Trifluoroacetate (TFA) and Pesticides:

Discussed during EQI Breakout Session, April 8, 2025

Article of interest that was published in November 2024:

Joerss et al., 2024: Pesticides can be a substantial source of trifluoroacetate (TFA) to water resources - ScienceDirect

Highlights

- Several plant protection products can form trifluoroacetate.
- Formation potential varies due to region, crop type, and parent compound.
- Field evidence confirms a significant contribution to overall levels in groundwater.

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.

Selected section:

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

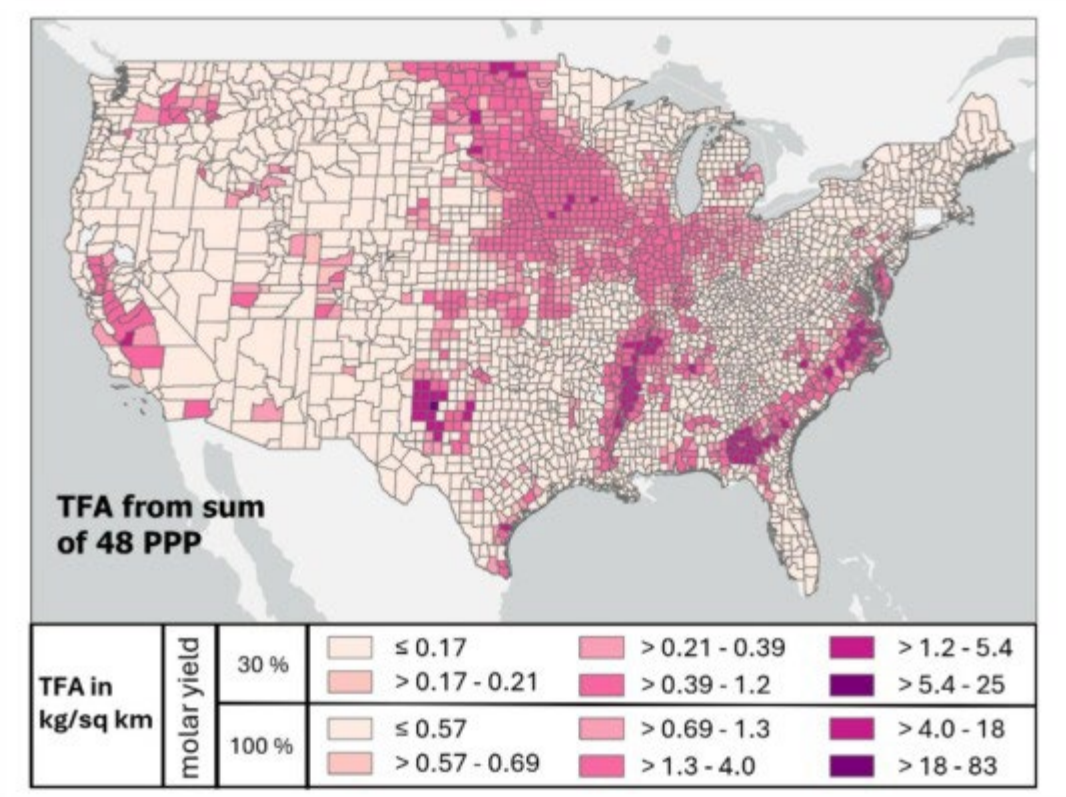

Fig. 3. *TFA formation potential from PPP in the continuous USA (excluding Hawaii and Alaska), based on the estimated amounts of 48 C-CF_3-containing PPP in each county in 2017* (USGS, 2024)*, assuming a molar TFA yield of 30 % and 100 %.*

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.

Given that the article described above cited the publication by Thomas Cahill (Arizona State University), it is of interest to consider that publication (2022) and a more recent study by Cahill published in 2024:

Cahill, 2022: **Increases in Trifluoroacetate Concentrations in Surface Waters over Two Decades | Environmental Science & Technology**

Abstract:

Trifluoroacetate (TFA) is a persistent perfluorinated alkanoic acid anion that has many anthropogenic sources, with fluorocarbon refrigerants being a major one. After an initial burst of research in the late 1990s and early 2000s, research on this ubiquitous pollutant declined as atmospheric emissions of the precursor compounds grew rapidly. Thus, there is little contemporaneous information about the concentrations of TFA in the environment and how they have changed over time. This research determined the change in TFA concentrations in streams by resampling a transect that was originally sampled in 1998. The transect was designed to determine the regional distribution of TFA both upwind and downwind of major metropolitan areas in Northern California as well as a set of globally remote sites in Alaska. The results showed that TFA concentrations increased by an average of 6-fold over the intervening 23 years, which resulted in a median concentration of 180 ng/L (range 21.3–2790). The highest concentrations were found in streams immediately downwind of the San Francisco Bay Area, while substantially lower concentrations were found in the upwind, regionally remote, and globally remote sites. The C_3 to C_5 perfluorinated alkanoic acids were also investigated, but they were rarely detected with this methodology.

This publication includes the following statement in the section ' Spatial Distribution of TFA':

Another potential source of TFA is pesticides that are used in the Central Valley. These chemicals may undergo atmospheric transport to the small watersheds before being converted to TFA. While this may be occurring, it is unlikely a dominant driver of the observed TFA concentrations since the concentrations from agriculture would be expected to highest downwind of the Central Valley, which was not observed in this study.

In the 2024 article, Cahill makes observations that do link pesticide use in agriculture to elevated TFA concentrations in water.

Cahill, 2024: Assessment of Potential Accumulation of Trifluoroacetate in Terminal Lakes | Environmental Science & Technology

Abstract:

Trifluoroacetate (TFA) is the anionic form of the shortest perfluorocarboxylic acid (PFCA) and is ubiquitous in the environment at concentrations that are typically much higher than those of other PFCAs. As a stable and nonvolatile anion, it is expected to accumulate in terminal lakes in endorheic basins. This research sampled eight terminal lakes in the Western United States to determine the degree to which TFA is concentrating in these lakes and compare the data to samples collected from three of these lakes 25 years ago. The first observation was that three of the six terminal lakes sampled had higher TFA concentrations than their input streams, while the last two lakes lacked surface water inputs at the sampling time. The TFA concentrations in Mono Lake effectively remained constant over 25 years despite the input stream concentrations increasing 6.5-fold. In contrast, Pyramid Lake concentrations increased approximately the expected amount based on a simplistic analysis of input flows and concentrations. An additional observation was that lakes in basins with agricultural activity appeared to have higher TFA concentrations, which suggests an agricultural input.

This article includes the following paragraph:

One observation was that basins with significant agricultural activity appeared to have higher concentrations of TFA. Some pesticides are known sources of TFA (10) and many more contain a trifluoromethyl group attached to a carbon (36) that might form TFA upon degradation. In particular, the high concentrations in the Salton Sea may have significant agricultural inputs due to the extensive and year-round agricultural activity in the basin. A recent publication has demonstrated the importance of presumed agricultural inputs of TFA by showing a pronounced seasonal trend in TFA concentrations in the Stever River, Germany, that corresponded to pesticide applications in the catchment. (11) Additionally, the Salton Sea may have been accumulating TFA from agricultural activity since the 1960s when some of the fluorinated pesticides (e.g., trifluralin) were introduced. More studies are

needed to investigate the relevance of agriculture (i.e., pesticide application) as a source of TFA in the aquatic environment and to determine the seasonal patterns of these emissions.