin	x	x	x						
Prosulfuron								x	
Pyroxsulam	x		x						

Active substances of PPP	Winter wheat	Winter oilseed rape	Winter barley	Sugar-beet	Apple	Hops	Potato	Maize	Wine
tau-fluvalinate	x	x							
Tembotrione								x	
Trifloxystrobin				x	x	x			x
Triflusulfuron				x					
Tritosulfuron	x		x					x	

Table 4 shows an example of the quantities of acitve substances of insecticides estimated by the JKI used on winter oilseed rape in Germany in 2019, as well as the potentially formed masses of TFA.

Table 4: Estimated quantities of acitve substances of insecticides applied in 2019 in Germany on the crop winter oilseed rape as well as the potentially formed masses of TFA. Active substances in bold are potential precursors of TFA. Data basis: JKI (2021).

PPP active ingredient	Amount of active ingredient in kg (estimated value)	Theoretically formed mass of TFA in kg[1]
Thiacloprid	42773	-
Etofenprox	20486	-
tau-fluvalinate	12858	2889
lambda-cyhalothrin	5949	1495
Cypermethrin	4492	-
Pymetrozine	3698	-
Indoxacarb	2757	-[2]
zeta-cypermethrin	2566	-
beta-Cyfluthrin	1225	-
Acetamiprid	1212	-
Deltamethrin	716	-
gamma-cyhalothrin	385	107
Esfenvalerat	161	-

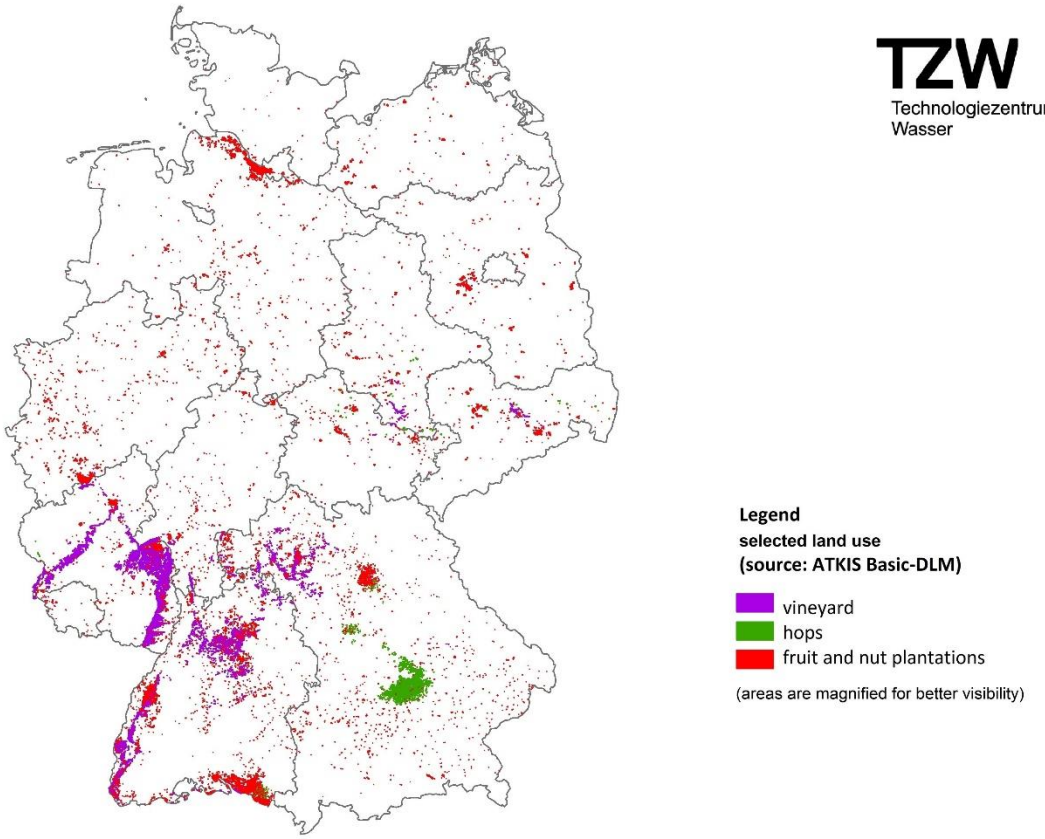
[1]Under the assumption of a molar TFA yield of 100 %.

[2] data were updated after the publication of the German report (last update: July 2023)

Assuming a molar TFA yield of 100 % and assuming that there are no regional differences in PPP application for various crops in Germany, the theoretical mass of TFA released from PPP degradation was calculated for each German county. As no data on the respective cultivated areas at county level was available for the crops hops, apple and wine in the 2016 agricultural structure survey, the ATKIS Basic-DLM data catalogue was used for these crops (see Figure 16). The ATKIS data were aggregated at the county level in order to obtain the same spatial

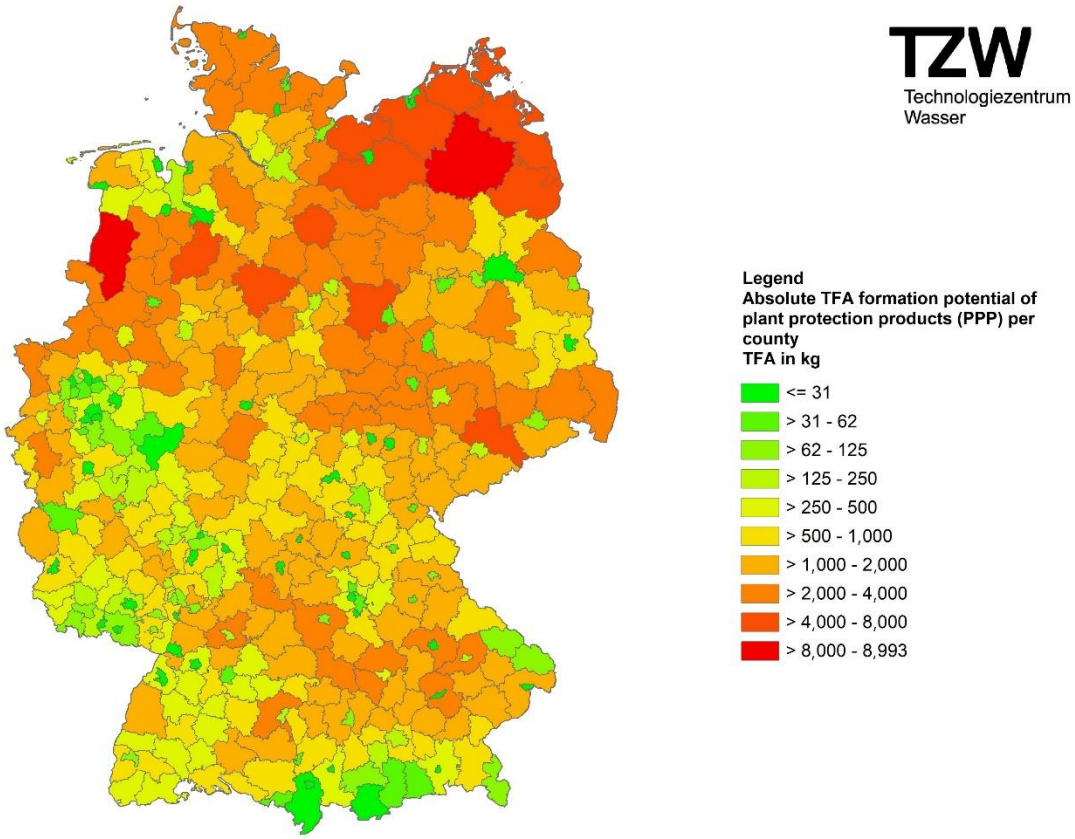
resolution for all agricultural crops. Table 5 shows the theoretical formation potential of potentially TFA-forming PPP for selected crops and years. The results show that winter wheat and winter barley contribute more than 60 % to the theoretical TFA-forming potential of all considered crops, while the crops vine, sugar beet, apple and hops play a minor role. It should be mentioned that the cultivation areas of the latter crops are, however, spatially more concentrated in Germany (Figure 16).

Figure 16: Cultivated areas of the crops vines, hops and fruit and nut plantations from the ATKIS-Basic-DLM within Germany



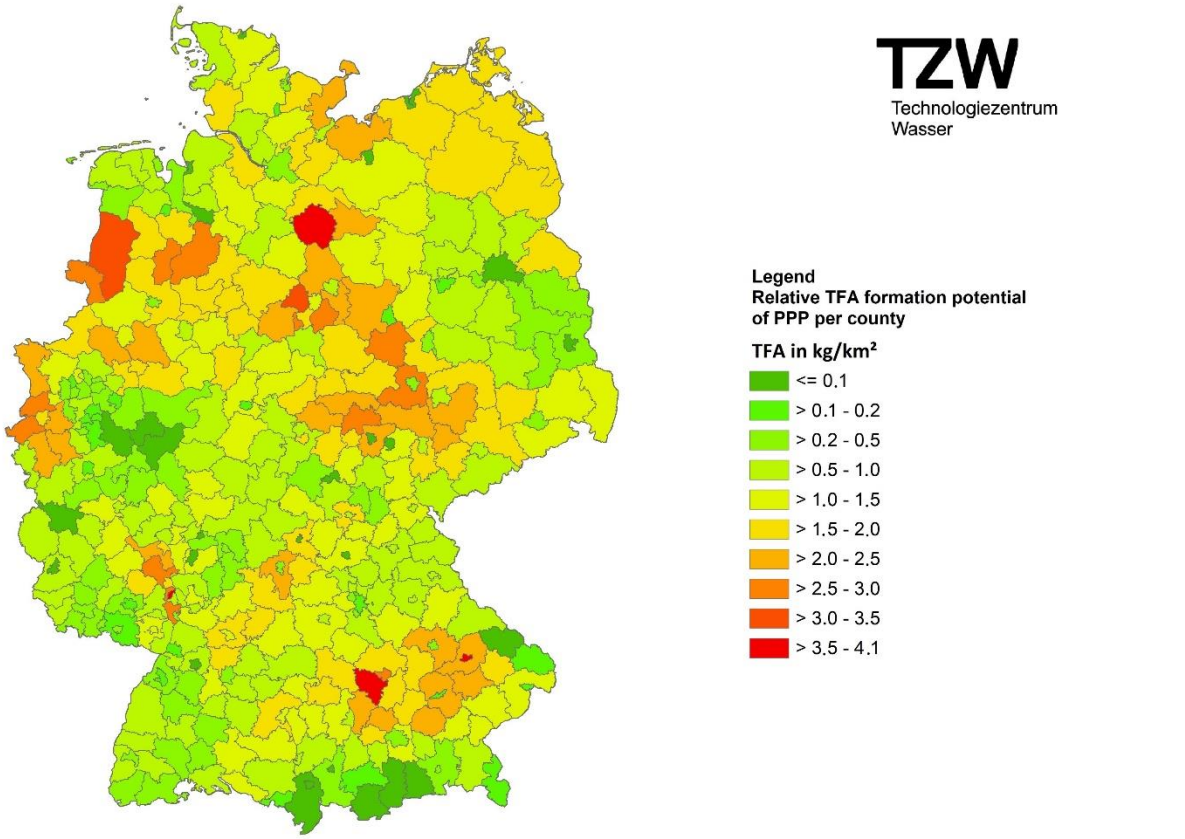
Source: own illustration, TZW; data basis: GeoBasis-DE / BKG (2021).

Figure 17: Absolute TFA formation potentials of applied plant protection products (PPP) of counties in Germany.



Source: own illustration, TZW; data basis: JKI (2021), Statistical Offices of the Federation and the Federal States (2021a).

Figure 18: Relative (i.e. area-normalized) TFA formation potentials of applied plant protection products (PPP) of counties in Germany.



Source: own illustration, TZW; data basis: JKI (2021), Statistical Offices of the Federation and the Federal States (2021a).

The theoretical mass of TFA (434 t TFA; mean value of the years 2016-2019) derived using the data from the JKI (JKI 2021) accounts for approx. 83 % of the TFA mass derived using data from the Federal Office of Consumer Protection and Food Safety (BVL) as an alternative source (521 t, mean value of the years 2016-2019) (BVL 2021). Differences in the theoretically formed TFA masses can be explained in particular by the fact that the JKI only provides estimates on the applied PPP amount for a selection of crops, whereas the BVL data represent the sale volumes of all PPP in Germany.

Table 5: Theoretical TFA mass of potential TFA-forming PPP for selected crops and years (in tonnes). Data basis: JKI (2021).

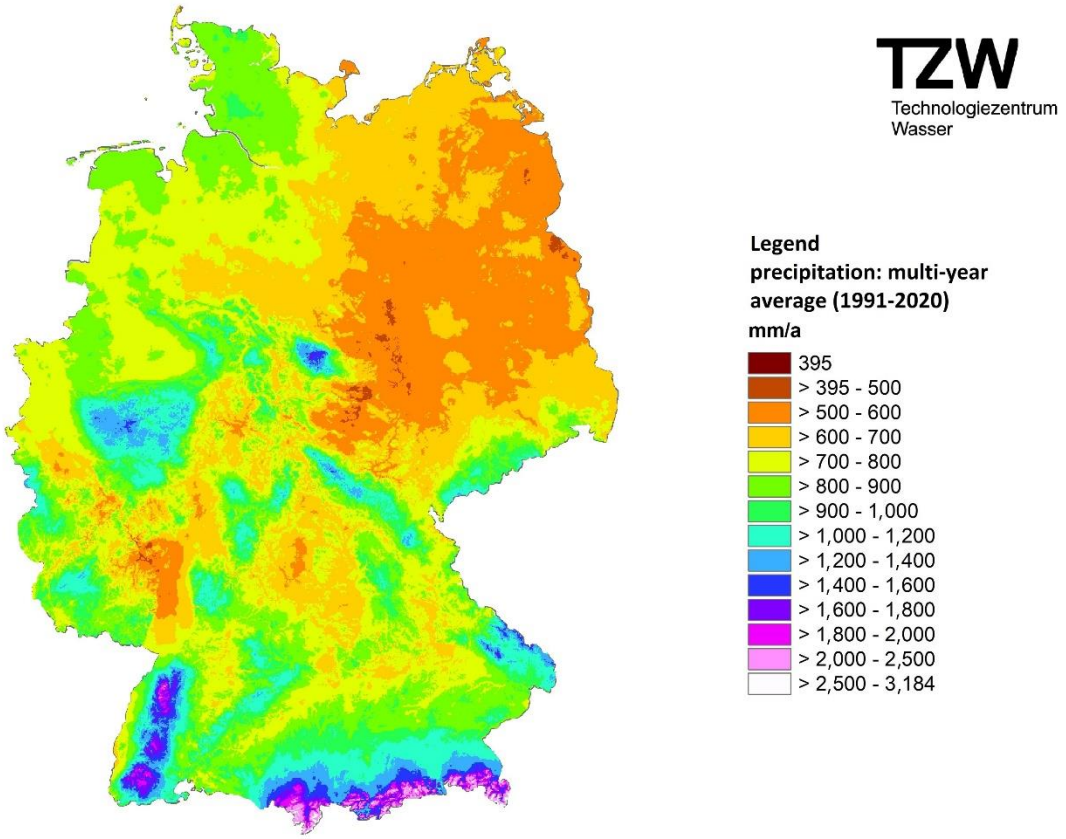
Culture	2016	2017	2018	2019	Mean value 2016-2019 (percentage share)
Winter wheat	148	154	164	191	164 (38%)
Winter barley	101	107	117	111	109 (25%)
Maize	44	60	77	71	63 (15%)
Potato	74	71	52	54	63 (15%)
Winter oilseed rape	22	28	24	14	22 (5%)
Wine	5.8	4.8	4.4	4.2	4.8 (1.1 %)
Sugar beet	2.2	3.7	4.8	4.5	3.8 (1.0%)
Apple	2.9	3.3	3.3	3.2	3.2 (0.7%)
Hops	0.8	0.9	1.3	0.7	0.9 (0.2 %)
Total	401	433	449	454	434 (100 %)

5.4 Precipitation

5.4.1 Data basis

The client provided precipitation data from the German Meteorological Service (Deutscher Wetterdienst, DWD) as .txt files. These data were imported into the GIS. Depending on the further evaluations, annual mean values (Figure 19) or seasonally differentiated values can be displayed.

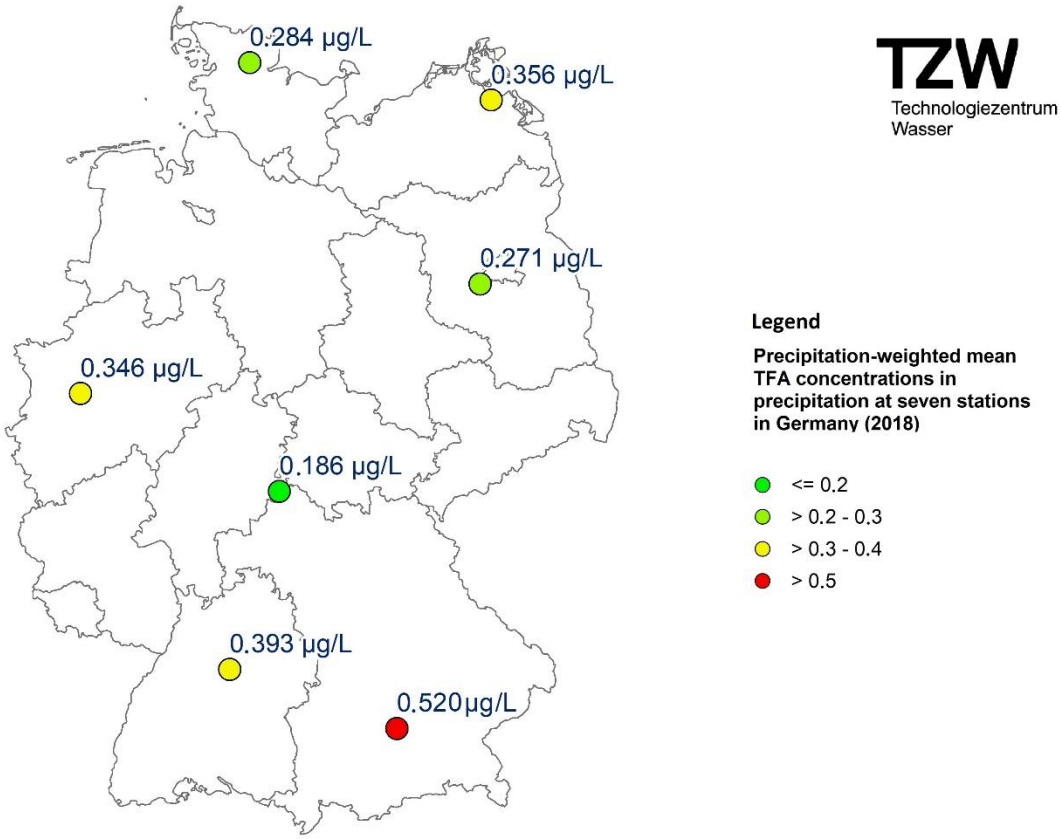
Figure 19: Multi-year precipitation averages (reference period 1991-2020) in Germany.



Source: own illustration, TZW; data basis: DWD (2020).

The concentrations of TFA in precipitation in Germany from the UBA project "Persistent Degradation Products of Halogenated Refrigerants and Blowing Agents in the Environment" (Behringer et al. 2021) were used. Figure 20 shows a selection of the dataset. In the report by Behringer et al. (2021), precipitation samples were collected at eight sampling sites in Germany and analysed for TFA. At one of the eight sampling sites (Brocken) an alternative sampling method was used. Consequently, at Brocken, the total atmospheric deposition (sum of dry and wet deposition) of TFA was determined instead of the wet deposition. Since only the wet deposition of TFA was considered in this project, the data points from the Brocken site were not used.

Figure 20: Precipitation-weighted mean TFA concentrations in precipitation at seven stations in Germany (2018).



Source: own illustration, TZW.

5.4.2 Precipitation distribution in Germany

Figure 19 shows the spatial distribution of precipitation in Germany for the time period 1991-2020. The mean annual precipitation totals range from approx. 400 mm to approx. 3,200 mm. The precipitation distribution in Germany is primarily characterised by an altitudinal gradient and an east-west gradient (decreasing hygric continentality). The lowest precipitation totals occur in lower-basin and lee locations in the eastern parts of Germany. The highest annual precipitation totals are recorded in the high altitudes of the low mountain ranges (e.g., Black Forest, Harz, Rhenish Slate Mountains) and especially in the Alps. The average annual precipitation total in Germany for the reference period 1991-2020 is approx. 790 mm.

5.4.3 TFA levels in precipitation in Germany

The input of TFA from the oxidative degradation of gaseous precursors in the atmosphere is considered to be one of the most important diffuse sources of TFA to the non-marine environment. Formation of TFA from the degradation of volatile precursors leads to diffuse and ubiquitous contamination of the environment., even in remote regions with very low anthropogenic activity (e.g. in the Arctic, see Pickard et al. (2020))

Klein (1997) reported precipitation-weighted TFA levels in Bayreuth of 0.079 µg/L (observation period: April 1995 to March 1996) and 0.106 µg/L (October 1995 to September 1996). A similar precipitation-weighted average TFA concentration of 0.116 µg/L was determined for

Switzerland for the period from May 1996 and July 1997. In the current study by Freeling et al. (2020), the precipitation-weighted average TFA concentration for Germany was 0.335 µg/L. This average concentration is three to four times higher than in the aforementioned monitoring studies from 1995/96, indicating a significant increase in TFA precipitation concentrations in Germany within the last decades. The analysis of archived tree leaf samples (observation period: 1989-2020) from the federal environmental sample bank also indicates a significant increase in the atmospheric deposition of TFA in Germany within the last three decades (Freeling et al. 2022b).

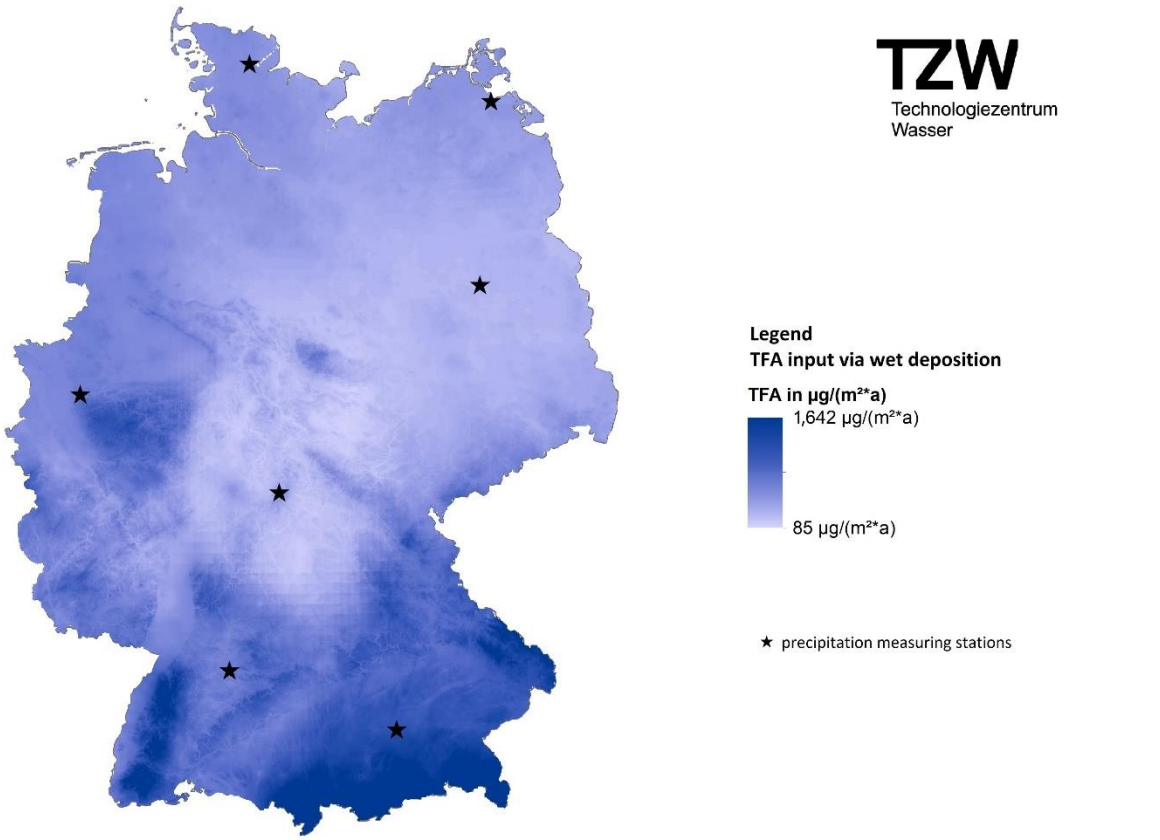
Increasing emissions of gaseous precursors of TFA are probably the main cause for the increasing atmospheric deposition of TFA. It can be assumed that the input of TFA via precipitation will increase globally. Halogenated refrigerants and blowing agents play a major role here. As described in the work of Behringer et al. (2021), a strong increase in the use and emission of these substances, in particular of refrigerants of the so-called 4th generation (e.g. u-HFKW-1234yf and u-HFKW-1234ze(E)), is expected for Europe (EU-28). According to model calculations, the total annual TFA input from the decomposition of halogenated refrigerants and blowing agents will increase by more than 300 % by the year 2050 compared to the year 2018 (Behringer et al. 2021). The estimates made here for the introduction of TFA via the precipitation pathway are based on the TFA levels determined during a one-year monitoring campaign conducted at seven sampling sites in Germany (observation period: February 2018 to January 2019) (Freeling et al. 2020a). In the study, each precipitation event during the observation period was analysed for TFA and the corresponding precipitation amounts of the sampled precipitation events were known. Hence, precise information on the wet deposition of TFA could be made for the specific sampling sites. However, no precise statements can be made regarding the spatial distribution of the atmospheric input of TFA within Germany.

The study by Freeling et al. (2020a) showed that that, at least, for the situation in Germany, the TFA concentration in precipitation depends more on the sampling date than on the sampling location. It can therefore be assumed that precipitation does not cause pronounced hotspots of elevated TFA concentrations in water bodies. It can be assumed that wet deposition leads to a background TFA contamination of approx. 0.3-0.4 µg/L TFA in surface waters in Germany, as this corresponds to the current average annual precipitation-weighted TFA concentration in precipitation in Germany (Freeling et al. 2020a). In the study by Behringer et al. (2021) TFA precipitation concentrations in Germany from the degradation of u-HFKW-1234yf were estimated using an atmospheric transport and chemistry simulation model, which was based on the model used by Henne et al. (2012). The modelling also revealed no substantial differences in the spatial distribution of TFA concentrations in precipitation in Germany. However, the simulated TFA deposition rates from u-HFKW-1234yf showed a north-south gradient, with higher inputs in Baden-Württemberg and Bavaria, caused by the larger precipitation totals in Southern Germany (Behringer et al. 2021). The results obtained of Freeling et al. (2020a) also indicate that at sites with low annual precipitation totals, less TFA tends to be introduced into the terrestrial environment via wet deposition. The authors assumed that at sites characterized by low amounts of annual rainfall there is a lower potential for TFA scavenging and local TFA deposition.

5.4.4 TFA wet deposition fluxes in Germany

To estimate the spatial TFA input via precipitation in Germany, the average precipitation-weighted TFA concentrations in precipitation of the seven measuring stations (point information) were first interpolated using an inverse distance weighting approach. In this interpolation procedure, the measured value is multiplied by a factor that is proportional to the inverse of the distance between the estimation point and the known points (i.e., the sampling sites). Subsequently, to obtain an estimate of the average annual wet deposition flux of TFA for each raster cell, the interpolated concentration values were multiplied by the long-term average annual precipitation total of the corresponding grid cell.

Figure 21: Modelled annual input of TFA via wet deposition in Germany and location of precipitation sampling sites in the study of Freeling et al. (2020a).



Source: own illustration, TZW.

Assuming an average precipitation-weighted TFA concentration of 0.335 µg/L and an average precipitation total of 790 mm, this results in an annual average wet TFA deposition of 264 µg/m^2 or a total of approx. 94 t for Germany. So far, there are no measured data on the mass of TFA that is deposited in Germany via dry deposition. Model calculations on the formation of TFA in Germany from the degradation of u-HFKW-1234yf showed a contribution of dry deposition to the total deposition of approx. 12 % (Behringer et al. 2021).

The study by Freeling et al. (2020) revealed a pronounced seasonality of the TFA concentration and wet deposition flux of collected samples with maximum values in the summer and minimum values in the winter. The difference between the lowest TFA median concentration (January 2019: 0.042 µg/L) and the highest TFA median concentration (July 2019: 0.789 µg/L) was 0.747 µg/L (Behringer et al. 2021). The observed diurnal and seasonal changes of TFA in precipitation and air are likely caused by the varying atmospheric concentrations of photochemically

generated oxidants, mainly hydroxyl radicals, which are responsible for the transformation of volatile TFA precursors in the troposphere. Despite the clear seasonality of TFA concentrations and loads in precipitation, it is unlikely that this source induces a seasonal pattern in the TFA concentrations in surface waters. This can be explained by the fact that TFA is introduced into the aquatic environment by a variety of other anthropogenic sources, which, according to current knowledge do not show seasonal changes in concentrations. It should also be mentioned that the total runoff of a surface water is not only formed by the direct runoff components surface runoff and interflow but also by the baseflow. The flow velocities of baseflow are generally significantly lower than those of the direct runoff components. The long-term base flow roughly corresponds to the groundwater recharge. Moreover, the total runoff depends not only on the precipitation but also on numerous physio-geographical and hydroclimatic factors, including topography, geomorphology, pedology, hydrogeology, land use, and evapotranspiration. Therefore, temporal changes in TFA concentrations in precipitation do not directly result in changes in TFA concentrations in water bodies. This is particularly true for groundwater bodies with long residence times and thus large mean groundwater ages. A seasonal differentiation of TFA inputs to groundwater and surface waters in Germany via precipitation is therefore not provided here.

5.5 Joint Consideration of Sources and Input Pathways

Table 6 gives an overview of the magnitudes of TFA release from the various sources and input pathways, which were considered in this current study. No figures are available for emissions from industrial plants (see Section 5.1.1). The examples explained for the Neckar and Alz Rivers (see Section 5.1.2) show, however, that industrial plants can have a formative influence on the TFA content of the surrounding surface and ground waters. With approx. 434 t/a of potential TFA emissions, the PPP used in agriculture probably contribute a significant part of all TFA inputs. It can be assumed that municipal wastewater treatment plants and liquid manure contribute to a quantitatively less share.

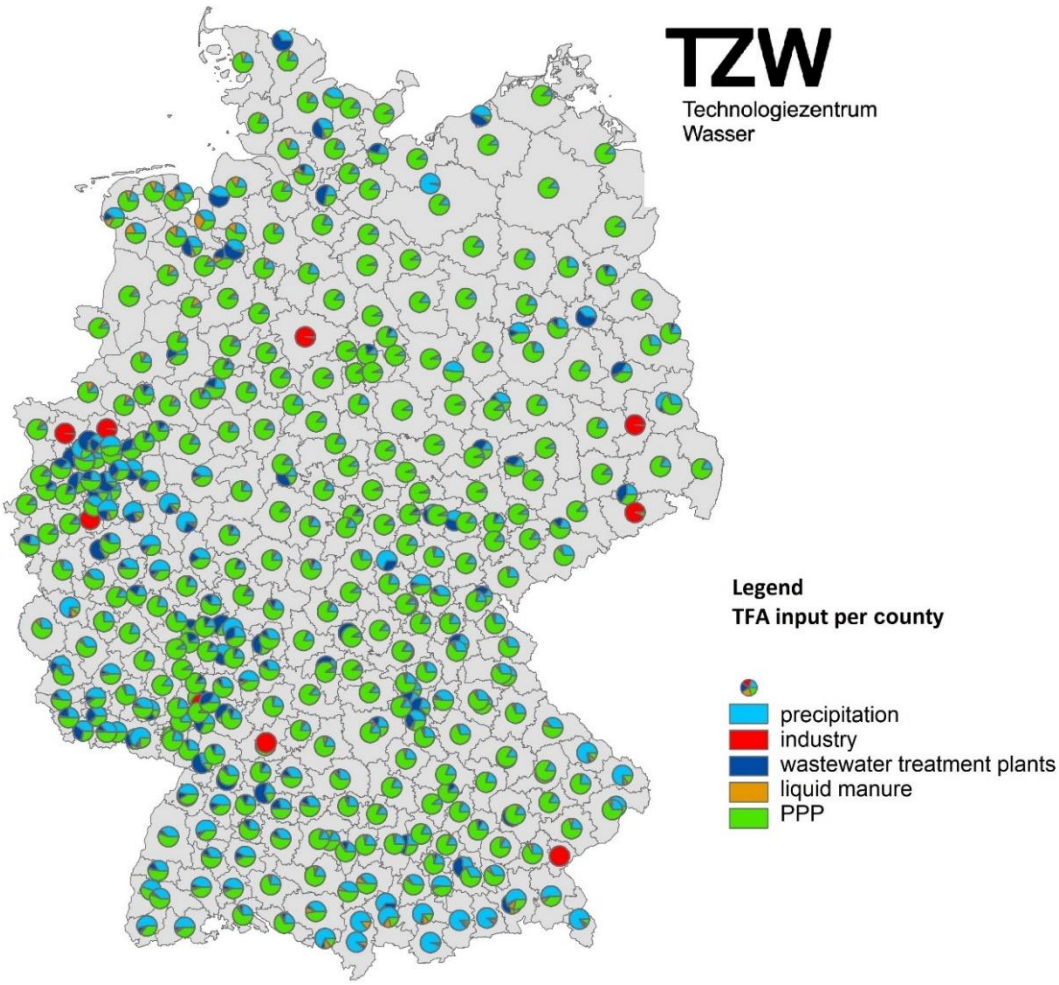
Table 6: Average theoretical annual TFA release from different sources and input pathways.

	Theoretical TFA release in t/a	Comment / Data source
Industry	Unknown	No values available (s. 5.1.1)
Municipal wastewater treatment plants	22	Theoretical quantity from human pharmaceuticals (s. 5.2.1)
Agriculture: PPP	434	JKI data (s. 5.3.1)
Agriculture: liquid manure	19	Based on the analysis of two samples of liquid manure (s. 5.3.1)
Precipitation	96	Mean values of the precipitation measurements (s. 5.4.1)

In order to be able to make a spatially differentiated statement on the significance of the various input pathways considered, the data shown in Table 6 were allocated among the counties. In order to determine kg/a-values, the data compiled in the chapters 5.1 to 5.4 were used. The industrial emissions were assigned to the categories listed in Table 1 which, according to the E-PRTR Regulation, release fluorides into water and are active in chemical synthesis. Figure 22 shows the shares of the assumed TFA emissions by the considered input pathways for each

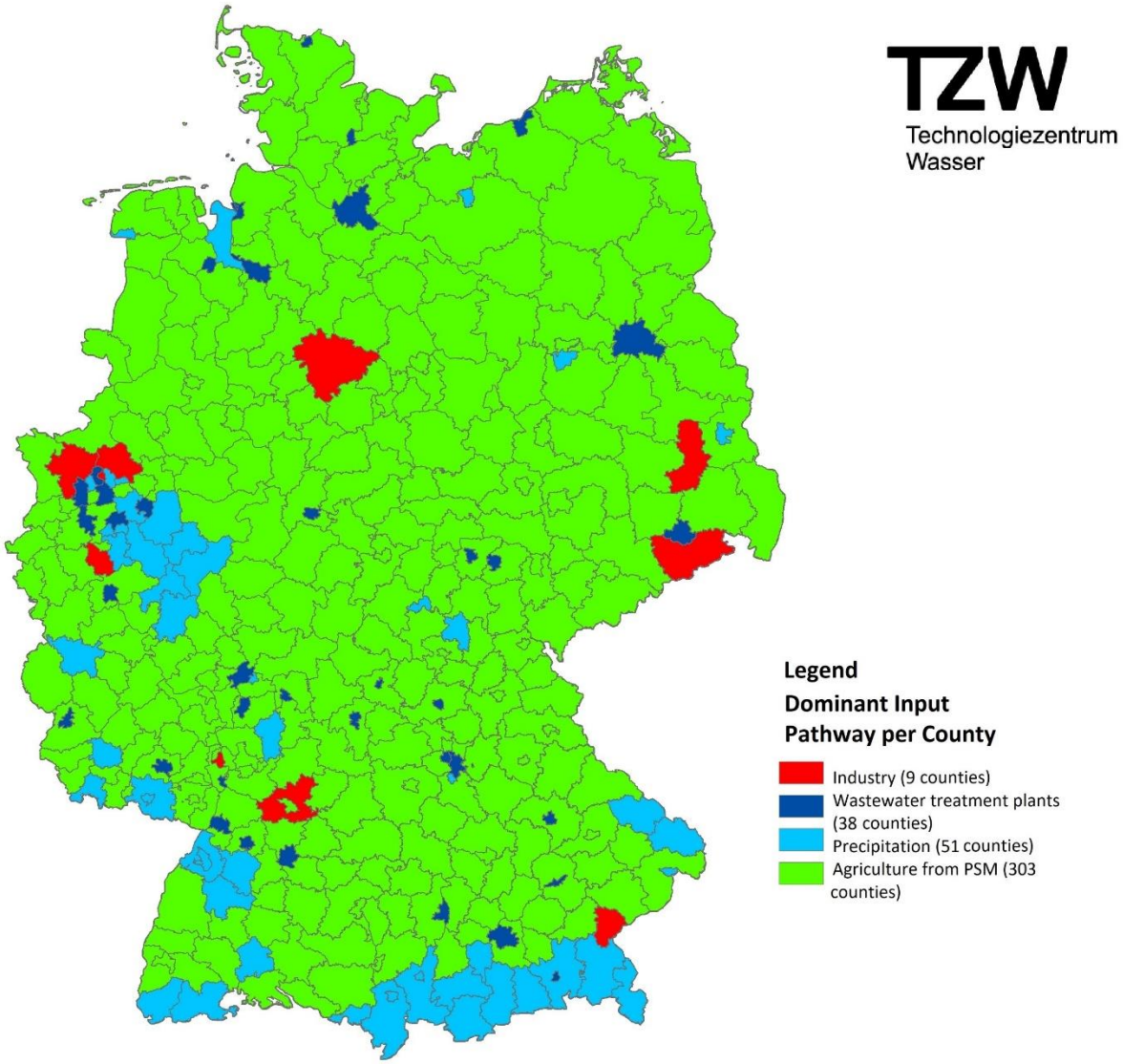
county. Due to the strong weighting of industrial emissions, these emissions dominate in the affected counties. In the other counties, PPP often appear to be the most significant TFA source. In regions with particularly high precipitation, where there is also a lower proportion of arable land, inputs via precipitation play a more important role (e.g., in the Allgäu region). In northwestern Germany, livestock density is comparatively high, so that TFA inputs from liquid manure are also relatively high there compared to most other regions. Inputs from wastewater treatment plants are dominant, especially in independent cities. Figure 23 shows the dominant pathway for each county. Each county is thus coloured according to the pathway that accounts for the largest share of TFA inputs, based on the calculations and considerations presented in Chapters 5.1 to 5.3. It should be mentioned that in the selected consideration of the input pathways at the county level, mass flows of TFA between the counties as a result of TFA transport with groundwater and surface water are not depicted, which can lead to certain spatial distortions. For example, inputs from an industrial plant are only assigned to the county in which the industrial plant is located, even though the TFA inputs naturally influence the TFA loads in downstream counties as well.

Figure 22: Potential TFA inputs from different sources/input pathways per county. Inputs were only considered in the county where they first enter a water body. TFA transport between counties via groundwater or surface water flow was not considered in this evaluation.



Source: own illustration, TZW.

Figure 23: Dominant TFA input pathway per county (inputs were only considered in the county where they first enter a water body. TFA transport from other counties via ground or surface waters was not included in this evaluation).



Source: own illustration, TZW.

6 Correlations between Input Paths and Monitoring Results

The theoretical considerations of possible TFA sources and input pathways were compared with measured TFA concentrations to reveal correlations between specific input pathways and elevated TFA concentrations.

6.1 Counties with the Same Dominant Input Pathway

The data described in chapter 5.5 were used to group the counties according to the dominant input pathway. For these units, the mean value of the (averaged) medians per county was determined for surface water and for groundwater, respectively (see Table 7). The mean value of these values across all counties is 1.65 µg/L. The corresponding value for counties in which relevant industrial plants are located (see Chap. 5.1) is 2.28 µg/L, which is significantly higher than the overall mean value. The measured concentrations in counties with a comparatively high proportion of arable land are significantly higher (1.66 µg/L) than in counties where inputs from wastewater treatment plants and precipitation dominate (1.06 and 0.67 µg/L, respectively).

Overall, TFA concentrations in groundwater are at a lower level than those in surface waters but show the same trends (see Table 7).

From this observation, it can be deduced that industry and PPP represent a significant source of TFA.

Table 7: Mean median auf measured TFA levels in counties with the same dominant input pathway (groundwater and surface water).

Dominant path per county	Mean of median per county (in µg/L) (surface water)	Mean of median per county (in µg/L) (groundwater)
Industry	2.28	1.82
Wastewater treatment plants	1.06	0.90
Precipitation	0.67	0.44
Agriculture (PPP)	1.66	1.12
Total	**1.65**	**1.09**

6.2 Correlation Analysis between TFA Concentrations and Potential TFA Inputs

To analyse the correlation between TFA concentrations in groundwater/surface waters and the calculated potential discharges via the described sources and input pathways, the rank correlation coefficient Spearman's Rho (ρ) was derived. For this purpose, the mean, median and maximum values of the TFA concentrations at the surface water monitoring sites of the individual counties were compared to the calculated theoretical discharges via the various input pathways.

With ρ-values between 0.34 and 0.38 (Table 8), there is a weakly positive, monotonic correlation between potential TFA inputs from PPP and the TFA levels in surface waters (p-value < 0.01). For the other input pathways, no or only very weak correlations could be found with this method.

The same evaluation for groundwater shows only weak correlations (see Table 9).

Table 8: Results of Spearman correlation analysis between TFA inputs and TFA concentrations in surface waters.

Correlation coefficient Spearman's ρ	Median per county	Mean value per county	Maximum value per county
Input via precipitation (kg/km²*a)	-0.03	0.01	-0.06
Input via industry (kg/km²*a)	0.07	0.08	0.07
Input via wastewater treatment plants (kg/km²*a)	-0.11	-0.06	-0.13
Input via liquid manure (kg/km²*a)	0.11	0.16	0.04
Input via PPP (kg/km²*a)	0.37	0.38	0.34

Table 9: Results of the Spearman correlation analysis between TFA inputs and TFA concentrations in groundwater.

Correlation coefficient Spearman's ρ	Median per county	Mean value per county	Maximum value per county
Input via precipitation (kg/km²*a)	-0.21	-0.21	-0.29
Input via industry (kg/km²*a)	0.14	0.14	0.14
Input via wastewater treatment plants (kg/km²*a)	-0.01	-0.01	-0.03
Input via liquid manure (kg/km²*a)	-0.06	-0.06	-0.08
Input via PPP (kg/km²*a)	0.20	0.20	0.23

6.3 PPP Inputs and TFA Concentrations in Surface Waters

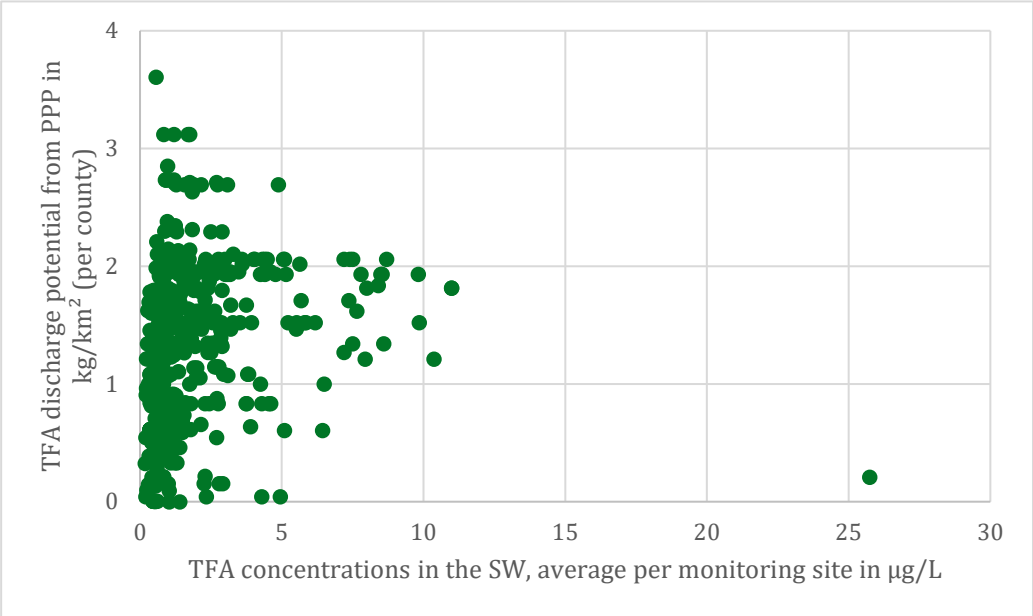
Since the evaluations shown so far suggest that pesticides are a significant source of TFA, this assumption was checked using further observations.

The graphical presentation of the mean values of the TFA concentrations of the individual surface water monitoring sites in relation to the potential TFA inputs from PPPs in the respective county shows that, irrespective of the calculated inputs, there are many monitoring sites with low TFA loads (Figure 24). This can be explained by the fact that the calculated potential TFA inputs are based on assumptions, which tend to overestimate the application of PPP: Since data

on actual PPP application were not available at the time of the analysis (as of November 2021), it was assumed that the maximum permissible amount of PPP was always applied (see Chapter 5.3.2.2), which does not necessarily correspond to a real-world scenario and therefore leads to an overestimation of the PPP application. Some monitoring sites are located in counties for which high potential TFA inputs from PPP application were calculated but had low environmental TFA concentrations. These are monitoring sites in Emsland and in the county of Uelzen, both of which are located in the headwaters of the respective streams. TFA measurements are available at two points in time. It is possible that these monitoring sites are located above the areas from which inputs could occur.

Figure 24 shows that monitoring sites with elevated TFA concentrations (>1 µg/L) occur more frequently in catchments with high potential TFA inputs from PPP application. In contrast, in counties where no or only small amounts of TFA-forming PPP are applied due to land use (<0.5 kg TFA from PPP/km^2), no monitoring sites with average TFA concentrations greater than 5 µg/L were recorded. The exception is one monitoring site with an average TFA concentration above 25 µg/L. It is located in a county with an E-PRTR-registered, potentially TFA-emitting industrial plant, which is presumably responsible for the high measured values.

Figure 24: Illustration of the relationship between TFA input potential from PPP and TFA concentrations in surface waters (OW).



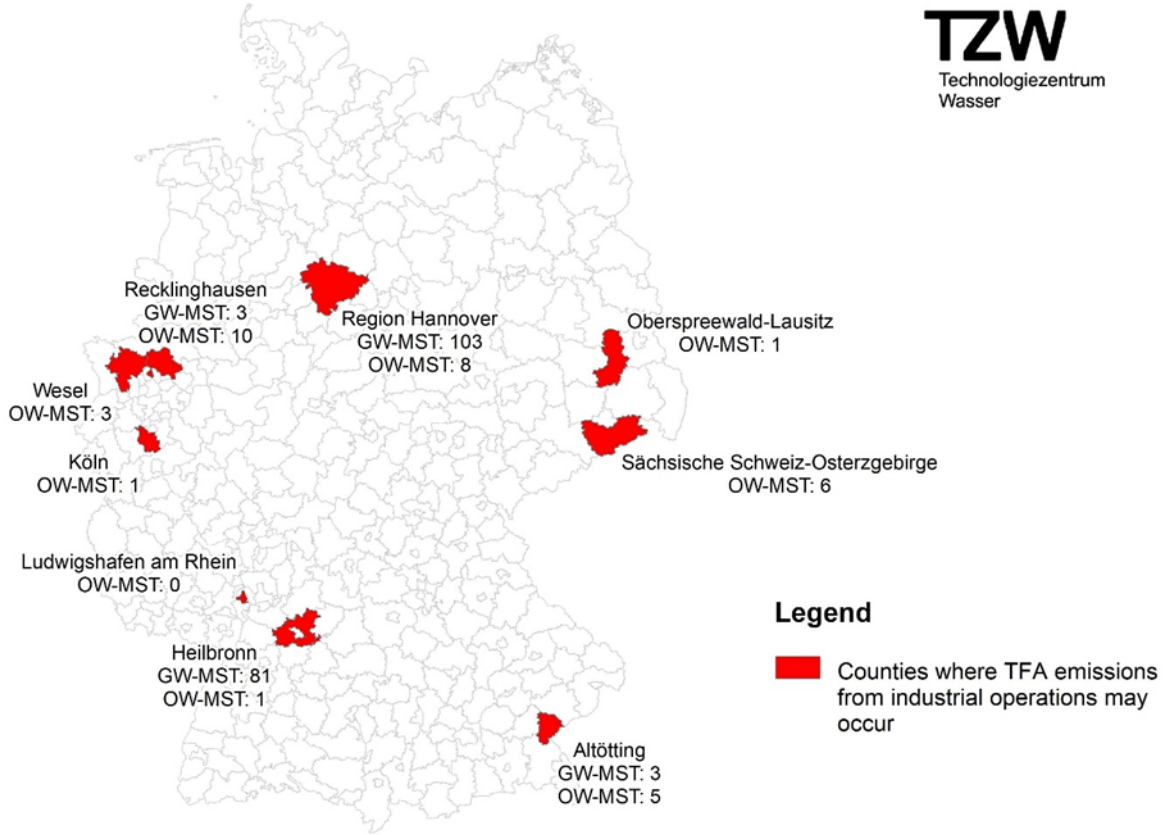
Source: own illustration, TZW.

Overall, these evaluations indicate that certain industrial operations as well as agricultural use of arable land contribute to elevated TFA concentrations.

6.4 TFA Concentrations in Industry-Influenced Counties

In addition to the mean value observations described above, the counties in which the potentially relevant industrial companies are located were analysed in more detail (see Figure 25). The data basis regarding TFA concentrations in water bodies is very heterogeneous: While 42 TFA analyses are available for eight surface water monitoring sites in the Hannover region and 203 TFA analyses are available for 103 groundwater monitoring sites, there are no TFA values for groundwater and only one TFA value for surface water in the county of Oberspreewald-Lausitz.

Figure 25: Counties where TFA emissions from industrial operations may occur, with number of groundwater monitoring sites (GW-MST) and surface water monitoring sites (OW-MST) for which TFA measurements are available.



Source: own illustration, TZW.

The averages, medians and maxima of all surface water monitoring sites within a county were averaged in each case, so that these statistical key figures are available for each of the counties listed in Figure 25 (see Table 10). The same procedure was followed for the groundwater monitoring sites in the respective counties (see Table 11).

The two evaluations show very large differences between the TFA concentrations in the different counties. Since, as described in chapter 5.1 only little information is available on the industrial plants, it is possible that plants are included in the list that work with fluorine-containing substances but do not emit TFA and TFA precursors. If this is indeed the case, elevated TFA concentrations are not to be expected in their vicinity.

In the counties of Altötting, Heilbronn and Recklinghausen, significantly elevated concentrations are present, especially in the sampled surface waters. The measured groundwater concentrations are clearly above the mean value, especially in the Altötting county and the Hannover region. Based on the available data, this cannot be attributed with certainty to the E-PRTR operations located there. However, a connection is probable.

Table 10: Mean TFA levels in surface waters in counties with industrial plants that release fluorides into the environmental compartment water according to the E-PRTR Regulation and are active in chemical synthesis.

Circle	Number of sampling points	Number of analyses	Mean value of the mean values (in µg/L)	Mean value of the medians (in µg/L)	Mean value of the maxima (in µg/L)
Altötting	5	53	3.89	3.86	9.63
Heilbronn	1	944	8.41	5.70	85.00
Cologne	1	65	1.05	0.99	2.30
Oberspreewald-Lausitz	1	2	1.40	1.40	1.80
Recklinghausen	10	642	3.19	3.00	4.91
Hanover region	8	42	1.15	1.13	1.64
Saxon. Schweiz-Osterzgebirge	6	37	1.69	1.52	2.83
Wesel	3	18	1.46	1.46	1.92
Total	35	1803	2.45	2.28	6.35

Table 11: Mean TFA levels in groundwater in counties with industrial plants that release fluorides into the environmental compartment water according to the E-PRTR Regulation and are active in chemical synthesis.

Circle	Number of sampling points	Number of analyses	Mean value of the mean values
Altötting	3	7	1.80
Heilbronn	81	85	1.05
Recklinghausen	3	3	0.50
Hanover region	103	203	2.46

6.5 Wastewater treatment plants and TFA concentrations in surface waters

The evaluations showed no connection between inputs from wastewater treatment plants and increased TFA concentrations. In contrast to many other data, the data on the wastewater treatment plants are available as point information including information on the capacity. This information was used to calculate the capacity-weighted density of wastewater treatment plants. GIS-based neighbourhood analyses were conducted using different parameters to vary the area that was regarded as potentially influenced by a water treatment plant (radius 6 km, 18 km, 30 km). The results of a correlation analysis showed no correlations between TFA concentrations measured in the surface waters and the number and capacity of wastewater treatment plants in the area.

7 Preparation of a cooperative mitigation strategy

Based on the compiled and evaluated data and findings from the data analysis on the entry and occurrence of TFA from various sources and in various environmental media , a spatial overall picture of TFA pollution was obtained and made accessible to a broad public utilising an interactive map and a StoryMap.

In addition, relevant input pathways and concrete fields of action were identified. On this basis, initial approaches for coordinated and cooperative mitigation strategies for TFA inputs to water bodies were to be discussed and prepared in a workshop with relevant stakeholders from the fields of action identified earlier.

In order to ensure goal-oriented discussions and to obtain results on which initial measures towards a coordinated, cooperative mitigation strategy can be derived, representatives of relevant sectors were specifically invited to the workshop. In order to ensure a successful professional exchange, the number of participants was limited to a maximum of 40 people, who were specifically invited by e-mail.

7.1 Prioritisation of the fields of action

Based on the results of data analysis, three priority fields of action were derived with regard to mitigate TFA water inputs:

1. Inputs from the agricultural application of critical PPPs
2. Inputs via precipitation resulting from the use of halogenated gases with TFA formation potential, especially refrigerants and blowing agents
3. Entries on emissions from fluorochemical industry

In the future, a higher prioritization of further fields of action from data analyses that have already been considered in some cases, cannot be excluded. The prioritisation presented is based on the current, incomplete data situation; with more available data, the priorities may change, so that further fields of action may become relevant.

7.2 Stakeholder workshop to prepare a cooperative mitigation strategy

The stakeholder workshop was held on 05th and 06th, October 2022 as lunch-to-lunch meeting at TZW in Karlsruhe.

In addition to representatives of the Federal Ministry of the Environment, primarily stakeholders from institutions and organisations involved in the production, testing and regulation of TFA and TFA precursors or affected by TFA contamination in their bodies of water were invited. These included stakeholders from federal and state authorities, representatives of companies and associations such as authorisation holders, users, WSC, NGOs and participants from the scientific community.

7.2.1 Methods

The program was customized up to the last minute to tailor it as much as possible to the participants and to allow for focused discussions. An overview of the final program for both days is shown in Table 12.

Table 12: Agenda TFA stakeholder workshop. D1 and D2 stands for the two discussion rounds held in parallel.

Wednesday, 5 October, 2:00 p.m. - 6:45 p.m. I Exchange: info, results, ideas and examples.
1:30 p.m. I Registration
2:00 p.m. I Welcome, introduction of participants and introduction to the day's program I *T. aus der Beek (IWW) / S. Sturm (TZW)*
2:10 p.m. I Introduction to the topic and objective I *F. Jentzsch UBA*
2:30 p.m. I Presentation of the project results I *F. Brauer & F. Freeling TZW*
35:45 p.m. I Coffee break
Presentations by the stakeholders
1 I 4:05 p.m. I Monitoring: " Findings of TFA in Mecklenburg-Vorpommern - ground and surface water, wastewater treatment plants" I *G. Burucker LUNG*
2 I 4:25 p.m. I Surveillance/monitoring: **"TFA inputs to waters Surveillance/monitoring Finds and Reconnaissance in Bavaria"** I *C. Becker LfU Bavaria*
3 I 4:47 p.m. I TFA in regulation - in the **field of plant protection products** I *K. Adlunger* UBA
4 I 5:05 p.m. p.m. I TFA in regulation - general chemicals/ **REACH** I D*. Sättler* UBA
5:20 - 5:30 p.m. I Coffee Break
5 I 5:40 p.m. I TFA from PPP - **Manufacturer's perspective in IVA** I *M. Winter IVA*
6 I 6:10 p.m. I Substitution **refrigerant** I *T. Frank Refolution*
7 I 6:25 p.m. I TFA from PPP - Case study agricultural cooperation "**Cause clarification for TFA entries in the Funne area (Northrhine Westphalia)**" I *A. Phelan Gelsenwasser*
6:30 p.m. I Summary and end of day

Thursday, 6 October, 9:00 a.m. -1:00 p.m. I "Discussion and development of possible mitigation strategies".
9:00 a.m. I Welcome, summary of the previous day, introduction to the day's program/ explanation of the objective I *T. aus der Beek (IWW) / S. Sturm (TZW)*
Strategy discussions in subgroups followed by a panel discussion
D 1 I **PPP as precursor for TFA**| Approval & application I *U. Karges (IWW) / S. Sturm (TZW)*
D 2 I **TFA & precursors under REACH** / refrigerants	emissions / precipitation I T*. aus der Beek (IWW) / F. Brauer (TZW)*
Plenary discussion I *T. aus der Beek; S. Sturm*
12:30 p.m. I Summary and conclusion I *UBA*

7.2.2 Round table discussions

The topics of the round table discussions on the second day of the workshop and the distribution of the participants to the two discussion groups (D1 and D2) was adapted to the interests of the stakeholders present and coordinated with them, as was the entire workshop process.

In preparation for the workshop and in order to create a common basis for discussion apart from the presentations, initial approaches for possible measures towards a cooperative mitigation strategy were compiled in bullet points on the basis of the project results and in consultation with UBA departments concerned and made available to the workshop participants in advance.

The agreed outcomes of the moderated discussions were recorded in writing and as photo documentation and then presented in plenary.

7.2.2.1 Results of discussion round D1 | PPP

The focus of discussion round D1 was on ways to reduce TFA inputs from PPPs. Accordingly, the round table consisted of representatives of manufacturers/industry association for agriculture (IVA), water management (especially water supply companies), representatives of environmental authorities of the federal states, the federal authorities for the environment and agriculture (UBA, BVL) and the chambers of agriculture, representing the interests of users.

D 1: PPP | Main points of discussion and statements

General statements from the discussion group:

- The remediation of TFA-contaminated media (end-of-pipe solution is excluded as a mitigation measure.
- The remediation of TFA-contaminated media (end-of-pipe solution) is excluded as a mitigation measure.
- Retroactive source attribution is not possible / difficult.
- The immediate substitution of the CF3-group in PPP active substances is not yet possible.
- Solutions can lie both in regulatory approaches or in cooperation.
- If TFA were regulated in the daughter directives to WFD (Groundwater Directive (2006/118/EC) and Directive on Environmental Quality Standards (EQS) in the Water Sector (2008/105/EC)) and in the associated national regulations, the prohibition of deterioration would apply.

There was consensus that different measures require very different time horizons and scales (EU - national - local) for implementation.

Approaches discussed at national and local level include:

- "Measure evaluation": Area-wise data on measures are required (analytics, monitoring, documentation, evaluation).
- "Cooperative approach": With the aim of further developing/expanding cooperative approaches and consultation; assessment and designation of particularly vulnerable areas.
- "Further development of integrated crop production"

- "TFA Information Campaign"

At the level of the European Union (EU), there has been controversial discussion on the question of only allowing organic farming in water protection areas. The current draft regulation on the sustainable use of plant protection products (SUR) within the framework of the European Green Deal, which calls for a ban on the use of all pesticides in sensitive areas to achieve the "50 %" target by 2030 (SUR 2022), provides for a similar approach.

Substitution options for TFA-forming PPPs were also discussed at various levels. These included the redistribution of cultivated areas (applications outside vulnerable areas), the mass reduction of active ingredient actually applied over time or per individual application, the targeted exclusion of certain crops and general restrictions on the use of acitve substances – e. g. in the form of an active ingredient account for certain areas.

Currently, there are no biological PPPs - i.e., substances of natural origin - that could be used as alternatives to flufenacet or others. Regarding the complex process that is necessary to bring innovations to the market, the need for corresponding funding and research was referred to several times. There was widespread agreement that these innovations can be mobilized, or have already been mobilized, e.g., in the area of the development of alternatives to PPP active substances with the C-CF3-group. Trials have also been initiated to convert cultivation in particularly vulnerable areas through land swaps in the form of cooperation between the pesticide industry, local water suppliers and farmers. This was explained earlier in the presentation on the Funne area.

Trends and open questions from the discussion:

- Manufacturing companies have joined forces in a TFA task force to address TFA in the authorisation of PPPs in the future.
- The already existing exchange between UBA and IVA is to be strengthened and extended to BVL and BfR in the future.
- When considered in isolation, the effects on other protection goals are often overlooked but this must be taken into account in the risk assessment.
- According to Regulation (EC) No 1107/2009 (Plant Protection Products Regulation), precaution ≠ risk

7.2.2.2 Results of discussion round D2 | RRP

The focus of discussion in subgroup D2 was, on the one hand, in the area of the fluorochemical industry on the mitigation of point emissions of TFA and TFA precursors that fall under the REACH Regulation. As another specific focus, this subgroup discussed fluorinated refrigerants, which also fall within the scope of the REACH Regulation and which contribute to the ubiquitous TFA input via precipitation. Due to a lack of feedback or cancellations by the invited industry representatives, the discussion in this group had to do without the views of the manufacturers/ distributors. In addition to UBA representatives from the relevant departments, the participants also included representatives from WSC, environmental science, refrigeration technology and NGOs.

D 2: RRP[5] I Main points of discussion and statements*

General statements:

- UBA should initiate the establishment of a targeted nationwide environmental monitoring that documents representative point and area discharges; consequences and measures should be linked to the results of this monitoring program.
- Water, environmental and plant legislation must be better linked, or should be more closely coordinated with each other, with access to data from chemical legislation, so that inputs that can be detected at least as a point source can be taken into account as far as possible.
- Raise awareness of the problem→ Mitigation requirement (e.g., from the European WFD) vs. 60 µg/L drinking water guide value[6] ; here, the various levels must be taken into account/addressed in measures: Local-State-National-EU
- A nationwide upgrade of municipal wastewater treatment plants, which primarily treat domestic wastewater, probably offers little potential for mitigation under socioeconomic factors.

(Fluorochemical) industry as an emission source:

- In the medium to long term, some regulation is expected via PFAS restriction/essential use
- Sharpening of the Groundwater Ordinance including the elaboration of consequences and measures
- Information to local authorities on chemicals and quantities
- Establishment of a flexible emission register
- Use of adapted air filters for exhaust gas treatment
- Lower discharge concentrations through improved wastewater treatment, e.g., reverse osmosis
- Inclusion of TFA in the company's own monitoring system

Refrigerants:

- Substitution of fluorinated greenhouse gases with natural refrigerants

Medical area

- Recommendation list for doctors for the substitution of human and veterinary medicinal products containing C-CF_3-groups
- Environmental behaviour actually taken into account in drug approval
- Consumer information should be adapted accordingly

*Order of prioritization by the discussants

[5] TFA precursor substances other than PPPs, these include: REACH regulated fluorinated chemicals, refrigerants and pharmaceuticals.

[6] For more information on the classification of the TFA drinking water conductance value, see: UBA classification TFA conductance (umweltbundesamt.de)

7.2.2.3 Overview of the plenary discussion

In the concluding plenary discussion, the question of fundamental, regulatory or cooperative, local measures was taken up again and weighed up against each other. There was widespread agreement that multiple approaches - at very different levels - are required to reduce TFA inputs into water bodies.

The cooperative approach was considered to be locally limited, but could be implemented quite quickly, as shown in presentation 7 (Table 12) in the Funne region. With the participation of concerned water suppliers, the local agricultural cooperation in the catchment area, the IVA and others, a cause clarification for TFA inputs in the Funne, a tributary of the drinking water-relevant Stever, was carried out. Through interviews and modelling of water and solute transport using the Soil & Water Assessment Tool (SWAT), the application of flufenacet was identified as the most important source, followed by diflufenican and tritosulfuron applications. From several mitigation scenarios on the identified most vulnerable areas, voluntary flufenacet abandonment in maize cultivation was identified as feasible for this cooperation and will be introduced as a mitigation measure from 2023. Even if no final results are available to quantify the success of the mitigation, the identification of the vulnerable areas and the most relevant active substances for each area is an essential step towards to assigning local TFA inputs to their sources and taking countermeasures.

By designating areas that are particularly vulnerable for drinking water supply and through the direct reduction path via the PPPs applied, drinking water supplies can be directly protected from TFA inputs. Thus, cooperative approaches offer the potential to alleviate the problems locally. In addition, successful cooperative approaches, could also be incorporated into future regulations as required. In general, cooperative individual projects (e.g., finds reconnaissance) are assessed as locally useful, but they do not solve the problem of the expected nationwide increase in TFA inputs in Germany. In order to find a final and comprehensive solution to the issue of TFA inputs, fundamental regulatory efforts are needed, also at EU level. Without a completed, harmonised assessment of the metabolite within the framework of the EU active substance approval procedure, it is difficult to issue conditions of use for products at national/zonal level. Currently, the re-approval of flufenacet is under review. Here, TFA has been identified for the first time as a soil metabolite for flufenacet and has therefore been taken into account in groundwater modelling (EFSA 2017). In the relevance assessment carried out due to the high groundwater values, TFA was classified as a non-relevant metabolite (nrM) for flufenacet. A metabolite is considered non-relevant if its pesticidal activity is less than 50 % of the parent substance, it has no evidence of toxicological properties that may pose a health risk to consumers in case of appropriate exposure (EC 2021). Nevertheless, there may be residual risks to these substances that are initially unpredictable and, in the case of sufficiently high persistence, even transcend generations. Also, the long-term risk of possible adverse impacts on the environment often cannot be assessed with sufficient accuracy or these effects cannot be easily reversed by regulatory measures (Hale et al. 2020).

The main difference in dealing with nrM and relevant metabolites (rM) is that rM are treated like active substances in the assessment of groundwater risk; a limit value of 0.1 µg/L applies to them under plant protection law in accordance with the Groundwater Directive. There are no uniform, binding limit values for the so-called nrM. The guideline value of 10 µg/L per year of application specified in the European Commission's assessment guideline is currently used in Germany as an assessment limit but is not currently (as of December 2022) anchored in groundwater or drinking water legislation.

The fact that PPPs with acitve substances containing C-CF_3-groups represent a source of input for TFA was generally regarded as undisputed in the plenary. However, there is still a need for clarification regarding the respective level of the contributions, i.e., the conversion or formation rate of the individual active substances to TFA. Due to the lack of publicly available data, a conservative approach to estimating the formation rates was chosen in data analysis of the project, which was necessary for precautionary reasons see Chapter 5.3.2.2). However, in the IVA presentation, formation rates of less than 100% conversion were shown for 12 of the 13 C-CF_3-containing PPPs shown, which were determined in specific metabolism studies for current re-approval procedures for PPP active substances. However, the formation rate for flufenacet, which is particularly relevant in terms of quantity as a TFA precursor in Germany, is also very high in these studies at 73%, while tritosulfuron, which was investigated in the example of the Funne cooperation, is even higher at 78 - 117% (contains two C-CF_3-groups). In contrast, TFA is not classified as a relevant soil metabolite for diflufenican, which was also identified as problematic in the example of the Funne area.

The plenary also intensively discussed the need for monitoring and surveillance of TFA inputs from other industries.

There is still a lack of knowledge about which (industrial) sites potentially emit TFA or TFA precursors and in what quantities. Therefore, the need to gain knowledge/information via a reporting register or a flexible emission register was emphasized. Although information on areas of use of industrial chemicals is part of the REACH registrations, these only describe the use generically and usually without reference to real locations in the EU. Accordingly, it is not possible to draw conclusions about individual emitters at national or EU level. In addition, in the case of drinking water supply via bank filtrate from surface waters, there is the problem that although vulnerable areas can be designated for drinking water supply. However, the relevant discharger of TFA or relevant TFA precursors into surface waters can also be located upstream, a few kilometers from the designated area, so that the protection goal is meaningless.

Due to the still inadequate information situation, a nationwide, long-term measurement program was advocated to secure evidence, but also to derive trends and as a means of gaining neutral information. In addition, data on emission values should be demanded via the Wastewater Ordinance and self-monitoring. In any case, the corresponding legal prerequisites would have to be created. Up to now, emission data has either not been collected by industry or has been withheld with reference to possible conclusions about production processes and thus company secrets.

8 Approaches to mitigation strategies - evaluation of data analysis, the pre-workshop literature review and the workshop outcomes.

Based on the results of the spatial data analysis, the discussions and workshop contributions, as well as the ideas collected prior to the workshop, some approaches for mitigation strategies are derived, but also gaps in knowledge gaps are identified and initial approaches to filling them are highlighted.

The extensive data research at the beginning of the project showed that only insufficient information is available in many areas. This concerns both data on TFA concentrations in different environmental matrices and information on the possible sources of TFA:

- Information on TFA concentrations in ground and surface waters is available in some federal states with good spatial and / or temporal resolution and could partly be supplemented by measurements carried out by water suppliers. In many regions, however, the data situation is not sufficient for statistically reliable evaluations.
- TFA measurements in precipitation have so far been carried out in Germany as part of a project funded by the Ministry of the Environment (Behringer et al. 2021) and are available with very good temporal resolution, but only for seven measuring sites distributed across Germany. Statements on atmospheric TFA input for the entire area of Germany are therefore subject to uncertainties.
- Information on the application of PPPs containing TFA-forming active substances could only be derived from estimated quantities of active substances applied and the information from the Federal Statistical Office on cultivated areas per county. Although actual PPP application quantities are recorded by the farms, they are generally not passed on and are therefore not available for scientific observations. However, starting in 2028, application data must be made available in digital form throughout the EU under the new Regulation on Statistics on Agricultural Input and Output (SAIO).
- Information on the location of industrial plants emitting TFA or its precursors and data on the amounts entering the aquatic environment via this pathway are not available. In order to identify potentially relevant industrial plants in Germany, only publicly available data from the PRTR pollutant register and REACH could be used. In the former, however, TFA is not reported as an individual substance, but at best is recorded under a non-specific sum parameter (e.g., via proportion of fluorides in wastewater), so that depending on the industry-specific reporting obligations, the inputs of TFA and its precursors can be both over- and underestimated. No information is available on (smaller) industrial sites not covered by the E-PRTR Regulation. Moreover, it is unknown whether and to what extent the identified facilities actually emit TFA into the aquatic environment. Under REACH, as already mentioned, there are almost exclusively generic descriptions of the conditions of use, so at best only rough estimates of the quantities of TFA or TFA precursors entering the aquatic environment are possible.
  Large-scale monitoring programs to determine TFA emissions by industry involve an unjustifiable effort, as each site emits different substances in different quantities at irregular times. Therefore, a large number of samples with a wide range of parameters would be required to reliably detect TFA precursors. Monitoring would therefore be particularly useful if information on possible emissions is already available, e.g., for the currently four

active registrants for trifluoroacetic acid under the REACH Regulation (ECHA 2022) that are located in Germany. The results of these monitoring programs could also help to better understand the influence of individual companies on environmental concentrations.

The results on sources and input pathways, which are substantiated with numerical values, are only partially reliable. The methods and approaches chosen for the correlation analysis nevertheless made it possible to identify weak correlations, which suggest the following conclusions:

- TFA in precipitation leads to a basic contamination of ground and surface waters. There is a ubiquitous input of TFA via precipitation, so that hardly any uncontaminated samples were recorded.
- PPPs are a hitherto underestimated, area-wide significant source of TFA.

Based on the available data, an influence of municipal wastewater treatment plants could not be determined. However, in view of the introduction of an oxidative, fourth treatment stage, further investigation of municipal wastewater treatment plant effluents as a potential input pathway is important. An oxidative fourth stage could increase the release of TFA from various fluorinated chemicals because oxidation can contribute to the formation of TFA (Scheurer et al. 2017).

Fundamentally, it is necessary to improve the data situation to further secure the previous results, but also to obtain reliable information at all on the input pathways that have been little documented so far, such as those via industrial point sources. This concerns both the information on potential TFA sources and the monitoring data.

8.1 Approaches to mitigation strategies

In principle, further monitoring in surface waters and groundwater is an important tool of gaining information. On the one hand, the purpose of monitoring is to identify further sources of TFA or TFA precursors; on the other hand, monitoring carried out over the longer term is also indispensable for deriving trends. To this end, federal and state authorities should enter into close exchange and create the basis for uniform standards and a central database.

8.1.1 Plant Protection Products

- At the regulatory level, the establishment of a harmonised, EU-wide binding limit value for nrM in groundwater as a criterion for product authorisation would be a milestone in order to be able to act in a nationally secured manner. With the Plant Protection Products Regulation, the Drinking Water Directive and the Groundwater Directive and their downstream legal acts, there are several legal frameworks at EU level of potential relevance for dealing with nrM of PPPs in connection with drinking water or groundwater. However, so far there is no binding limit value for nrM.
- For TFA as a nrM of PPPs, there is also no national limit value; rather, the guideline value of 10 µg/L is applied as the assessment limit, according to the recommendation of the European Guideline (EC 2003) and Michalski et al. (2004). However, a corresponding political initiative would make it possible to set a national statutory limit value for TFA (or all nrM) in groundwater. From a drinking water perspective, this could lead to greater legal certainty. Before doing so, however, the risk of volume problems possibly arising should be examined. With regard to a concrete mitigation of TFA inputs into water bodies, an amendment of the data requirement for PPP would be effective. Here, the data requirements for degradation studies of PPP active substances containing C-CF_3 should be adapted and

specified. For a corresponding guideline, concrete test requirements and study designs would have to be developed by an independent scientific institution.

- A fundamental reduction in the use of PPPs, as called for in the EU Commission's draft of a new SUR, would certainly also have a reducing effect on the use of TFA-forming PPP active substances, or possibly even completely ban the use of PPPs in "sensitive (vulnerable) areas". However, since no decision has yet been taken on this draft and the components do not yet appear to be an attractive option for many farmers without corresponding promotion and safety, users and politicians (and possibly water suppliers) as relevant actors would have to further clarify under which aspects the reduction of PPPs would be feasible, at least in vulnerable areas.

- Another viable short-term option for reducing TFA inputs is to make greater use of existing instruments such as the issuing of application regulations, especially NG356 and subforms, which limit the application rate of PPPs containing flufenacet on an area within a defined period of time. Instead of specifically testing and listing individual areas, these application regulations could be extended to water protection areas, for example, by amending the regulations. Since flufenacet is the most important PPP active ingredient in terms of volume in relation to TFA inputs throughout Germany, with the highest tonnages and growth rates (cf. BVL sales figures in BVL 2021), such a restriction would be particularly effective. For example, between 2008 and 2018, the sales volume of the active ingredient flufenacet increased by 80% (BVL 2021) and in 2022 a total of 31 PPPs containing flufenacet are authorisded in Germany.

- Measures that can also be implemented in the short term include local efforts to expand cooperative approaches and targeted advice/support for risk management for particularly vulnerable areas by local actors from plant protection services, agriculture, WSC and, where appropriate, authorities who are also experts for their areas.

The release of application data on active substances with C-CF_3-groups could be regulated at a similar level as long as no legal regulation exists. However, this should be created at the federal level and regulate the release and dissemination, collection and processing of data for environmental/water risk assessment by central agencies of the federal government or federal states.

8.1.2 Chemicals registered under REACH

The stakeholder workshop once again made it clear that there are far too many gaps in the information on industrial enterprises that produce or use TFA or TFA precursors and on the quantities discharged into the aquatic environment as a result of these activities. As a result, a reliable identification of sources and input pathways is not possible with the existing database.

In addition to developing mitigation strategies for the paths and sources, which can be assumed to be quite secure, the importance of information gathering must be emphasised here as a matter of priority and ways of gaining knowledge must be pointed out.

This includes, in particular, knowledge of which chemical industry sites can potentially emit TFA or TFA precursors in relevant quantities.

- To this end, federal policy would have to create the legal basis for a nationwide database into which companies would have to enter information on substances and quantities they process and produce. The data requested should necessarily include structural information from which a general TFA formation potential can be concluded.

- In view of the large number of substances, that are potentially introduced into water bodies and that may pose a concern for the environmental organisms, or which potentially can reach the raw water sources used for drinking water productionfor drinking water supplies, it is obvious that the reporting obligations associated with this database should not only include TFA and its precursors.
- Further development of the Technical Guidance Document (TGD) on the derivation of WFD EQS (EC-TGD 2018) is necessary to ensure the long-term protection of water bodies and to extend the WFD's prohibition of deterioration to substances such as TFA. The Industrial Emissions Directive 2010/75/EU and the National Waste Water Ordinance (WWO) should also be extended to TFA. The latter should also regulate self-monitoring by the companies and the dissemination of data.
- The possible action option of identifying TFA as a substance of very high concern (SVHC) according to Article 57 of REACH on the criteria of wide environmental distribution and the fulfilment of the criteria for very persistent, very mobile substances (vPvM criteria) would not result in a ban on production and use, but would have an impact on the communication obligations under REACH according to the requirements of Articles 31ff: Informing customers in the supply chain if TFA concentrations >0.1 wt.% are contained in a substance/mixture; informing consumers on demand if TFA is contained in articles in concentrations >0.1 wt.%. Furthermore, a so-called "black listing" effect would have to be expected: applications/products with TFA would have to be checked for substitution possibilities; effects on business agreements at company level would be expected - e.g. if the customer demands products without contained SVHC from his supplier.
- Far-reaching restriction of the use of TFA precursors: the assessment authorities in Germany are currently (as of November 2022) preparing a far-reaching restriction proposal for PFAS (regarding production and use) under REACH together with competent authorities from the Netherlands, Denmark, Sweden and Norway. If this proposal is accepted by the relevant committees of the EU Commission and the restriction is adopted accordingly, the restriction of PFAS as potential TFA precursors would also have a reducing effect on TFA emissions from the affected applications after a transition period.

8.1.3 Refrigerants and other fluorinated gases

Fluorinated gases are a subgroup of chemicals, which fall within the scope of REACH as well. By 2050, the use of short-lived fluorinated refrigerants and blowing agents with higher TFA formation potential will continue to increase sharply. This trend can only be stopped if manufacturers and operators consistently focus on more sustainable solutions and systems that use natural substances such as hydrocarbons, carbon dioxide, water, air or ammonia. In addition, the need for cooling by refrigeration and air conditioning should be reduced as much as possible, e.g., through construction measures and greening.

Possible steps towards reduction:

- No exemption of refrigerants from the PFAS restriction proposal. In particular, if alternatives are available, no exemptions are to be provided for these applications in new installations. Substitution/use requirement for natural refrigerants if they can be considered as alternatives (e.g., for mobile air conditioning, CO_2 or hydrocarbons).
- Extend the reporting obligations in Regulation (EC) 1005/2009 on substances that deplete the ozone layer and Regulation (EU) 517/2014 on fluorinated greenhouse gases. Here, the

reporting obligations should be extended to include halogenated alternatives that have a low ozone depletion potential or a low global warming potential but are clear TFA formers.

- Regulations on the use of non-halogenated refrigerants at EU level, such as the standards of the International Electrotechnical Commission (IEC), should be rapidly transposed into national law. Regulations should be harmonised across the EU.
- Promoting education and training for the refrigeration and air-conditioning technicians in fluorine-free alternatives, accompanying an ambitious amendment of Regulation (EU) 517/2014 on fluorinated greenhouse gases. The aim should be to switch immediately to systems using halogen-free refrigerants, ensuring that sufficient staff capacity is available for the rapid installation of new systems and for expert maintenance and repair.
- Expansion of a targeted national and international information policy for halogen-free technologies and products. Financial and human resources must be made available for information on natural refrigerants and advice on possible applications and energy benefits. Existing information portals for natural refrigerants with examples of use must be kept up to date and should cover further areas of application.
- The existing state support, e.g., for stationary refrigeration and air-conditioning systems (currently supported in the German Refrigeration and Air-conditioning Directive) must be maintained and as soon as possible, extended to transport refrigeration systems with natural refrigerants.
- In all existing funding programs for new plants and processes, only the use of halogen-free gases should be eligible for funding. In new funding programs (e.g., for the air conditioning of data centers), strict attention must be paid to ensuring that only such technologies and systems that use halogen-free refrigerants, or do not use refrigerants at all, are included.
- Refrain from promoting or supporting projects that use halogenated substances as refrigerants or as working fluids, such as stationary and mobile refrigeration and air conditioning systems, heat pumps and organic Rankine cycle (ORC) systems. Similarly, discontinue the promotion of solvents, fire extinguishing agents and aerosol propellants containing halogenated substances. Discontinuation of subsidies for electric buses that cool with halogenated refrigerants.

Germany shall continue to support events to disseminate the knowledge about new technologies both nationally and internationally. In developing countries in particular, this can lead to a direct switch from ozone-depleting substances (CFCs and HCFCs) to natural substances without first introducing fluorinated greenhouse gases (PFCs and HFCs) (so-called leap frog). Platforms are provided, for example, by the Montreal Protocol and the Climate & Clean Air Coalition (CCAC) as well as relevant events such as the Green Cooling Summit organised by the German Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection (BMUV)/UBA and the German Society for International Cooperation.

9 Conclusion and outlook

TFA, as a very persistent and highly mobile chemical in waters, accumulates increasingly in the water cycle in the long term and cannot be removed with economic means, even in drinking water treatment.

The findings of this project represent an important first step towards reducing TFA inputs: The spatial data analysis carried out on concentrations of TFA in water bodies underlines the explosive nature of TFA as a previously underestimated contaminant and thus also the need for prompt mitigation of inputs. The results of data analysis provide a basis for identifying causes and sources and show which input pathways for TFA in the aquatic environment are relevant. In the course of the project, it has been confirmed that the data situation on TFA emissions is very patchy so far, so that the project results are subject to some uncertainty. It can be assumed, however, that significant area-wide inputs occur primarily through the application of Plant Protection Products (PPP) and gaseous TFA precursors (e.g., refrigerants), while industrial operations sometimes cause very high local loads.

From the compiled and evaluated data and findings on the input and occurrence of TFA from various sources and in various environmental media, a spatial overall picture of TFA exposure was emerged and made accessible to a broad public utilising an interactive map and a storymap. This are intended to inform as well as sensitise and show that even substances of little toxicological relevance are not necessarily harmless.

The project results emphatically show that TFA is rightly described as a "substance of multiple sources". The steady increase in the use of some known TFA precursors - such as the herbicide flufenacet or the refrigerant R1234yf - contribute to the prediction of a continuing upward trend for TFA as an environmental chemical. This increases concern about this substance as a contaminant in water bodies and drinking water, particularly from a precautionary perspective.

As TFA is currently classified as of no toxicological concern and low ecotoxicological concern, many stakeholders see a low priority to initiate measures to restrict use and release limited by the means of current legislation. The multitude of sources and pathways of TFA also complicate the development of effective measures to reduce and regulate the input of TFA into the environment, especially into the water cycle.

The relevant input pathways and concrete fields of action identified in the project formed a basis for a workshop in which initial approaches for coordinated and cooperative mitigation strategies were discussed by various stakeholders. An important point is the mandate to politicians and authorities to increasingly advocate for the inclusion of TFA and other very persistent and very mobile substances in legal regulations, both at national and EU level - especially if these substances also cause toxic effects in humans or environmental organisms even at low concentrations. Especially in the area of PPP, existing approaches were named that should be continued and expanded. Detection in cooperation with WSC and PPP manufacturers was identified as a locally effective instrument, even if it is not able to solve the problem of the expected area-wide increase in TFA inputs. The existing proven exchange between UBA and IVA (German Crop Protection Association) should be intensified and extended to BVL (German Federal Office of Consumer Protection and Food Safety) and BfR (German Federal Institute for Risk Assessment) in the future. The existing monitoring programs of the federal states formed an important basis for this project. In order to continue to quickly identify causes and trends and, if necessary, to be able to initiate concrete measures, further monitoring programs are important.

10 List of References

BAuA (2021): Datenbank der zugelassenen Biozidprodukte. Bundesanstalt für Arbeitsschutz und Arbeitsmedizin. Verfügbar unter: https://www.baua.de/DE/Themen/Anwendungssichere-Chemikalien-und-Produkte/Chemikalienrecht/Biozide/Zugelassene-Biozidprodukte.html. Letzter Zugriff: 19.11.2021.

Behringer, D.; Heydel, F.; Gschrey, B.; Osterheld, S.; Schwarz, W.; Warncke, K.; Freeling, F.; Nödler, K.; Henne, S.; Reimann, S.; Blepp, M.; Jörß, W.; Liu, R.; Ludig, S.; Rüdenauer, I.; Gartiser, S. (2021): Persistente Abbauprodukte halogenierter Kälte- und Treibmittel in der Umwelt: Art, Umwelt-konzentrationen und Verbleib unter besonderer Berücksichtigung neuer halogenierter Ersatz-stoffe mit kleinem Treibhauspotenzial. Umweltbundesamt TEXTE 36/2021. Forschungskennzahl 3717 41 305 0.

BfG (2021): Geoportal der BfG. Bundesanstalt für Gewässerkunde (BfG). Verfügbar unter: https://geoportal.bafg.de/CSWView/od.xhtml. Letzter Zugriff: 15.10.2021.

Bowden, D.J.; Clegg, S.L.; Brimblecombe, P. (1996): The Henry's law constant of trifluoroacetic acid and its partitioning into liquid water in the atmosphere. In: Chemosphere, 32, 2, S. 405 – 420.

BVL (2021): Absatzmengen von Wirkstoffen in Pflanzenschutzmitteln in der Bundesrepublik Deutschland von 1987 bis 2020. Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (BVL). Verfügbar unter: https://www.bvl.bund.de/SharedDocs/Downloads/04_Pflanzenschutzmittel/meld_par_64_Wirkstoffabsatz_seit_1987.xlsx.

CAS (2021): SciFinder, a CAS Solution, American Chemical Society. Verfügbar unter: https://scifinder-n.cas.org/. Letzter Zugriff: 18.06.2021.

Cui, J.'n.; Guo, J.; Zhai, Z.; Zhang, J. (2019): The contribution of fluoropolymer thermolysis to trifluoroacetic acid (TFA) in environmental media. In: Chemosphere, 222, S. 637 – 644.

DrugBank (2021): Chemical Structure Search. Verfügbar unter: https://go.drugbank.com/structures/search/small_molecule_drugs/structure. Letzter Zugriff: 19.11.2021.

ECHA (2022): SCIP Database. European Chemicals Agency (ECHA). https://echa.europa.eu/de/search-for-chemicals (29.03.2022).

EFSA (2017): Flufenacet: Draft Renewal Assessment Report Flufenacet, Volume 3, Annex B.8 (AS) Fate and Behaviour in the Environment. https://www.efsa.europa.eu/en/consultations/call/170920

Ellis, D.A.; Mabury, S.A.; Martin, J.W.; Muir, D.C. (2001): Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. In: Nature, 412, 6844, S. 321 – 324.

EURL-SRM (2017): EURL-SRM – Residue Findings Report - Residues of DFA and TFA in Samples of Plant Origin. Verfügbar unter: https://www.eurl-pesticides.eu/userfiles/file/eurlsrm/eurlsrm_residue-observation_tfa-dfa.pdf. Letzter Zu-griff:11.04.2020.

Frank, H.; Christoph, E.H.; Holm-Hansen, O.; Bullister, J.L. (2002): Trifluoroacetate in ocean waters. In: Environmental Science & Technology, 36, 1, S. 12 – 15.

Freeling, F.; Behringer, D.; Heydel, F.; Scheurer, M.; Ternes, T.A.; Nödler, K. (2020a): Trifluoroacetate in precipitation – deriving a benchmark data set. In: Environmental Science & Technology, 54, 18, S. 11210 – 11219.

Freeling, F.; Scheurer, M.; Koschorreck, J.; Hoffmann, G.; Ternes, T.A.; Nödler, K. (2022a): Levels and Temporal Trends of Trifluoroacetate (TFA) in Archived Plants – Evidence for Increasing Emissions of Gaseous TFA Precursors over the Last Decades. In: Environmental Science & Technology Letters, 9, 5, S. 400 – 405.

Freeling, F.; Scheurer, M.; Koschorrek, J.; Hoffmann, G.; Ternes, T.A.; Nödler, K. (2022b): Levels and temporal trends of trifluoroacetate (TFA) in archived plants: Evidence for increasing emissions of gaseous TFA precursors over the last decades. Submitted to Environmental Science & Technology Letters.

Freeling, F.; Scheurer, M.; Sandholzer, A.; Armbruster, D.; Nödler, K.; Schulz, M.; Ternes, T.A.; Wick, A. (2020): Under the radar - Exceptionally high environmental concentrations of the high production volume chemical sulfamic acid in the urban water cycle. In: Water research, 175, S. 115706.

Füßler, C. (2011): Wenn die Gülle sauer wird. DIE ZEIT Nr. 24/2011. Artikel vom 9. Juni 2011. Verfügbar unter: https://www.zeit.de/2011/24/Weg-der-Guelle/komplettansicht. Letzter Zu-griff: 11.04.2020.

Hydrologischer Atlas von Deutschland/BfG (2003). Verfügbar unter: https://geoportal.bafg.de/smartfinderClient/?lang=de#/datasets/iso/c21d4842-39b0-469d-9828-956a583213e2. Letzter Zugriff: 23.03.2022.

JKI (2021): Wirkstoffmengen Pestizide. Julius Kühn-Institut (JKI) Bundesforschungsinstitut für Kulturpflanzen. Verfügbar unter: https://papa.julius-kuehn.de/index.php?menuid=33. Letzter Zugriff: 19.11.2021.

Joudan, S.; Silva, A.O. de; Young, C.J. (2021): Insufficient evidence for the existence of natural trifluoroacetic acid. In: Environmental science. Processes & impacts.

Klein, A. (1997): Halogenierte Essigsäuren in der Umwelt. Dissertation, Shaker, Aachen. ISBN 3-8265-3299-6.

Nödler, K.; Freeling, F.; Sandholzer, A.; Schaffer, M.; Schmid, R.; Scheurer, M. (2019): Untersuchungen zum „Vorkommen und Bildungspotential von Trifluoracetat (TFA) in niedersächsischen Oberflächengewässern". Landesweiter Überblick und Identifikation von Belastungsschwerpunk-ten. Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz.

Nödler, K.; Scheurer, M. (2019): Substances from Multiple Sources (SMS) – The Presence of Mul-tiple Primary and Secondary Sources of Persistent and Mobile Organic Contaminants Is an Up-coming Challenge for the Drinking Water Sector and Regulatory Frameworks. In: Environmental science & technology, 53, 19, S. 11061 – 11062.

Ogawa, Y.; Tokunaga, E.; Kobayashi, O.; Hirai, K.; Shibata, N. (2020): Current Contributions of 284 Organofluorine Compounds to the Agrochemical Industry. In: iScience, 23, 9, S. 101467.

Pickard, H.M.; Criscitiello, A.S.; Persaud, D.; Spencer, C.; Muir, D.C.G.; Lehnherr, I.; Sharp, M.J.; Sil-va, A.O. de; Young, C.J. (2020): Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids – Evidence of the Impact From Global Environmental Regulations. In: Geophysical Research Letters, 47, 10, S. 65.

Sacher, F.; Lange, F.T.; Nödler, K.; Scheurer, M.; Müller, J.; Nürenberg, G.; Janda, J.; Freeling, F.; Muschket, M.; Keltsch, N.; Paschke, H.; Reemtsma, T.; Berger, U.; Zwiener, C.; Tisler, S.; Bugsel, B.; Schlummer, M.; Gruber, L.; Breuer, J.; Mechler, M.; Beiser, D.; Köhler, H.-R.; Wilhelm, S.; Lorenz, C. (2019): Forschungsbericht BWPLUS – Optimierung der EOF-Analytik unter Berücksichtigung der Beiträge verschiedener Stoffklassen poly- und perfluorierter Verbindungen. Förderkennzeichen: L7517011 - 16.

Scheurer, M.; Brauch, H.-J.; Schmidt, C.K.; Sacher, F. (2016): Occurrence and fate of nitrification and urease inhibitors in the aquatic environment. In: Environmental science. Processes & im-pacts, 18, 8, S. 999 – 1010.

Scheurer, M.; Nödler, K. (2021): Ultrashort-chain perfluoroalkyl substance trifluoroacetate (TFA) in beer and tea - An unintended aqueous extraction. In: Food Chemistry, 351, S. 129304.

Scheurer, M.; Nödler, K.; Freeling, F.; Janda, J.; Happel, O.; Riegel, M.; Müller, U.; Storck, F.R.; Fleig, M.; Lange, F.T.; Brunsch, A.; Brauch, H.-J. (2017): Small, mobile, persistent: Trifluoroacetate in the water cycle – Overlooked sources, pathways, and consequences for drinking water supply. In: Water Research, 126, S. 460 – 471.

Scott, B.F.; Macdonald, R.W.; Kannan, K.; Fisk, A.; Witter, A.; Yamashita, N.; Durham, L.; Spencer, C.; Muir, D.C.G. (2005): Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans. In: Environmental science & technology, 39, 17, S. 6555 – 6560.

Solomon, K.R.; Velders, G.J.M.; Wilson, S.R.; Madronich, S.; Longstreth, J.; Aucamp, P.J.; Bornman, J.F. (2016): Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts – Relevance to substances regulated under the Montreal and Kyoto Protocols. In: Journal of toxicology and environmental health. Part B, Critical reviews, 19, 7, S. 289 – 304.

Statistische Ämter des Bundes und der Länder (2021a): Anbau auf dem Ackerland in landwirtschaftlichen Betrieben nach Fruchtarten - Jahr - regionale Tiefe: Kreise und krfr. Städte (bis 2016). Code: 41141-02-02-4. Regionaldatenbank Deutschland. Verfügbar unter: https://www.regionalstatistik.de/. Letzter Zugriff: 11.03.2022.

Statistische Ämter des Bundes und der Länder (2021b): Landwirtschaftliche Betriebe mit Vieh-haltung und Zahl der Tiere - Stichtag - regionale Tiefe: Kreise und krfr. Städte (bis 2016). Code: 41141-03-01-4. Regionaldatenbank Deutschland. Verfügbar unter: https://www.regionalstatistik.de/. Letzter Zugriff: 11.03.2022.

Statistisches Bundesamt (2020): Wirtschaftsdünger tierischer Herkunft in landwirtschaftlichen Betrieben / Landwirtschaftszählung - Fachserie 3 Reihe 2.2.2 - 2020. Verfügbar unter: https://www.destatis.de/DE/Themen/Branchen-Unternehmen/Landwirtschaft-Forstwirtschaft-Fischerei/Produktionsmethoden/Publikationen/Downloads-Produktionsmethoden/wirtschaftsduenger-2030222209005.xlsx;jsessionid=84ADBBCA2692680214088FF99CE85984.live731?__blob=publicationFile. Letzter Zugriff: 30.03.2022.

Tisler, S.; Zindler, F.; Freeling, F.; Nödler, K.; Toelgyesi, L.; Braunbeck, T.; Zwiener, C. (2019): Transformation Products of Fluoxetine Formed by Photodegradation in Water and Biodegrada-tion in Zebrafish Embryos (Danio rerio). In: Environmental science & technology, 53, 13, S. 7400 – 7409.

Tong, W.; Huang, Q.; Li, M.; Wang, J.-b. (2019): Enzyme-catalyzed C–F bond formation and cleav-age. In: Bioresources and Bioprocessing, 6, 1, S. 61.

UBA (2021a): Öffentliche Abwasserentsorgung. Verfügbar unter: https://www.umweltbundesamt.de/daten/wasser/wasserwirtschaft/oeffentliche-abwasserentsorgung#rund-10-milliarden-kubikmeter-abwasser-jahrlich. Letzter Zugriff: 29.03.2022.

UBA (2021b): UBA-Hintergrundpapier: Chemikalieneintrag in Gewässer vermindern – Trifluoracetat (TFA) als persistente und mobile Substanz aus vielen Quellen. Entwurfsfassung. –Quellen, Eintragspfade, Umweltkonzentrationen von TFA und regulatorische Ansätze.

UBA (2022): PRTR-Gesamtdatenbestand (Stand 14.12.2021) der Berichtsjahre 2007 bis 2019. Verfügbar unter: https://thru.de/fileadmin/SITE_MASTER/content/Dokumente/Downloads/01_Topthemen/PRTR-Daten_2019/XLSX_PRTR-Export_GERMANY_2021-12-15.zip. Letzter Zugriff: 28.03.2022.

Zhang, L.; Sun, H.; Wang, Q.; Chen, H.; Yao, Y.; Zhao, Z.; Alder, A.C. (2019): Uptake mechanisms of perfluoroalkyl acids with different carbon chain lengths (C2-C8) by wheat (Triticum acstivnm L.). In: The Science of the total environment, 654, S. 19 – 27.

ZSE (2020): Emissionsdatenbank des Umweltbundesamtes des Umweltbundesamtes zu Treibhausgasen und klassischen Luftschadstoffen. Zentrales System Emissionen (ZSE).

11 List of legal bases

AbWV (2004): Abwasserverordnung in der Fassung der Bekanntmachung vom 17. Juni 2004 (BGBl. I S. 1108, 2625), die zuletzt durch Artikel 1 der Verordnung vom 20. Januar 2022 (BGBl. I S. 87) geändert worden ist.

EC (2021): Guidance document on the assessment of the relevance of metabolites of substances in groundwater regulated under the Regulation (EC) No 1107/2009 (Sanco/221/2000 – rev.11).

EC-TGD (2018): TGD EQS Nr. 27 - Europäische Kommission, Generaldirektion Gesundheit und Lebensmittelsicherheit, Technical guidance for deriving environmental quality standards, European Commission, 2018.

EG-Pflanzenschutzmittelverordnung (2009): Verordnung (EG) Nr. 1107/2009 des Europäischen Parlaments und des Rates vom 21. Oktober 2009 über das Inverkehrbringen von Pflanzenschutzmitteln und zur Aufhebung der Richtlinien 79/117/EWG und 91/414/EWG des Rates.

EG-WRRL (2000): Richtlinie 2000/60/EG des Europäischen Parlamentes und des Rates vom 23. Oktober 2000 zur Schaffung eines Ordnungsrahmens für Maßnahmen der Gemeinschaft im Bereich der Wasserpolitik.

EG-VO (2009): REGULATION (EC) No 1005/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 September 2009 on substances that deplete the ozone layer.

E-PRTR-Verordnung (2006): Verordnung (EG) Nr. 166/2006 des Europäischen Parlaments und des Rates vom 18.1.06 über die Schaffung eines Europäischen Schadstofffreisetzungs- und -verbringungsregisters und zur Änderung der Richtlinien 91/689/EWG und 96/61/EG des Rates.

F-Gas VO (2014): Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006.

German Refrigeration and Air-conditioning Directive - Kälte-Klima-Richtlinie (2022): Richtlinie zur Förderung von Kälte- und Klimaanlagen mit nicht-halogenierten Kältemitteln in stationären und Fahrzeug-Anwendungen im Rahmen der Nationalen Klimaschutzinitiative.

REACH-VO (2006): Verordnung (EG) Nr. 1907/2006 des Europäischen Parlaments und des Rates vom 18. Dezember 2006 zur Registrierung, Bewertung, Zulassung und Beschränkung chemischer Stoffe (REACH), zur Schaffung einer Europäischen Agentur für chemische Stoffe, zur Änderung der Richtlinie 1999/45/EG und zur Aufhebung der Verordnung (EWG) Nr. 793/93 des Rates, der Verordnung (EG) Nr. 1488/94 der Kommission, der Richtlinie 76/769/EWG des Rates sowie der Richtlinien 91/155/EWG, 93/67/EWG, 93/105/EG und 2000/21/EG der Kommission.

SUR (2022): Vorschlag über eine Verordnung des Europäischen Parlaments und des Rates zur nachhaltigen Anwendung von Pflanzenschutzmitteln 2022/0196 (COD) – orig.: Proposal for a regulation of the European Parliament and of the Council on the sustainable use of plant protection products and amending Regulation (EU) 2021/2115, 2022/0196 (COD).