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ENVIRONMENTAL MODELING OF TRIFLUOROACETIC ACID (TFA) ORIGINATING FROM HYDROFLUOROLEFINS

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1.0 BACKGROUND

Ramboll, on behalf of Honeywell Performance Materials & Technologies (Honeywell), has conducted an environmental fate and transport modeling study to provide a simple characterization of trifluoroacetic acid (TFA, CAS 76-05-1) in the freshwater aquatic environment resulting from the degradation of specific fluorinated refrigerant gases emissions and subsequent atmospheric deposition through a case study for the Rhine River basin.

PFAS are a large class of thousands of chemicals that are commonly used globally. Due to their highly persistent nature PFAS are increasingly detected as environmental pollutants and certain PFAS can be linked to negative effects on human health.

An Annex XV REACH Restriction proposal[1] prepared by the European Union (EU) Competent Authorities from Denmark, Germany, the Netherlands, Norway, and Sweden was submitted to ECHA on 13 January 2023. The proposal introduces a comprehensive set of actions to address the use of and contamination with PFAS. It aims to reduce PFAS emissions into the environment and make products and processes safer for people by phasing out the use of PFAS in the EU, unless it is proven essential for society. On 22 March 2023 ECHA announced a six-month public consultation on the PFAS Annex XV Restriction proposal, which will run from 22 March 2023 until September 2023. The consultation is open to anyone with information on PFAS relevant to risks, socio-economic aspects, and alternative substances. ECHA’s scientific Committee for Risk Assessment (RAC) and for Socio-Economic Analysis (SEAC) will use the consultation input to evaluate the proposed restriction and to form an opinion and make decisions on the extent and implementation of use derogations.

Honeywell is a global manufacturer and importer of various fluorinated gases to the EU, including hydrofluorocarbons (HFC) and hydrofluoroolefins (HFO) and their mixtures (blends), primarily used in refrigeration, heating, ventilation and air conditioning (RHVAC), mobile air conditioning (MAC), thermal management systems (TMS) in electric vehicles (EV), as propellants in metered-dose inhalers (MDI) and blowing agents in insulation foam applications.

2,3,3,3-tetrafluoropropene [HFO-1234yf; CAS 754-12-1], the key MAC refrigerant, degrade in the atmospheric environment to trifluoroacetyl fluoride which then hydrolyses to form TFA. The high water solubility of TFA together with its ability to spread rapidly in the environment via the water cycle makes it widespread and ubiquitous in nature. TFA does not appear to accumulate in humans or animals, unlike some other PFAS that are known to accumulate in the fatty tissue of mammals.[2] However, given its widespread presence in the water systems there is potential for contamination of water and consequently drinking water.

Ramboll performed a fate and transport modeling study to assess the fate and transport of TFA in the freshwater aquatic environment resulting from the emission and atmospheric degradation of HFO-1234yf and subsequent atmospheric deposition in the Rhine River basin; the Rhine River basin was selected as a case study as it represents a prominent watershed in western Europe with a large population.

The methods and results of the modeling study are provided in the following sections.

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[1] Version 2, uploaded 22nd March 2023 can be found here: https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea

[2] Solomon, K. R., et al. 2016. "Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols." Journal of Toxicology and Environmental Health, Part B 19(7): 289-304.

2.0 ESTIMATION OF HFO AIR EMISSIONS AND TFA DEPOSITION

While the fluorinated gas/refrigerant 2,3,3,3-tetrafluoropropene (HFO-1234yf)[3] and its predecessor 1,1,1,2-tetrafluoroethane (HFC-134a)[4] are both anthropogenic sources for the atmospheric formation of TFA, there is also strong evidence that TFA is a naturally occurring substance.[5] TFA is formed in the atmosphere and subsequently reacts and deposits into the water and soil, eventually entering marine systems. This study was conducted based on the assumption of constant and ongoing HFO-1234yf emissions, which through atmospheric degradation in turn leads to a constant deposition of TFA.

2.1 Air Emissions of HFO-1234yf

The projected annual emissions rate of HFO-1234yf from its use as a cooling agent in MACs in the European vehicle fleet was obtained from the 2023 REACH Dossier Chemical Safety Report (CSR).[6] This includes releases during MAC service life, leakage, end-of-life recovery and MAC filling and re-fueling, and formulation. Table 1 presents the estimated distribution of emissions from these categories. The projected total emissions of HFO-1234yf in Europe in 2030 is 7,090 tonnes. It is expected that by year 2030, HFO-1234yf would be fully implemented in the European vehicle fleet and hence this year represents a reasonable upper bound on future annual HFO-1234yf releases.

Table 1. Estimated emissions of HFO-1234yf from mobile air conditioners in European vehicle fleet in 2030

Activity/Use	**Emissions (tonnes/year)**
Regular usage (all vehicles)	2697
Irregular leakage	3202
Release during recovery	950
MAC filling at OEM (new vehicles)	29
Refilling professional	140
Formulation	71
TOTAL	**7090**

Source: Honeywell Advanced Limited, REACH Dossier Chemical Safety Report, 2023.

2.2 Atmospheric Conversion to TFA

In the atmosphere, HFO-1234yf is oxidized to trifluoroacetyl fluoride that hydrolyses in cloud water droplets to form TFA, which then undergoes gas-phase removal by oxidation, wet deposition through precipitation (rain, snow, and fog) and dry deposition under non-precipitating conditions. The conversion rate of HFO-1234yf to TFA is almost 1:1 on a molar basis, with ~100% molar yield. In this study, it is conservatively assumed (i.e., upper bound on impacts) that all of the HFO-1234yf emissions are converted to TFA and subsequently deposited.

[3] Polyhaloalkene, EC no: 468-710-7, CAS no.: 754-12-1, Mol. formula: $C3H2F4$

[4] Norflurane, 1,1,1,2-tetrafluoroethane, EC no: 212-377-0, CAS no: 811-97-2, Mol. formula: $C2H2F4$

[5] See also EFCTC summary publication Naturally Occurring TFA: https://www.fluorocarbons.org/wp-content/uploads/2020/08/EFCTC-TheEvidenceThatTFAoccursNaturally_A4.pdf

[6] Honeywell Advanced Limited, 2023. REACH Dossier. Chemical Safety Report 2,3,3,3-tetrafluoropropene (HFO-1234yf). January.

2.3 Atmospheric Deposition of TFA

An atmospheric modeling study was previously conducted by Henne et al.[7] (2012) to study the deposition of TFA resulting from emissions of HFO-1234yf from mobile air conditioners in Europe. Taking leakage rate assumptions and predicted vehicle numbers for the year 2020 into account, they estimated an upper limit for total HFO-1234yf emissions to be 19,212 tonnes/yr and assessed resulting TFA wet and dry deposition rates over Europe using the Lagrangian particle dispersion model FLEXPART[8]. Because TFA deposition is expected to vary linearly with emissions of HFO-1234yf, the modeled TFA deposition results from Henne et al. (2012) are applied in the current study after reducing by a factor of 2.71 to account for the emissions over-estimate in Henne et al. (2012) compared to the current best estimate of 7,090 tonnes reported in the REACH Dossier CSR. Table 2 presents the resulting estimated gridded total (wet + dry) deposition of TFA at 5^0 by 5^0 spatial resolution over Europe.

Table 2. Estimated total (wet + dry) deposition flux of TFA over Europe (kg/km^2-yr)

Latitude (degree)	**Longitude (degree)**								
	-10	**-5**	**0**	**5**	**10**	**15**	**20**	**25**	**30**
65	0.04	0.04	0.06	0.06	0.06	0.06	0.06	0.13	0.09
60	0.06	0.06	0.11	0.15	0.17	0.24	0.15	0.20	0.13
55	0.07	0.11	0.15	0.22	0.37	0.37	0.44	0.20	0.17
50	0.07	0.11	0.18	0.31	0.59	0.57	0.48	0.24	0.15
45	0.13	0.17	0.24	0.30	0.65	0.54	0.31	0.37	0.18
40	0.07	0.13	0.22	0.24	0.37	0.37	0.24	0.18	0.18
35	0.07	0.11	0.09	0.09	0.11	0.18	0.18	0.17	0.09

Note:

kg/km^2-yr = kilogram per square kilometer per year

To obtain the relative fractions of wet and dry deposition, the ratio of wet to total deposition was assumed to be 0.77 consistent with the wet deposition fraction used by Henne et al. in FLEXPART modeling.

2.4 Estimated Atmospheric Deposition of TFA in Rhine River Sub-Basins

As shown in Table 3, the annual average atmospheric dry, wet, and total deposition rates (microgram per square meter per year [μg/m^2-yr]) of TFA in each of the Rhine River sub-basins[9] were then estimated using the deposition rates at 5^0 by 5^0 spatial resolution over Europe presented in Table 2. These deposition rates were used as inputs in the subsequent environmental fate and transport modeling of TFA after it deposits on the soil or waterbody in the Rhine River watershed.

[7] Henne, S.; Shallcross, D.E.; Reimann, S.; Xiao, P.; Brunner, D.; O'Doherty, S.; Buchmann, B. 2012. Future Emissions and Atmospheric Fate of -1234yf from Mobile Air Conditioners in Europe. Environ. Sci. Technol. 46, 1650-1658.

[8] Stohl, A.; Forster, C.; Frank, A.; Seibert, P.; Wotawa, G. 2005. Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2. Atmos. Chem. Phys. 5, 2461-2474.

[9] The Moezel/Saar sub-basin was evaluated as part of the Middle-Rhine sub-basin; the Main and Neckar sub-basins were evaluated as part of the Upper-Rhine sub-basin.

Table 3. Annual Average Atmospheric Deposition of TFA in the Waterbody of Rhine River Sub-Basins

Sub-Basin	Total Deposition ($\mu g/m^2$-yr)	Dry Deposition ($\mu g/m^2$-yr)	Wet Deposition ($\mu g/m^2$-yr)
Alpine Rhine/Lake Constance	6.46E+02	1.49E+02	4.98E+02
High Rhine	2.95E+02	6.79E+01	2.27E+02
Upper Rhine	5.91E+02	1.36E+02	4.55E+02
Middle Rhine	3.14E+02	7.22E+01	2.42E+02
Lower Rhine	3.14E+02	7.22E+01	2.42E+02
Delta Rhine	2.22E+02	5.10E+01	1.71E+02

Note:

$\mu g/m^2$-yr = microgram per square meter per year

3.0 ENVIRONMENTAL FATE AND TRANSPORT MODELING OF TFA

Assuming a continuous emission of HFOs into the atmosphere, and the degradation of HFO into TFA, there will be a continuous deposition (mostly through wet deposition, or precipitation) of TFA on soil and freshwater aquatic environment, which typically will eventually accumulate in the marine system where it is considered an infinite terminal sink and the increase of TFA concentration is expected to be very slow (except for inland salt lakes). An environmental modeling case study for the Rhine River was conducted to characterize the fate and transport of TFA in the freshwater aquatic environment resulting from the degradation of HFO emissions and subsequent atmospheric deposition.

3.1 Fate and Transport Modeling Methodology

A fate and transport modeling to simulate TFA concentrations in the Rhine River was conducted based on the annual average deposition rates provided in Table 3 in the air analysis described above, and following the methodology recommended by the United States Environmental Protection Agency's (USEPA) Human Health Risk Assessment Protocol (HHRAP) for Hazardous Waste Combustion Facilities.[10]

The following mechanisms were considered in determining the TFA loading of the water column:

- Direct deposition,
- Runoff from surfaces within the watershed,
- Soil erosion over the total watershed,
- Benthic burial,
- Inputs from the upstream river segment, and
- Discharge to ocean.

It is assumed that contributions from other potential mechanisms are negligible compared to the most relevant ones listed above. Moreover, since TFA is persistent in the environment, meaning it does not readily break down or degrade, the model does not account for any chemical or biological transformation of TFA that may occur after its deposition on the ground or water surface. Although TFA is quite volatile as a neat solution, once it is in water, it will ionize and should not evaporate; therefore, the loss of TFA through evaporation will not be considered in the model.

A series of compartment models that represent the following six sub-basins within the Rhine River were modeled to simulate the transport of TFA in a river system from the beginning till the end where it discharges into the ocean:

- Sub-basin #1: Alpine Rhine/Lake Constance sub-basin
- Sub-basin #2: High Rhine sub-basin
- Sub-basin #3: Upper Rhine sub-basin (including the Main and Neckar sub-basins)
- Sub-basin #4: Middle Rhine sub-basin (including the Moezel/Saar sub-basin)
- Sub-basin #5: Lower Rhine sub-basin
- Sub-basin #6: Delta Rhine sub-basin

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[10] USEPA. 2005. Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, Final EPA530-R-05-006: Solid Waste and Emergency Response, Washington, D.C.

The methods for modeling TFA loading to a water body represent a simple steady state model to solve for a water column in equilibrium with the upper sediment layer. The model predicts the steady state mass of contaminants in the water column and underlying sediments and does not address the dynamic exchange of contaminants between the water body and sediments following changes in external loadings. The total concentration of TFA partitions between the sediment and the water column. The HHRAP uses the Universal Soil Loss Equation (USLE) and a sediment delivery ratio to estimate the rate of soil erosion from the watershed. The total estimated water column TFA concentration is the sum of the TFA concentration dissolved in water and the TFA concentration associated with suspended solids.

3.2 Chemical-Specific Properties and Modeling Parameters

The selection of chemical-specific properties for TFA and other modeling parameters were based on the best science available and professional judgment and discussed below:

3.2.1 Physical/Chemical Properties for TFA:

TFA is poorly adsorbed to the soil and is considered a mobile organic compound. The physical and chemical properties of TFA used in the modeling are shown in Table 4. As documented in the notes of this table, these parameters are from ECHA. If not available on the ECHA website, they were either collected from literature or guidance or estimated following the approach recommended in the USEPA HHRAP Guidance.

Table 4. Physical/Chemical Properties for TFA

Chemical	Organic Carbon-Water Partition Coefficient [1]	Soil-Water Partition Coefficient [2]	Soil Enrichment Ratio [3]	Suspended Sediment/ Surface Water Partition Coefficient [4]	Bed Sediment/ Sediment Pore Water Partition Coefficient [5]	Diffusivity in Water [6]
	Koc L/kg	Kd_s L/kg	ER unitless	Kd_{sw} L/kg	Kd_{bs} L/kg	D_w cm^2/s
TFA	6.22	0.94	3.00	0.47	0.25	8.00E-06

Notes:

ECHA: European Chemicals Agency
cm^2/s: Square centimeter per second
foc: Fraction organic carbon
L/kg: Liter per kilogram

[1] Koc at 20 °C for trifluoroacetic acid, calculated according to the equation from Sabljic and Güsten (1995), as reported in the EU TGD (2003), using the class of non-hydrophobic chemicals. In the case of trifluoacetic acid, the class "organic acid" is more relevant. Therefore the Koc is calculated as follows: logKoc = 0.6 * logKow + 0.32, with LogKow = 0.79 (European Chemical Agency [ECHA] Trifluoroacetic Acid Endpoint Summary for Transport and Distribution - Adsorption/Desorption: https://echa.europa.eu/registration-dossier/-/registered-dossier/5203/5/5/2).

[2] Adsorption/desorption tests results show that TFA is poorly adsorbed to the soil and is considered as a mobile organic compound in the majority of soils investigated. The Kd ranged between 0.17 to 20 L/kg for organic and mineral soils (the organic horizon exhibiting greater retention) giving a geometric mean of 0.94 L/kg (SD=4.86, n= 20) (ECHA Trifluoroacetic Acid Endpoint Summary for Transport and Distribution - Adsorption/Desorption: https://echa.europa.eu/registration-dossier/-/registered-dossier/5203/5/5/2).

[3] Default value for organic compounds (USEPA 2005, Appendix B, Table B-4-11)

[4] Calculated using the Koc and a default mid-range value of surface water foc of 0.075 (USEPA 2005, Appendix A-2)

[5] Calculated using the Koc and a default mid-range value of sediment foc of 0.04 (USEPA 2005, Appendix A-2)

[6] George Ch., 1994.

Sources:
United States Environmental Protection Agency (USEPA). 2005. Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, Final EPA530-R-05-006:Solid Waste and Emergency Response,

George Ch., J.Y. Saison, etc. 1994. Kinetics of mass transfer of carbonyl fluoride, trifluoroacetyl fluoride, and trifluoroacetyl chloride at the air/water interface. J. Phys. Chem. 1994, 98, 42, 10857–10862.

3.2.1.1 Watershed and Waterbody Parameters:

The watershed and waterbody parameters for each of the six sub-basins of the Rhine River from the EU-Hydro River Network Database[11] were used in the transport modeling to estimate the surface water TFA concentrations for each sub-basin evaluated in this analysis, as shown in Table 5 below. The default Empirical intercept coefficient of 0.6 for watersheds larger than 1000 mile^2 (or 2560 kilometer^2) from the USEPA HHRAP was used.

Table 5. Waterbody/Watershed Parameters

Parameter	Alpine Rhine/ Lake Constance	High Rhine	Upper Rhine	Middle Rhine	Lower Rhine	Delta Rhine
Waterbody surface area (m^2)	2.88E+07	2.74E+07	1.85E+08	1.18E+08	2.13E+08	4.78E+07
Impervious watershed area receiving deposition (m^2)	5.89E+08	6.93E+08	4.06E+09	2.59E+09	2.88E+09	1.85E+09
Total watershed area receiving deposition (m^2)	1.59E+10	1.76E+10	6.49E+10	3.98E+10	2.54E+10	2.53E+10
Waterbody temperature (K)	287	287	287	287	287	287
Average volumetric flow rate through waterbody (m^3/yr)	7.73E+09	3.43E+10	7.88E+10	7.88E+10	9.15E+10	9.15E+10
Depth of water column (m)	4	4	5	7	6	6
Total suspended solids concentration (mg/L)	134	15	19	26	29	29
Total waterbody depth (m)[1]	4.03	4.03	5.03	7.03	6.03	6.03
Current velocity (m/s)	1.5	1.5	1.0	1.8	1.7	1.5
Average annual precipitation (cm/yr)	164	149	72	83	80	76
Empirical intercept coefficient (unitless) [2]	0.6	0.6	0.6	0.6	0.6	0.6

Notes:
cm: Centimeter
K: Kelvin
M: Meter
m^2: Square meter
m^3: Cubic meter
m/s: Meter per second
mg/L: Miligram per liter
yr: Year
USEPA: United States Environmental Protection Agency.

[1] Depth of water column plus 0.03 m (USEPA 2005).
[2] Default empirical intercept coefficient for watersheds larger than 1000 mile^2 (or 2560 km^2) from the USEPA HHRAP (USEPA 2005).

Sources:
EU-Hydro River Network Database: https://land.copernicus.eu/imagery-in-situ/eu-hydro/eu-hydro-river-network-database?tab=download
United States Environmental Protection Agency (USEPA). 2005. Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, Final EPA530-R-05-006:Solid Waste and Emergency Response, Washington, D.C. September.

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[11] https://land.copernicus.eu/imagery-in-situ/eu-hydro/eu-hydro-river-network-database?tab=download

3.2.1.2 Other Modeling Parameters:

Other modeling parameters used in transport modeling to predict the TFA concentrations in soil and surface water from air deposition are summarized in Table 6. The model simulated a time series between 0 to 30 years and assumed that the TFA deposition rates (see Table 3) did not change during the modeled time frame. As noted in Table 6 below, the parameters that are either constant or are not expected to vary significantly, or cause a significant impact on the results, are based on default recommended values from the HHRAP. Other parameters are based on average values for the Rhine River basin.

Table 6. Modeling Parameters Used in Soil Deposition Calculation

Parameter	Unit	Symbol	Value	Source
Time period of deposition	year	tD	0-30	Site-specific
Time period at the beginning of deposition	year	T_1	0	USEPA 2005
Soil mixing zone depth	cm	Z_s	2	USEPA 2005, untilled soil
Soil bulk density	g/cm^3	BD	1.5	USEPA 2005
Loss Constant Due to Soil Erosion	$year^{-1}$	kse	0	USEPA 2005
Soil volumetric water content	mL/cm^3	θ_{sw}	0.2	USEPA 2005
Average annual surface runoff from pervious areas	cm/year	RO	28.6	Site-specific
Average annual irrigation	cm/year	I	20	Site-specific
Average annual evapotranspiration	cm/year	E_v	55	Site-specific
Ambient air temperature	K	T_a	284	Site-specific
Solids particle density	g/cm^3	ρ_s	2.7	USEPA 2005
USLE rainfall (or erosivity) factor [1]	$year^{-1}$	RF	26.4	Site-specific, in Panos Panagos et al., 2015: Rainfall Erosivity in Europe.
USLE erodibility factor	ton/acre	K	0.36	USEPA 2005
USLE length-slope factor	unitless	LS	1.5	USEPA 2005
USLE cover management factor	unitless	C	1	USEPA 2005, bare soil
USLE supporting practice factor	unitless	PF	1	USEPA 2005, no control measures
Empirical slope coefficient	unitless	b	0.125	USEPA 2005
Depth of upper benthic sediment layer	m	d_{bs}	0.03	USEPA 2005
Bed sediment concentration	g/cm^3	C_{BS}	1	USEPA 2005
Bed sediment porosity	unitless	θ_{bs}	0.225	Site-specific
Temperature correction factor	unitless	θ	1.026	USEPA 2005
Drag coefficient	unitless	C_d	0.0011	USEPA 2005
Average annual wind speed	m/s	W	6.5	Site-specific
Density of air	g/cm^3	ρ_a	0.0012	USEPA 2005
Density of water	g/cm^3	ρ_w	1	USEPA 2005
von Karman’s constant	unitless	k	0.4	USEPA 2005
Dimensionless viscous sublayer thickness	unitless	λ_z	4	USEPA 2005

Parameter	Unit	Symbol	Value	Source
Viscosity of water corresponding to water temperature	g/cm/s	μ_w	0.0169	USEPA 2005
Viscosity of air	g/cm/s	μ_a	0.00018	USEPA 2005

Notes:
cm: Centimeter
cm/year: Centimeter per year
g/cm^3: Gram per cubic centimeter
g/cm/s: Gram per centimeter-second
K: Kelvin
m: Meter
m/s: Meter per second
mL/cm^3: Milliliter per cubic centimeter
USLE: Universal Soil Loss Equation

[1] The average rainfall factor (RF) of 26.4 (year^{-1}) in Europe was converted from 450 (MJ mm)/(ha-h-yr) (Estimated from graph from Panos Panagos et al., 2015: Rainfall Erosivity in Europe) divided by 17.02 using the method recommended by USLE (Foster G.R. 1981, and Benavidez R., 2018).

Sources:

Benavidez R. et al., 2018. A review of the (Revised) Universal Soil Loss Equation ((R)USLE): with a view to increasing its global applicability and improving soil loss estimates. Hydrology and Earth System Sciences, 22(11), 6059-6086.

Foster. G.R. et al., 1981. Conversion of the Universal Soil Loss Equation to SI Metric Units. Journal of Soil and water conservation, 36(6), 355-359.

Panagos et al., 2015. Rainfall Erosivity in Europe. Science of the Total Environment, 511, 801-814.

United States Environmental Protection Agency (USEPA). 2005. Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, Final EPA530-R-05-006: Solid Waste and Emergency Response, Washington, D.C. September.

4.0 RESULTS AND DISCUSSION

An environmental fate and transport modeling was conducted to simulate the TFA concentrations in each of the six sub-basins in the Rhine River between 0 to 30 years using the methodology and assumptions discussed above. Based on the simulation results (as shown in Table 7, and Figure 1), the TFA concentrations in the river system would reach steady state within a few months (two to seven months). The upper stream sub-basins would reach steady state faster than the downstream sub-basins. The model predicted steady state TFA concentrations in the Rhine River sub-basins range from 0.11 µg/L for the upstream sub-basin (i.e., the High Rhine sub-basin) to 0.57 µg/L for the Delta Basin where the Rhine River reaches the North Sea. In general, the TFA concentration in the river system increases from the upstream sub-basins to the downstream basins. The expectation for this is that the TFA concentrations predicted for the Alpine Rhine / Lake Constance sub-basin are higher than the High Rhine sub-basin due to lower volumetric flow rate and high total suspended solids in the Alpine Rhine / Lake Constance sub-basin than the other sub-basins. Similarly, as shown in Figure 2, the TFA concentrations in surface soil receiving deposition also reach steady state within a few months (two to seven months. Based on the simulation results of the TFA mass allocation in soil, river system, and the ocean (see Attachment A), a very small percentage (<1 %) of the TFA mass deposited from the air would remain in the river system or the mixing zone of surface soil receiving deposition (i.e., assumed to be the top 2 centimeters of soil for this study) after the TFA concentrations reach steady state in the surface water and in the mixing zone of surface soil, the majority of the TFA would enter the ocean.

Based on the mean and maximum measured TFA concentrations in the Rhine River[12], the modeled TFA concentrations in surface water estimated based on the TFA deposition rates are within a reasonable range given there are other sources contributing to the TFA concentrations in the river system (e.g., leaching or direct discharge).

Table 7. Time Series of Model-Predicted TFA Concentrations in Surface Water

Time (Year)	Peak Total Surface Water Concentration (µg/L)					
	Alpine Rhine/Lake Constance	**High Rhine**	**Upper Rhine**	**Middle Rhine**	**Lower Rhine**	**Delta Rhine**
0.005	1.04E-01	3.56E-02	6.73E-02	8.44E-02	8.69E-02	9.39E-02
0.01	1.47E-01	5.02E-02	9.24E-02	1.15E-01	1.17E-01	1.26E-01
0.06	3.13E-01	1.09E-01	2.57E-01	3.20E-01	3.15E-01	3.41E-01
0.12	3.36E-01	1.18E-01	3.50E-01	4.35E-01	4.26E-01	4.62E-01
0.18	3.39E-01	1.19E-01	3.96E-01	4.90E-01	4.79E-01	5.19E-01
0.24	3.39E-01	1.19E-01	4.19E-01	5.16E-01	5.04E-01	5.46E-01
0.3	3.39E-01	1.19E-01	4.31E-01	5.29E-01	5.16E-01	5.59E-01
0.4	3.39E-01	1.19E-01	4.39E-01	5.38E-01	5.25E-01	5.68E-01
0.5	3.39E-01	1.19E-01	4.41E-01	5.41E-01	5.27E-01	5.71E-01
0.6	3.39E-01	1.19E-01	4.42E-01	5.42E-01	5.28E-01	5.72E-01
0.7	3.39E-01	1.19E-01	4.42E-01	5.42E-01	5.28E-01	5.72E-01
0.8	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01
0.9	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01
1	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01
5	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01
10	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01
15	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01

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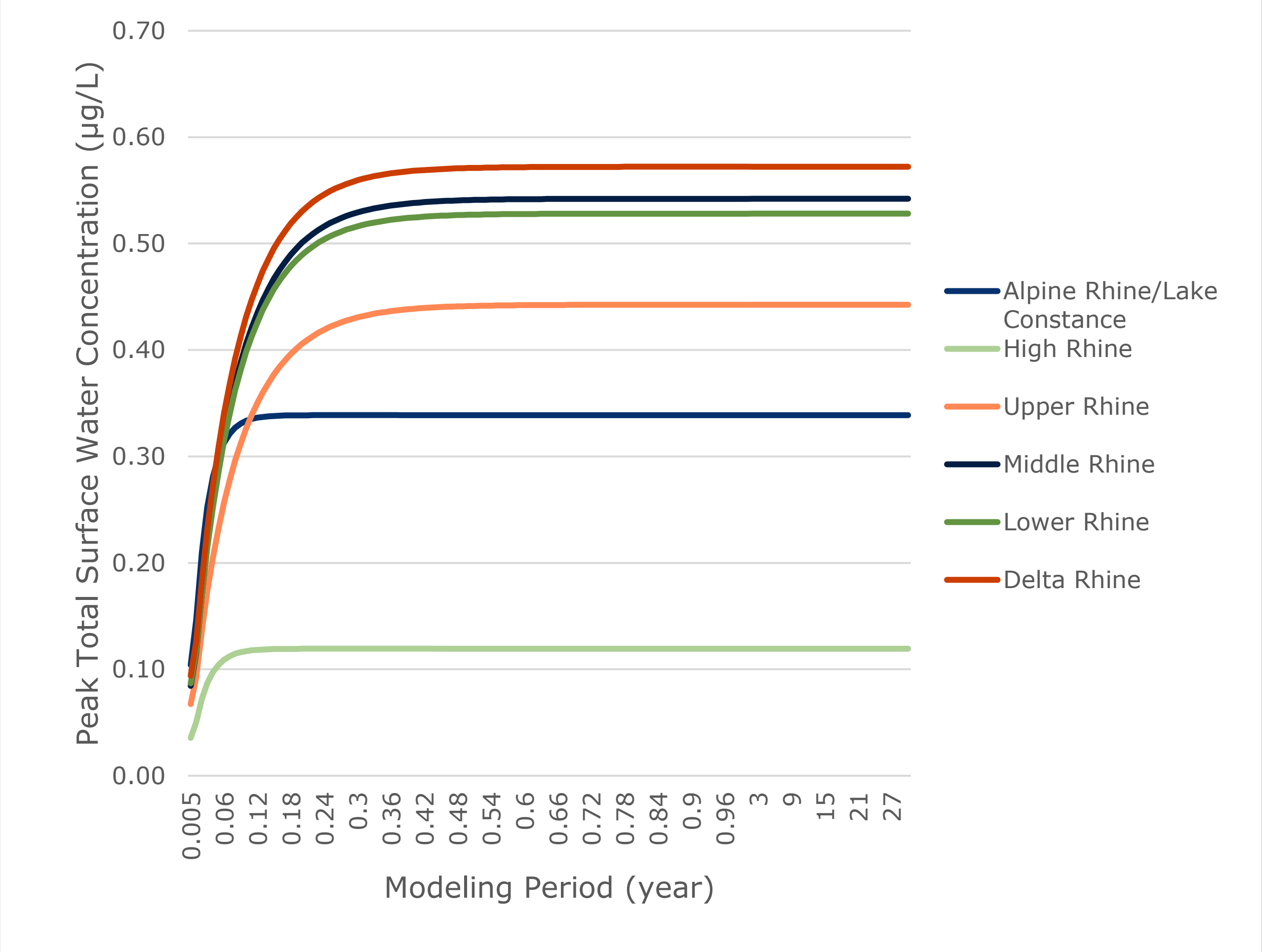
[12] https://gis.uba.de/maps/resources/apps/TFA-Herkunft-und-Belastungen/index.html?lang=en&vm=2D&s=9244648.868618&c=246236.57895956002%2C6515669.535245592&r=0

Time (Year)	Peak Total Surface Water Concentration (µg/L)					
	Alpine Rhine/Lake Constance	High Rhine	Upper Rhine	Middle Rhine	Lower Rhine	Delta Rhine
20	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01
25	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01
30	3.39E-01	1.19E-01	4.43E-01	5.42E-01	5.28E-01	5.72E-01

Note:

µg /L	microgram per liter

Figure 1. Model Predicted TFA Surface Water Concentration (0 - 30 Years)



These findings reflect the results from a simplified compartment model with assumptions and modeling parameters based on average estimates of each sub-basin or the Rhine River watershed and annual averaged deposition rates. They are aimed to provide rough estimates at the regional level but not accurate high-resolution modeling results for specific areas.

A sensitivity analysis was performed to understand the impact of some of the key input parameters on the modeling outputs (i.e., TFA concentrations in the surface water). The selected input parameters and the observation of the sensitivity analysis are summarized in Table 8 below.

Figure 2. Model Predicted TFA Soil Concentration (0 - 30 Years)

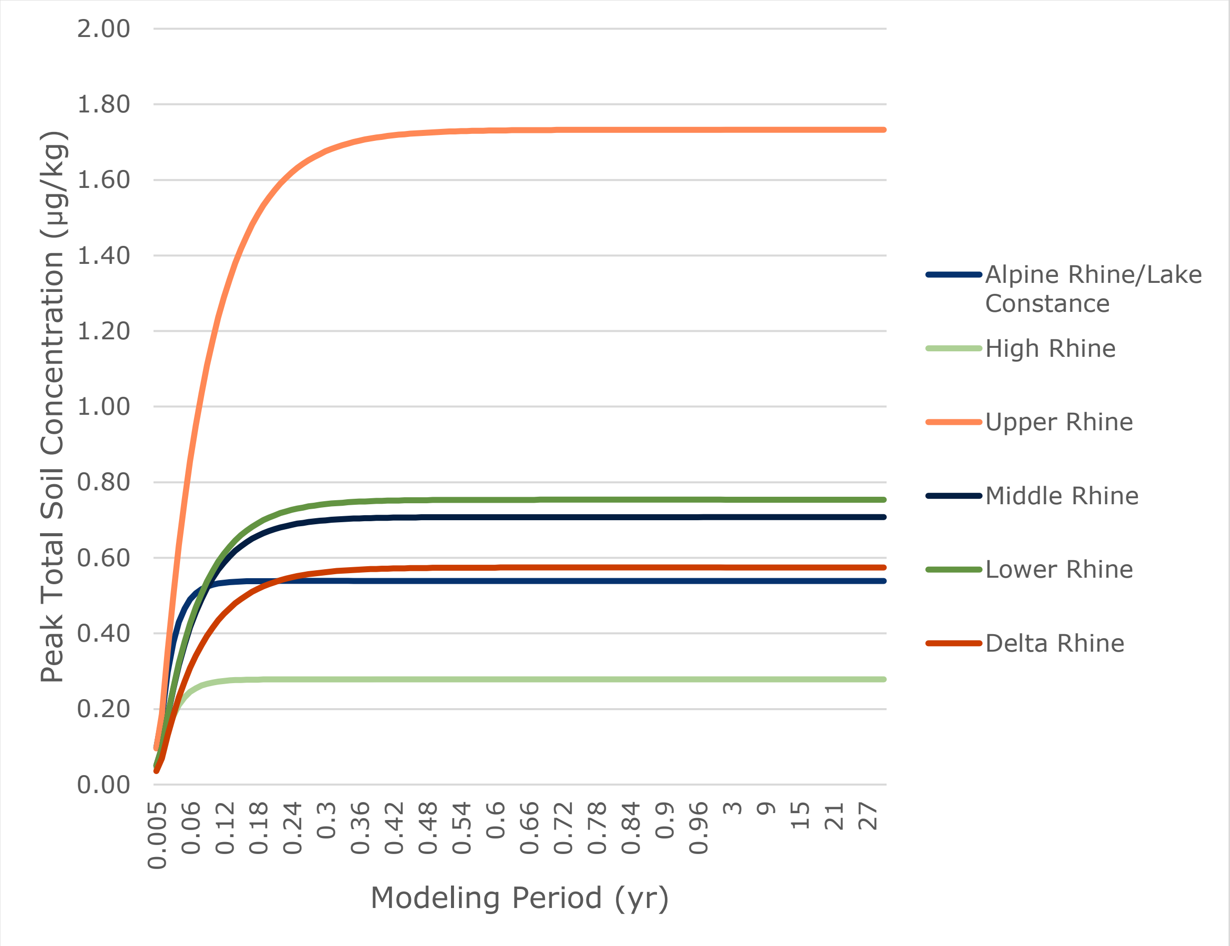


Table 8. Summary of Sensitivity Analysis

Parameter	Observation
Total TFA deposition rate (wet and dry)	The TFA concentration in surface water changes linearly with the total air deposition rates; no impact on time to reach steady state.
Waterbody area	The TFA concentration in surface water increases slightly with the increase of the waterbody area; no impact on time to reach steady state.
Total watershed area	The TFA concentration in surface water increases significantly with the increase of the watershed area; the impact on the TFA concentration in surface water due to % change in the watershed area is more significant than the water body because the contribution of TFA load from the soil in the watershed is much larger than the direct deposition from the air on the water body. No impact on time to reach steady state.
Precipitation	The modeled TFA concentration in surface water concentration decreases significantly when precipitation increases (assuming the same deposition rate), primarily due to increased loss of TFA in soil by leaching which results in lower TFA concentrations in soil (note that the contribution of TFA to surface water from groundwater discharge is not simulated in this model); reaches steady state sooner with higher precipitation.

Parameter	**Observation**
Flow rate (Vfx)	The modeled TFA concentration in surface water decreases significantly when the river flow rate increases, no impact on time to reach steady state.
Rainfall factor (RF)	This parameter ranges from 20 to 43 in Europe. It has a very low impact on the modeled TFA concentrations in surface water and the time to reach steady state.
Soil Organic Carbon-Water Partition Coefficient (Koc)	The TFA concentration in surface water increases with lower Koc (which also resulted in lower partition coefficients between soil and soil pore water (Kd_s), suspended sediment and surface water (Kd_{sw}), and bed sediment and sediment pore water (Kd_{bs}); the % changes in TFA concentrations decreases quickly over time and the difference is minimum when reaching steady state. Therefore, the long-term impact of Koc on TFA concentrations in surface water is insignificant. Lower Koc also results in reaching steady state slightly sooner.

The detailed modeling results of the sensitivity analysis are included in Attachment B.

5.0 CONCLUSIONS

Environmental fate and transport modeling of TFA in the freshwater aquatic environment was conducted based on the assumption of constant and ongoing HFO emissions, which through atmospheric degradation in turn leads to a constant deposition of TFA. Modeling results demonstrate that within a short timeframe (i.e., of the order of months) a steady state concentration of TFA is reached, which does not further increase over time. This is illustrated in a case study of the Rhine basin, for which TFA concentrations below 0.6 µg/L are predicted under the conditions assumed in this TFA environmental modeling study.

Importantly, this study contests the assumption made in the REACH PFAS Restriction Proposal that freshwater TFA concentrations would continue to increase until "inevitably" a toxic level would be reached. Moreover, the TFA concentrations modeled are reasonably within the mean and maximum measured TFA concentrations in the Rhine River.