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# Pesticides can be a substantial source of trifluoroacetate (TFA) to water resources

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ABSTRACT

Through the application of C-$CF_3$-containing plant protection products (PPP) in agriculture, a substantial quantity of trifluoroacetate (TFA) can be formed and emitted. We here present estimations of TFA formation potentials from PPP across three important economical regions, namely Europe, the United States of America and China. PPP with TFA formation potential vary in type and use profile across those regions, but can be found throughout, with the estimated maximum TFA emissions ranging from 0 to 83 kg/km$^2$ per year. Therein, some PPP are only used for specific crops in specific regions, while others are used more widely. The importance of PPP as a TFA source is supported by the field data from a region in Germany, which revealed a significant increase in TFA groundwater concentrations with agriculture compared to other land uses. Substance-specific TFA formation rates and field studies are necessary to characterize the formation of TFA from precursors under environmental conditions and to rank and prioritize PPP of concern for potential (regulatory) action.

## 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of anthropogenic chemicals that are used in a broad range of industrial applications and consumer products (Wang et al., 2017). More than 200 uses have been identified and associated with over 1,400 PFAS (Glüge et al., 2020). PFAS are of particular concern due to the high persistence of themselves or their transformation products, which has led to practically irreversible environmental exposure (Cousins et al., 2022) and subsequently a broad range of adverse effects on human health and the environment (Kwiatkowski et al., 2020). Consequently, many PFAS are now internationally restricted and being phased out based on their inclusion in the Stockholm Convention (SCC, 2023) and a number of regional and national regulations. A restriction of the entire class of PFAS unless a specific use is proven essential for society has been proposed under REACH, the European chemicals regulation (ECHA, 2024a). However, active ingredients in pesticides or plant protection products (PPP) have been excluded from the proposed restriction (ECHA, 2023). Similarly, pesticides are regulated separately from other chemicals also in other major economic regions such as the United States of America (USA) and the People's Republic of China (PRC).

Ogawa et al. (Ogawa et al., 2020) reported that approximately 16 % of PPP are fluorinated and identified 424 organofluorine PPP in 2020. As of February 2024, 202 of 1934 entries in the Pesticide Properties DataBase (UH, 2024) contained a $-CF_3$ group. This smaller group are PFAS according to the revised definition by the Organisation for Economic Co-operation and Development (OECD) (Wang et al., 2021). A total of 143 of these entries contained a $-CF_3$ group linked to a carbon

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atom that is not fully fluorinated, making them potential parent compounds (*i.e.* precursors) for trifluoroacetate (TFA) formation. Of them, 39 substances are currently approved in the European Union, 48 are registered in the USA, and 68 are registered in China.

Introducing the $-CF_3$ group in a molecular structure can alter properties such as stability and lipophilicity, and increase bioavailability (Abula et al., 2020). As a side effect, if the $-CF_3$ group is linked to another carbon atom (C-$CF_3$), TFA can be formed as a major transformation product in biological and chemical processes. TFA is the perfluorocarboxylic acid (PFCA) with the shortest chain length and the final transformation product from a range of precursors. For example, degradation studies for the PPP flurtamone and flufenacet showed the formation of TFA as part of the approval process under the PPP Regulation (EC) No 1107/2009 (UBA, 2022). Also, during ozonation and in the OECD 302B test on inherent biodegradability of organic substances (Zahn-Wellens/EMPA test), the formation of TFA has been reported for the PPP tembotrione, flufenacet, flurtamone and fluopyram (Scheurer et al., 2017). Direct and indirect photolytic processes for four fluorinated pesticides in aqueous laboratory experiments also yielded TFA (Bhat et al., 2022). Increased TFA formation rates were observed with a pesticide containing a benzylic $CF_3$ group (penoxsulam) and one containing a $CF_3$-substituted heteroaromatic group (fluroxypyr). For penoxsulam, fluoride was also formed, which may be due to defluorination from the benzylic $CF_3$ group (up to 53 % depending on the aqueous photolysis conditions). This example shows that the presence of a C-$CF_3$ moiety in a compound does not necessarily imply a 100 % molar TFA yield upon its degradation. The microbial metabolism of fluorinated pesticides is characterized by highly inefficient catabolic processes that rarely ensure complete defluorination, leading to the formation of secondary fluorinated transformation products. Alexandrino et al., (2022) reported that in their investigations on $CF_3$-substituted PPP, certain dead-end metabolites still contained C-$CF_3$ moieties, suggesting that no TFA was formed. However, it is uncertain whether the study designs (e.g., test durations) and chemical analyses used in these studies were adequate to track potential TFA formation and thus whether the results are representative of real-world conditions. In contrast, TFA was detected as a transformation product of PPP in field studies, such as flurtamone (EFSA, 2017a), saflufenacil (EFSA, 2014), and tritosulfuron (EFSA, 2023).

Formation rates of TFA in terms of molar equivalents from $CF_3$-containing PPP-molecules in biotic and abiotic transformation studies are, however, still largely unknown. The German agrochemical industry association, *Industrieverband Agrar* (IVA), reported an average TFA formation rate in metabolism studies of approximately 0.3 per $CF_3$ moiety (range: <0.05–0.73) for 13 $CF_3$-containing pesticides (IVA, 2022). The studies are part of the approval of active substances of PPP in the EU. It is important to note that these formation rates could not be verified, as the review of most of the submitted data by the Rapporteur Member States (RMS) and the European Food Safety Authority (EFSA) is still in progress.

TFA is a PFAS (Wang et al., 2021) with continuously increasing concentrations in the environment (Cahill, 2022; Freeling et al., 2022; Pickard et al., 2020; Zhai et al., 2015) that are higher compared to many other PFAS (Björnsdotter et al., 2022; Janda et al., 2019; RIWA, 2022a, 2022b). TFA has been identified as a "substance from multiple sources" (Nödler and Scheurer, 2019). Atmospheric photooxidation of fluorinated refrigerants and propellants is a substantial diffusive source of TFA (Holland et al., 2021). Monitoring has shown that atmospheric deposition leads to ubiquitous contamination of the aquatic and terrestrial environment with TFA (Freeling et al., 2020a). In addition, industrial sites producing and using fluorochemicals including TFA, municipal and industrial waste and wastewater management facilities, and firefighting training sites, among others, may act as hotspots for TFA releases (Freeling and Björnsdotter, 2023; UBA, 2023). A comprehensive understanding of TFA's (eco)toxicological impacts has just started. While the European Food Safety Authority (EFSA) pointed out that an ecotoxicological risk assessment for TFA (as a metabolite of saflufenacil) could not be finalized due to data gaps (EFSA, 2023), Germany has recently added TFA (i.e., trifluoroacetic acid and its inorganic salts) to the registry of intentions for harmonized classification and labelling under the EU Classification, Labelling and Packaging (CLP) regulation, with a proposal for addition of reproductive toxicity (Repr. 1B, H360Df), persistent, mobile and toxic (PMT, EUH450) and very persistent, very mobile (vPvM, EUH451) hazard classes (ECHA, 2024b, 2024c). The German Environmental Agency (UBA) has already introduced limits to drinking water (60 μg/L) based on a possible liver toxicity through the activation of the enzyme alanin-amino-transferase (UBA, 2022). UBA also proposed an environmental quality standard (EQS) of 21 μg/L (annual average) for inland surface waters (UBA, 2020). TFA is very persistent and very mobile in the environment (Freeling et al., 2020a; Scheurer et al., 2017), and thus has a high likelihood of contaminating (ground)water resources. Due to these properties, it is extremely challenging to remove TFA from water resources (Neuwald et al., 2022; Scheurer et al., 2017). Thus, it is urgent and critical to address TFA from all sources to avoid further accumulation in the environment.

In an earlier study, the TFA pollution of waterbodies in Germany and its sources were spatially and quantitatively analyzed to assess the contributions of various possible input pathways for TFA. The application of PPP was considered to be the biggest source of TFA to the aquatic environment in Germany (UBA, 2023). This was the starting point for this study, in which we assess PPP as a potential source of TFA in groundwaters of Europe and the USA (mass-based estimates) and in China (qualitative approach). Due to the very low soil sorption affinity of TFA, we here considered groundwater as a key receiving phase of TFA formed in agricultural soils. For a more detailed evaluation, highly resolved monitoring data were used to correlate TFA concentrations in groundwater to land use categories and nitrate concentrations for a German federal state with a PPP usage typical for Germany. Finally, implications for future research and action are discussed.

## 2. Materials and methods

### 2.1. Estimation of TFA formation potential from PPP

For Europe, a European-wide dataset of the estimated quantities of 152 PPP applied on crops (called "emissions") was taken as a basis (Udias et al., 2023, 2022). The estimates were derived from data on the PPP sales provided by eight European countries and extrapolated to other European countries applying regression models under consideration of land use and climate variables. The authors reported total amounts (in kg/year) of each PPP within the EU corresponding to level 3 of the European Nomenclature of Territorial Units for Statistics, NUTS3 (Eurostat, 2024a). As the estimates were based on heterogeneous data reported during 2011 to 2017, the authors stressed that the emissions do not reflect a specific year but should be considered as reference of PPP usage during this period (Udias et al., 2023).

Out of the 152 PPP, 18 contained one or more C-$CF_3$ groups (acrinathrin, benfluralin, bifenthrin, cyflufenamid, diflufenican, fluazifop-*p*-butyl, fluazinam, flufenacet, fluopicolide, flurtamone, isoxaflutole, metaflumizone, oxyflurfen, penoxsulam, picolinafen, tau-fluvalinate, tembotrione, trifloxystrobine). Information on the date of first approval and the current registration status is included in the Supporting Information, Table S1. Based on the reported emission estimates for these C-$CF_3$-containing PPP, we calculated the TFA formation potential assuming stoichiometric TFA formation in the same year. This worst-case scenario was chosen due to the lack of robust data on TFA formation rates of C-$CF_3$-containing PPP under environmentally relevant conditions. To consider an alternative, less conservative approach, we compare these estimates with calculations using an average TFA formation rate of 30 %, based on the above-mentioned estimate.

Using ArcGIS Pro, we joined the absolute TFA formation potential per NUTS Level 3 region (in kg/year) with a GISCO statistical unit dataset representing the NUTS and statistical regions by means of multipart polygon, polyline and point topology (Eurostat, 2024b). Because the NUTS legislation has been periodically amended, we used the "NUTS 2013" classification as in the PPP emission dataset. The TFA formation potential per NUTS Level 3 region was normalized to the region's area (km$^2$) (=relative TFA formation potential).

For Switzerland, data on the sales of individual PPP reported by the Swiss Federal Office for Agriculture were used. Out of the 18 PPP considered from the European Union dataset, 14 PPP were also approved and sold in Switzerland. The Swiss data were averaged for the years 2011 to 2017 to align with the dataset for the European Union. To report TFA formation potential (also stoichiometric worst-case scenario) per NUTS Level 3 region, *i.e.* cantons of Switzerland, it was assumed that PPP were used evenly and only on agricultural areas. The average percentage of agriculture per canton during 2011 to 2017 (excluding summer pastures) was taken from the Farm Structure Survey of the Swiss Federal Statistics Office (BFS, 2024).

For the USA, the estimated amounts (EPest-high method) of 408 PPP applied in 3,037 counties in 2017 reported from the Pesticide National Synthesis Project were taken as a basis (USGS, 2024). For the 48 PPP containing at least one C-CF$_3$-group, the TFA formation potential was calculated as for the European data. To report data at the county level and create joins in ArcGIS Pro, the Federal Information Processing Standard (FIPS) code was used.

For China, where no national data could be obtained, we used fomesafen application rate estimates for cotton from the PEST-CHEMGRIDS dataset for 2015 (Maggi et al., 2020, 2019). Application rates in kilogram per hectare per year at 5 arc-min resolution were summed up for all individual grid cells in China with a value $> 0$.

### 2.2. Contribution of PPP compared to other TFA sources

Public monitoring data on TFA and nitrate in groundwater of the German state of Baden-Württemberg (2016 to 2022) was provided by the Baden-Württemberg State Institute for the Environment (LUBW) (LUBW, 2024). To elucidate a potential influence of land use on the TFA concentration in groundwater samples, the percentage shares of agricultural land use were derived for each groundwater body located within Baden-Württemberg using GIS analysis. Information on the identities and spatial extents (in x- and y-direction) of groundwater bodies defined under the Water Framework Directive (WFD) was retrieved from the German Federal Agency for Cartography and Geodesy. The information was merged with land cover data from the CORINE Land Cover (CLC) project (reference year: 2018) (CLMS, 2024). Subsequently, the percentage share of agriculture (CORINE land cover classes: arable land (2.1); permanent crops (2.2); heterogeneous agricultural land (2.4)) on total land was calculated for each groundwater body. Pasture (CORINE land cover class 2.3) was not considered in the evaluations as PPP are generally not applied to areas in Germany which are intended to be grazed by domesticated livestock.

## 3. Results and Discussion

### 3.1. Estimated TFA formation potential from PPP in Europe

Based on the estimated amounts of 152 PPP sold in 1,360 European regions between 2011 and 2017 (Udias et al., 2023), Fig. 1 shows the relative TFA formation potential of the 18 C-CF$_3$-containing PPP discussed in the aforementioned study. The regions correspond to level 3 of the European Nomenclature of Territorial Units for Statistics, NUTS3, with an average population size of 150,000 to 800,000 (Eurostat, 2024a). Assuming a molar TFA yield of 100 % and 30 %, the median total TFA formation potential per NUTS Level 3 region was 0.9 kg TFA per square kilometer (km$^2$) per year (mean 1.9, maximum 83) and 0.3 kg TFA (km$^2$ × year) (mean 0.6, maximum 25), respectively. With a mean of 3.5 kg TFA (km$^2$ × year), the maximum TFA formation potential was highest in Germany, followed by the United Kingdom (3.0) and Poland (1.7), and lowest in Finland and Ireland (0.1 each). Detailed data on a NUTS3 level is included in the Supporting Information, Table S2 (100 %) and Table S3 (30 %).

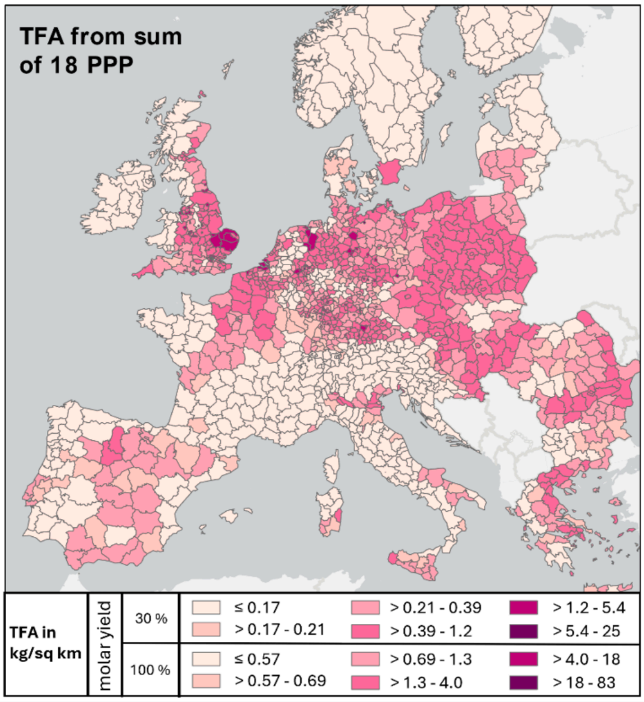

**Fig. 1.** Total TFA formation potential from PPP in Europe per year, based on the estimated amounts of 18 C-CF$_3$-containing PPP sold in each NUTS Level 3 region of the EU between 2011–2017 (Udias et al., 2023) and sales data from Switzerland (2011–2017), assuming a molar TFA yield of 30 % and 100 %.

Based on a molar TFA yield of 30 % or 100 % a total of 970 t or 3,200 t TFA per year could be emitted due to application of the 18 C-CF$_3$-containing PPP with reported sales and emission estimates. The largest contributions come from Poland (17 %), Germany (16 %), Spain (10 %), France (9 %) and the United Kingdom (9 %). The five PPP representing the most important sources regarding PPP-induced TFA load on a European scale can form a maximum (100 % molar TFA yield) of 657 t TFA/year (flufenacet), 627 t TFA/year (diflufenican), 482 t TFA/year (fluazinam), 364 t TFA/year (isoxaflutole), and 324 t TFA/year (oxyfluorfen).

As shown in Fig. 2A, flufenacet-induced TFA is of higher relevance in Northern Europe (on average 0.5 to 1.5 kg/km$^2$ in Germany, United Kingdom, Belgium, Poland, and the Netherlands with a 100 % molar TFA yield) compared to Southern Europe (on average $<$ 0.06 kg/km$^2$ in Spain, Italy, and Greece with a 100 % molar TFA yield). In contrast, oxyfluorfen is more important with regard to TFA emissions in Southern Europe (on average 0.2 to 0.5 kg/km$^2$ in Greece, Portugal, and Cyprus with a 100 % molar TFA yield) compared to Northern Europe (no reported sales in Germany, the United Kingdom and other Northern European countries) (Fig. 2B). While flufenacet is used to control grasses and broad-leaved weeds in crops such as winter cereals, oxyfluorfen is used to control certain annual weeds in nuts, fruits, vegetables, and cotton (BVL, 2024). In addition to the predominant crop types, the dual approval process of PPP in the European Union can explain differences between the European regions. While active substances are approved on a European level, PPP commercial products containing one or more active substances are authorized at the Member State level. PPP containing flufenacet, diflufenican, and fluazinam are authorized in 25 to 27 Member States, whereas PPP with oxyfluorfen are only authorized in ten Southern European countries (EC, 2024).

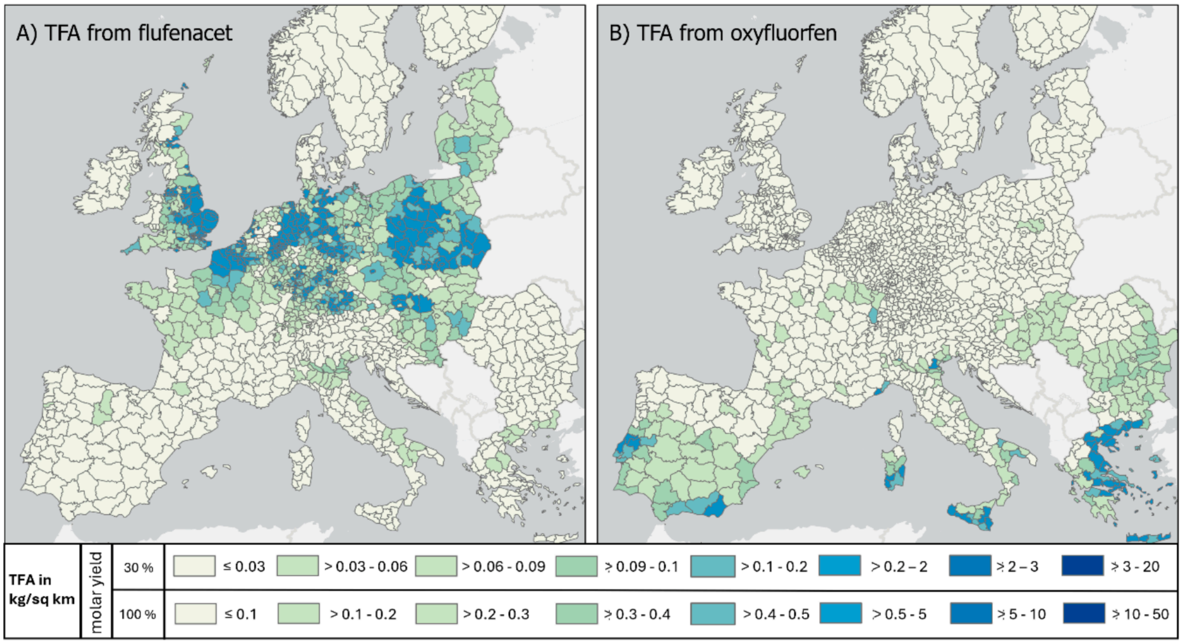

**Fig. 2.** Relative TFA formation potential in Europe per year from A) flufenacet and B) oxyfluorfen, based on the estimated amounts sold in each NUTS Level 3 region of the EU (Udias et al., 2023) and sales data from Switzerland (2011–2017), a molar TFA yield of 30 % and 100 %.

The European-wide dataset of the estimated quantities of selected PPP applied on crops, which was used to calculate the TFA formation potential, include land use and climate variables in the applied regression models. However, factors such as agricultural practices, soil types and associated PPP application rates and use frequency were not considered. Comparing maximum approved quantities of various PPP per hectare of agricultural land, in particular fluazinam-induced TFA, can be of high local relevance (UBA, 2022). As an example, fluazinam (relative molecular ratio of the two TFA moieties: 0.49) quantities can be applied as high as 2000 g/(hectare × year) compared to flufenacet (relative molecular ratio of the TFA moiety: 0.31) with 250 g/(hectare × year), considering the active substance content of commercial PPP, recommended dose and number of treatments approved in Germany (BVL, 2024). However, on a European scale, flufenacet remains the PPP of highest relevance regarding TFA inputs to the environment due to its widespread use.

Additional uncertainties are related to the fact that the used pesticide emission dataset is based on the heterogeneous sales data reported by eight Member States and extrapolated to all European regions using regression models and based on the assumption that the amounts of PPP sold are equivalent to the amounts used in the fields. A comparison of the estimated TFA formation potentials in Germany (mean 2016–2019), showed a good agreement of the total TFA formation potential with 525 t/year (this study) versus 521 t/year (derived using sales volumes of PPP, no regression models), versus 434 t/year (derived using the application estimates for certain PPP and field crops) (UBA, 2023). The authors of the pesticide emission dataset underline that the predictions have a higher degree of uncertainty in the Northern and Eastern European countries compared to the Western and Southern European countries (Udias et al., 2023, 2022). This is because the Northern and Eastern European countries are underrepresented among the eight reference countries with available data, and the PPP usage patterns may vary substantially. The comparison of the emission estimates with aggregated data provided by EUROSTAT and with independent data for the United Kingdom on a NUTS 3 level showed an error typically within one order of magnitude (Udias et al., 2023).

To calculate the theoretical TFA formation potential from a specific site in a given year, a 100 % molar TFA yield was assumed as a worst-case scenario and complemented with a 30 % molar TFA yield scenario as suggested by the German agrochemical industry association. Due to lack of publicly available data, we could neither consider the molar formation potentials nor the kinetics of the transformation reactions. Flufenacet is one of the few C-$CF_3$-containing PPP for which laboratory results on the TFA formation during chemical oxidation (ozonation) and aerobic biodegradation (OECD 302B: Zahn-Wellens test) are publicly available (Scheurer et al., 2017). The Zahn-Wellens test is used for testing the inherent biodegradability of organic substances. It has also been successfully applied to elucidate the formation of soluble, weakly adsorbing, non-volatile transformation products during the aerobic biodegradation of precursor compounds, as also shown for sulfamate (Freeling et al., 2020b). In the assessment report for the re-approval of flufenacet, TFA was identified as a soil metabolite with an estimated maximum occurrence fraction of about 82 % (of total applied on a molar basis) in the laboratory studies on aerobic soils (EFSA, 2017b). For other PPP, needed information about the transformation product formation in soil is not available, as underlined in the peer review of the pesticide risk assessment of tritosulfuron (EFSA, 2023).

It is important to note that relocation processes of PPP, intermediates, and TFA (e.g. due to groundwater and surface water transport) after PPP application were not considered in our estimations. This can also lead to certain uncertainties in the theoretical TFA formation potential of a specific region/county in a given year.

### 3.2. Estimated TFA formation potential from PPP in the USA

Based on the estimated amounts (EPest-high method) of PPP applied in 3,037 counties of the continuous (excluding Alaska and Hawaii) United States in 2017 (USGS, 2024), Fig. 3 shows the relative TFA formation potential of 48 C-$CF_3$-containing PPP. Assuming a molar TFA yield of 30 % and 100 %, the median TFA formation potential per county was 0.1 kg (km$^2$ × year) (mean 0.3, maximum 5), and 0.3 kg/(km$^2$ × year) (mean 0.9, maximum 18), respectively. This is in the same order of magnitude but slightly lower than in Europe. Detailed data on a county level is included in the Supporting Information, Table S4 (100 %) and Table S5 (30 %). Counties with the highest relative TFA formation

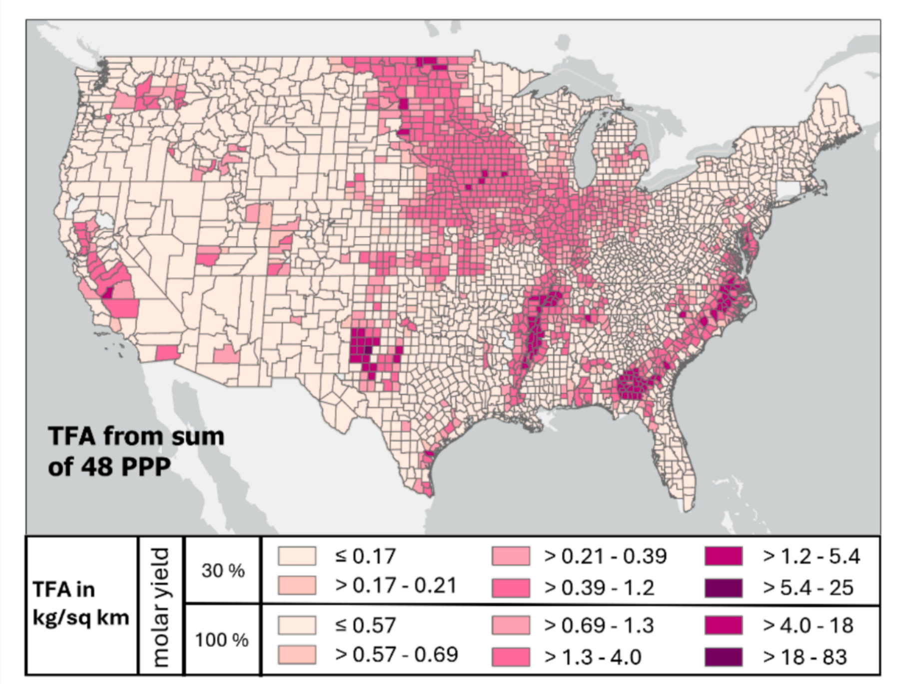

**Fig. 3.** *TFA formation potential from PPP in the continuous USA (excluding Hawaii and Alaska), based on the estimated amounts of 48 C-CF$_3$-containing PPP in each county in 2017* (USGS, 2024)*, assuming a molar TFA yield of 30 % and 100 %.*

potential are located within the USDA farm resource regions Fruitful Rim, Heartland, Mississippi Portal, Prairie Gateway, and Southern Seaboard (USDA, 2024a).

Our estimations indicate that based on a molar TFA yield of 30 % and 100 %, up to 1,500 t and 5,000 t TFA, respectively, could be formed and emitted from PPP throughout the continuous USA in a single year (Fig. 3). The five most important PPP, which account for around two-thirds of this formation potential, can form a maximum of 1,537 t TFA/year (trifluralin), 811 t TFA/year (fomesafen), 605 t TFA/year (ethalfluralin), 219 t TFA/year (fluometuron), and 213 t TFA/year (bifenthrin). In the USA, these PPP are mainly applied in cotton, soybeans as well as in vegetables and fruits. Fluometuron is only approved for cotton, explaining its significance in the southern-tiered "Cotton Belt" States, (USDA, 2024b) in contrast to the country-level relevance of trifluralin (Fig. 4). Apart from fluometuron, which is authorized in Greece and Spain, none of the other four top PPP are currently registered for use in the European Union, highlighting the regional differences of PPP as potential precursors to TFA.

Current monitoring studies on TFA in surface and groundwaters in the USA are scarce. Cahill (2022) investigated the increase of TFA concentrations in surface waters in California over 23 years (Cahill, 2022). This was accomplished by re-sampling a transect originally sampled in 1998 (Wallington and Schneider, 1994). The author reported an approximate 6-fold increase in TFA concentrations in the investigated surface waters (median TFA concentration: 0.18 μg/L; range 0.02–2.79 μg/L). According to the author, the increase was mainly attributed to increases in atmospheric depositions, while the usage of PPP in the study area was considered to be a non-relevant TFA source.

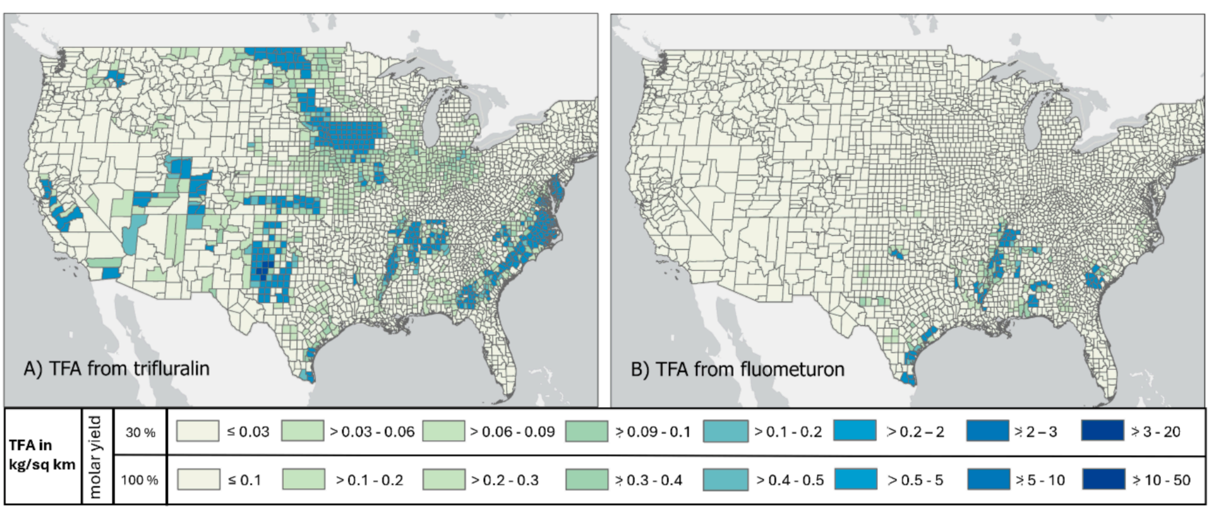

**Fig. 4.** *Relative TFA formation potential in the USA (excluding Hawaii and Alaska) from A) trifluralin and B) fluometuron, based on the estimated amounts applied in each county in 2017* (USGS, 2024)*, assuming a molar TFA yield of 30 % and 100 %.*

### 3.3. TFA formation potential from PPP in China

As of April 2024, a total of 68 PPP containing one or more C-$CF_3$ have been registered in China. Among them, 13 PPP have more than 100 registered formulation products. The two most widely used C-$CF_3$ containing PPP are fomesafen and penoxsulam with 363 and 360 registered formulations, respectively. Fomesafen is used in soybean, cotton and potato crop production, whereas penoxsulam is used in paddy field weeding. Unfortunately, we were not able to acquire the necessary use and application data to allow for sufficiently resolved mass-based estimates of TFA formation. Using the PEST-CHEMGRIDS dataset (Maggi et al., 2020, 2019), which contains data for fomesafen, a formation potential of up to 180 t TFA/year (molar TFA yield 30 %) and 604 t TFA/year (molar TFA yield 100 %) across China was calculated from this single PPP for the crop cotton. The TFA formation potential from PPP in China may thus be in a similar order of magnitude as in the US, where we estimated a maximum of 811 t TFA/year from fomesafen.

Similar to other regions of the world, TFA concentrations in Chinese water bodies substantially increased over the last decades (Zhai et al., 2015). However, comprehensive groundwater monitoring data are lacking. Still, available data from surface waters suggest that TFA is ubiquitous and of concern in many Chinese water bodies, as concentrations of TFA in 36 sampled waters ranged from 0.03 to 0.29 μg/L in 2007 (Yang et al., 2010). In urban landscape waters, TFA concentrations increased from 0.023 to 0.098 μg/L in 2002 to 0.35–0.83 μg/L in 2012 (Zhai et al., 2015). In regions with fluorochemical production industries, concentrations in surface waters were even higher. For example, in the industrially affected Jinan region in 2016, TFA concentrations in surface waters were 0.93 ± 0.056, 1.0 ± 0.079, and 0.590 ± 0.072 μg/L for the Tuhai River, the Yellow River, and the Xiaoqing River, respectively (Xie et al., 2020).

### 3.4. The contribution of PPP compared to other sources

The estimations of potential PPP-induced TFA emissions were complemented with field data to further evaluate evidence of PPP as a TFA source, using a comprehensive groundwater monitoring dataset from the German state Baden-Württemberg. In total, 1,598 TFA data points from 1,011 measurement sites were available from 2016 to 2022 (LUBW, 2024). To differentiate between sites predominated by agricultural land use and other types of land use, information on the identities and spatial extents of groundwater bodies defined under the Water Framework Directive (WFD) was merged with land cover data from the CORINE Land Cover (CLC) project.

Fig. 5A shows censored boxplots of the TFA concentration grouped by a proportion of agricultural land use $\leq$ 50 % and $>$ 50 %. A non-parametric two-sample permutation test showed a significantly ($p < 0.001$) higher average TFA concentration in the samples of groundwater bodies located in agricultural areas (mean = 1.59 μg/L; median = 1.1 μg/L; $n = 411$; proportion of agricultural land use: $>$ 50 %) than in the samples of groundwater bodies located in areas with lower degrees of agricultural activity (mean = 1.14 μg/L; median: 0.61 μg/L; $n = 1187$; proportion of agricultural land use: $\leq$ 50 %). The latter median concentration is close to the average range of atmospheric deposition reported from precipitation in Germany (Freeling et al., 2020a). The significantly higher average concentration of TFA at the sites with a higher than 50 % proportion of agricultural land use indicates that agriculture contributes to elevated TFA concentrations.

Because the spatial extents of groundwater bodies were only considered in x- and y-direction and no hydrogeological information was reviewed, the land use characteristics of the different groundwater catchment areas could only be determined as a rough approximation. In addition to the land cover data, elevated nitrate concentrations indicate agricultural land use (Wick et al., 2012). For 1,577 out of the 1,598 samples with reported TFA concentrations, nitrate measurements were also available. Consequently, the relationship between TFA and nitrate concentration was evaluated as a second approach for investigating a potential link between agriculture and TFA concentration. The nitrate values were grouped into classes included in the reporting under the European Nitrates Directive (EEA, 2024). A non-parametric two-sample permutation test showed a significantly ($p < 0.0001$) higher average TFA concentration in the groundwater samples containing elevated nitrate concentrations $>$ 25 mg/L (mean = 1.84 μg/L; median = 1.30 μg/L; $n = 556$) than in the samples containing $\leq$ 25 mg/L of nitrate (mean =

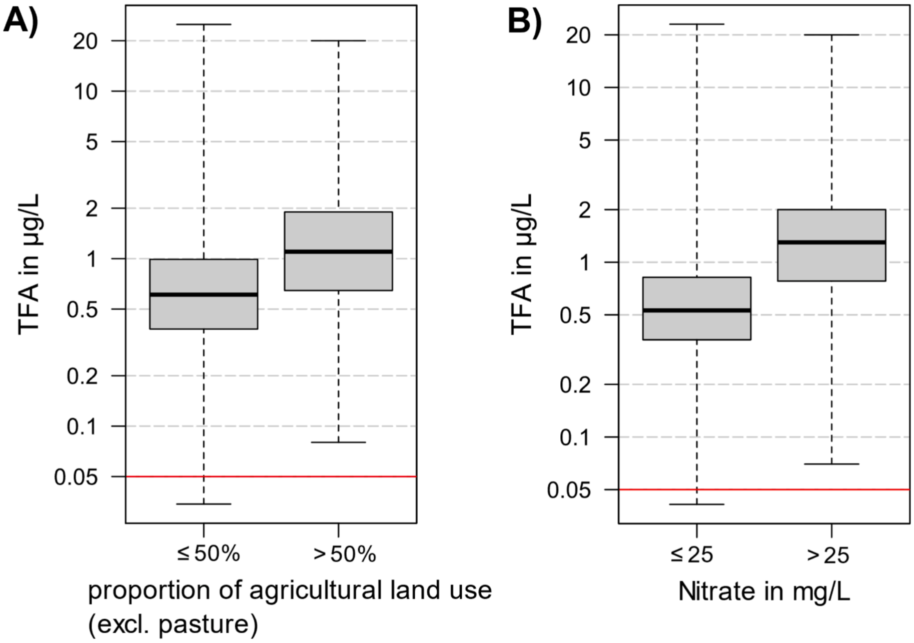

**Fig. 5.** A) Censored boxplots of the TFA concentration grouped by proportion of agricultural land use $\leq$ 50 % and $>$ 50 % ($n = 1598$). B) Censored boxplots of the TFA concentration with data grouped by the nitrate concentration of the samples ($n = 1577$). Percentiles below the limit of quantification were estimated using regression on order (ROS) statistics. The horizontal red line depicts the LOQ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.92 µg/L; median = 0.53 µg/L; $n = 1021$) (Fig. 5B). These results also indicate that agricultural land use is linked to elevated TFA concentrations.

In addition to C-$CF_3$-containing PPP, the application of liquid manure can also be a potential source of TFA in agricultural areas, given the reported high levels of TFA in plants (EURL, 2017). Analyses of a small number of cattle and pig slurry samples as well as of fermentation residues showed a TFA content of approximately 100 µg/L (UBA, 2023). Based on application volumes, liquid manure could be of local relevance, but C-$CF_3$-containing PPP are considered the more important TFA source in agricultural areas on a larger country-level scale (UBA, 2023).

Besides atmospheric deposition and runoff from agricultural land, industrial discharges can be a significant source for TFA in ground and surface water (Freeling and Björnsdotter, 2023). As such, the groundwater dataset used in our present study includes sampling sites which are likely influenced by a fluorochemical industrial plant close to the city of Bad Wimpfen. Industrial discharges of this plant into the Neckar River resulted in surface water TFA concentrations of up to 140 µg/L as well as elevated TFA concentrations in the groundwater near the city of Heidelberg (Scheurer et al., 2017). In fact, the three groundwater bodies with the highest average TFA concentration in the dataset are all located in the Neckar River catchment downstream of the plant. Despite this known non-agricultural point source of TFA, we decided against excluding data from specific groundwater sampling sites from the statistical analysis to minimize bias.

TFA formation and release to water bodies does not solely depend on the chemical structure of the PPP, but also on local conditions such as the soil type and hydrological conditions (Lischeid et al., 2023). Consequently, local case studies investigating direct causal relationships, timely and spatially resolved, combining measurements and modelling data are needed to understand the underlying processes. Moreover, case studies investigating the link between PPP application and TFA levels in crops could further consolidate the hypothesis of PPP as a significant TFA source. For example, the European Reference Laboratories for Residues of PPP analyzed TFA in more than 1,600 food samples from 2016 and 2017. The results show that the overall frequency of TFA findings exceeding the reporting limit is clearly higher in conventionally produced products compared to organic food (EURL, 2017). The use of C-$CF_3$-containing PPP in conventional farming is a potential explanation for this finding.

## 4. Implications for future research and action

Through the application of C-$CF_3$-containing PPP, which vary regionally in type and application rate, PPP are a widespread, diffuse, and continuous source of TFA to water resources. We here presented a first estimation of the TFA formation potentials across three important economical regions (Europe, USA, China). However, a substantial data gap persists relating to the actually applied PPP across many regions, and these estimates can only be a first step to capturing the full extent of the issue of PPP as a source of TFA.

Importantly, actual TFA formation rates are lacking for most PPP and are urgently needed to better assess the actual formation potential of individual PPP. With known formation rates, only a small number of PPP may need to be restricted to result in lower TFA emissions. It should be noted that the test durations used in simulation degradation studies may be insufficient to adequately address the often-complex microbial degradation pathways of these biologically recalcitrant substances and to identify small fluorinated dead-end metabolites such as TFA, which may escape detection. Further research is required to determine whether modifications to current degradation tests, such as OECD 307 for the aerobic and anaerobic transformation of chemicals in soil, are necessary for a more accurate assessment of TFA and other transformation products.

Single PPP, such as fluazinam and oxyfluorfen, can be of high relevance and potential concern for specific regions and crops, whereas other PPP, such as flufenacet, may be more widely used in a generic manner. Identifying those PPP that have a high TFA formation rate under different regional conditions (i.e., climate, soil type, crop type, etc.), would be crucial to curbing TFA emissions from PPP in a targeted manner both regionally as well as more broadly.

Similarly, analysis of TFA should be included in regular water and soil monitoring programs to close the widespread data gap on the TFA occurrence, also in relation to agricultural inputs. While analytical methods to enable such measurements exist (e.g. ion exchange chromatography coupled to mass spectrometry) (Freeling et al., 2020a; Schorr et al., 2023), harmonization and standardization is still ongoing.

Because TFA is very persistent and very mobile, it will remain in the environment long after chemical management measures take place. Therefore, regulatory actions that consider all (major) TFA sources are urgently needed. The widespread use of large quantities of PPP with a TFA formation potential may be one of those sources. To date, to the best of our knowledge, PPP have not been restricted based on their TFA formation potential anywhere in the world. We recommend that the formation of TFA and other highly persistent and mobile transformation products should be considered during the development and authorization of PPP. For example, flufenacet is not only the most significant PPP with respect to TFA emissions in Europe, but also one of the few substances for which a substantial TFA formation has been proven in laboratory studies. Consequently, not prolonging its approval would be an important first step towards decreasing TFA emissions from PPP use. Thereby, regrettable substitution of TFA-forming PPP with potentially more hazardous or otherwise problematic compounds needs to be avoided, by carefully considering the hazards of individual alternatives and all their transformation products.

## CRediT authorship contribution statement

**Hanna Joerss:** Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Finnian Freeling:** Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Stefan van Leeuwen:** Writing – review & editing, Investigation, Conceptualization. **Juliane Hollender:** Writing – review & editing, Investigation, Data curation. **Xingang Liu:** Investigation. **Karsten Nödler:** Writing – review & editing. **Zhanyun Wang:** Writing – review & editing. **Bochi Yu:** Investigation. **Daniel Zahn:** Writing – review & editing. **Gabriel Sigmund:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2024.109061.

## Data availability

All data used are made available in the supporting information.

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