

Estimation of environmental concentrations and deposition fluxes of R-1234-YF and its decomposition products emitted from air conditioning equipment to atmosphere

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Abstract: The use of hydrofluorocarbons (HFCs) as refrigerants in air conditioning equipment is of great concern because this could lead to global warming since the global warming potential (GWP) of HFCs is high. Therefore, substances with high reactivities and shorter lifetimes in the troposphere have been considered as candidates for next-generation refrigerants. However, substances with shorter lifetimes may cause the decomposed products to have high local concentrations, which, in turn, may affect the atmospheric environment. Hence, concentration estimation and environmental impact assessment of the decomposed products of refrigerants must be conducted. R-1234-YF ($\text{CF}_3\text{CF}=\text{CH}_2$), is a next-generation refrigerant candidate with a low GWP of four. However, the photochemical reaction of R-1234-YF due to its high reactivity with OH radicals can contribute to ozone production in the troposphere. Moreover, trifluoroacetic acid (TFA), which is the final product of R-1234-YF decomposition, is strongly acidic and hence could cause ecological effects. In this paper, we assume that R-1234-YF is used as the refrigerant in air conditioning equipment in Japan, and we estimate the environmental concentrations of the refrigerant and its decomposed products by using an atmospheric dispersion model.

Keywords: *trifluoroacetic acid (TFA), R-1234-YF, atmospheric dispersion model, photochemical reaction*

1 INTRODUCTION

In order to prevent ozone depletion, since the 1990s, the refrigerant gases used in air conditioning equipment, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), have been replaced by hydrofluorocarbons (HFCs). However, HFCs have been designated as a greenhouse gas under the Kyoto Protocol, and further, it has high global warming potential (GWP).

R-1234-YF, ($\text{CF}_3\text{CF}=\text{CH}_2$), is a new important candidate for use as a refrigerant because of its low GWP (GWP = 4); however, R-1234-YF might promote the generation of photochemical oxidants in the troposphere due to its high reactivity with OH radicals. Moreover, trifluoroacetic acid (TFA), which is the final decomposed product of R-1234-YF, has strong acidity and could cause ecological damages. TFA obtained from the decomposition of HCFCs and HFCs has been studied by numerical simulations previously[1], but TFA from R-1234YF has not yet been studied. In this report, we estimate the environmental concentrations of a refrigerant and its decomposed products by using an atmospheric dispersion model; we consider the refrigerant R-1234-YF and consider its emission from air conditioning equipment in Japan.

2 METHOD

2.1 Estimation of Emission Amount of R-1234YF

The future emission amounts of R-1234YF discharged from three types of air-conditioning (A/C) equipments—home A/C, institutional A/C (e.g., buildings, stores), and mobile A/C (e.g., car)—were estimated for each life-cycle stage. It is assumed that R-1234YF is used in all A/C equipments manufactured after 2011 in place of HFC and HCFC. The fill ratio of refrigerants per equipment, emission coefficient of refrigerants to the atmospheric environment, and the lifetime of the equipments were assumed to be constant. The emission coefficients used for estimating the amount of refrigerants emitted from each type of A/C for each life-cycle are shown in Table 1. The estimated time trend of

the amount of refrigerant emission from the three A/C equipments is shown in Fig.1. It was found that the emission amount increases and then reaches a steady state. Emissions from home A/Cs and institutional A/Cs were dominant. In this report, the emission amount in 2050, which is 15,172 ton/year as shown in Table 2, was used as the input data for the atmospheric chemical transport model.

Table 1 Emission coefficient used for estimating the amount of refrigerants emitted from A/Cs

Type of A/C		Life-cycle stage of A/C			
		Production		Consumer use	Disposal
		Refrigerants at the A/C production factory	Refrigerants at the A/C operation location	Refrigerants at work	
		[-/year]	[-/year]	[-/year]	[-]
Home A/C		0.002	—	0.02	0.73
Institutional A/C	Stores	0.002	—	0.03	0.72
	Buildings	0.002	0.0222	0.035	
	Facilities	0.002	0.0225	0.045	
Mobile A/C		3 [g/car]	—	15~100 [g/car/year]*	0.232

*) variation corresponding to the type of vehicle

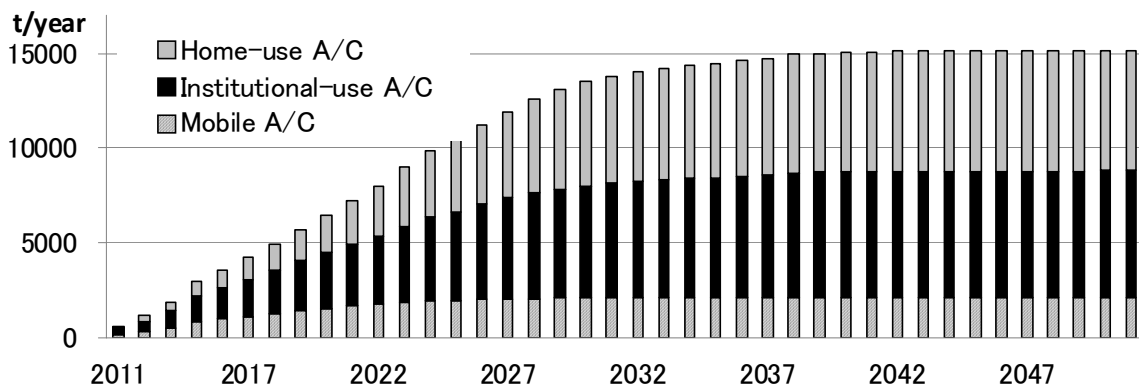


Fig.1 Variation in the R-1234YF emission amount to air, discharged from three types of A/Cs in Japan, with time [t/year]

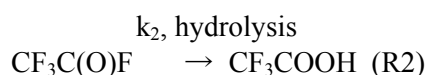
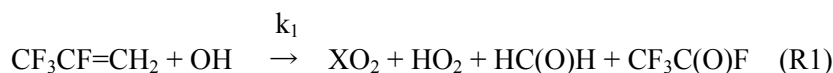
Table 2 Refrigerant emission amount in 2050 estimated for each equipment and life-cycle stage in Japan [t/year]

Type of A/C		Life-cycle stage of A/C			Total	
		Production		Consumer use		Disposal
		Refrigerants filling at the A/C production factory	Refrigerants filling at the A/C operation location			
Home A/C		8	—	1,903	4,454	6,366
Institutional A/C	Stores	5	—	724	1,238	1,967
	Buildings	2	24	1,380	2,005	3,410
	Facilities	1	2	632	722	1,357
Mobile A/C		34	—	1,713	325	2,072
Total		50	26	6,352	8,744	15,172

2.2 Atmospheric dispersion model for estimating concentration and dry/wet deposition

We used an on-line meteorology-coupled chemical transport model to simulate the atmospheric concentrations of the target chemicals. The main concept of this model consists of a meteorological model, Regional Atmospheric Modeling System version 4.4[2], and a chemistry model, updated Carbon Bond Mechanism IV[3]. Dry deposition was also considered using the model of Zhang et al. [4]. Wet deposition was calculated only for TFA by the CAL-PUFF scheme [5]. The simulations were conducted in Kanto, Japan, and meteorological data in 2005 was used as the input data.

The target chemicals were R-1234YF, ozone, formaldehyde, $\text{CF}_3\text{C}(\text{O})\text{F}$, and TFA. Only for TFA, dry and wet deposition flux amounts were estimated besides atmospheric concentration. Here, Dry and wet deposition rates for TFA were set at the same rates as nitric acid. Chemical reactions between R-1234-YF and OH radical by Hurley et al. [6] were set in as shown below with attention to the consistency with the chemistry model CB-99.



Here, the reaction rate constants k_1 and k_2 were set as $k_1 = 1.05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [7] and $k_2 = 1.16 \times 10^{-6} \text{ s}^{-1}$ [6]. XO_2 represents a universal peroxy radical operator that acts as a counter species to keep track of the rate of NO to NO_2 conversion, and hence of ozone formation.

The R-1234-YF emission amount shown in Table 2 was distributed geographically to each grid based on the index corresponding to the type of A/C and life-cycle stage. The index used for the emission distribution was the night-time population for home A/Cs, daytime population for institutional A/Cs, and traffic volume for mobile A/Cs except the disposal stage. In the case of the disposal stage for all the A/Cs, the number of employees in a waste-disposal industry was used for the distribution index. Emission amounts of other pollutants, nitrogen oxides (NO_x), volatile organic compounds (VOCs), and carbon monoxide (CO), were calculated with the similar method described in Kannari et al. (2007)[8] for each grid cell.

The TFA concentrations in rainwater were calculated by dividing the wet-deposition flux with the precipitation rate. The TFA concentrations in surface water were calculated by dividing the sum of dry-deposition and wet-deposition fluxes with the precipitation rate.

3 RESULTS AND DISCUSSION

The estimated gaseous concentration of R-1234YF and its photochemical reaction products in the lower atmosphere from ground level to 50-m height are shown in Table 3. The maximum concentration of R-1234YF was 0.28 ppb, which is more than 10^7 times lower than the no observed

adverse effect level (NOAEL) (4000 ppm) of the developmental toxicity for rabbits[9]. This implies that the health effects caused by the direct inhalational exposure of R-1234YF in atmosphere can be ignored. Since the increases in O₃ and HCHO, as compared to the control case, were estimated to be approximately 0.005% and 0.02%, respectively, for the spatially averaged concentrations, the effects of R-1234YF on oxidant formation in the troposphere in Japan appears to be very small.

Table 3 Estimated annual average concentration of R-1234YF and photochemical reaction products in air in Kanto [ppb]

	R-1234YF	O ₃		HCHO		CF ₃ C(O)F	TFA
		-	Increment from control case	-	Increment from control case		
Max.	0.28	45.2	0.005	2.9	0.0011	0.0035	9.1 × 10 ⁻⁵
Min.	0.0063	11.1	0.001	0.7	0.0002	0.00085	1.8 × 10 ⁻⁵
Average	0.045	34.6	0.002	1.8	0.0004	0.0018	5.3 × 10 ⁻⁵

The estimated concentration distributions of R-1234YF, CF₃C(O)F, and TFA are shown in Fig.2. It was found that the concentration distributions of CF₃C(O)F and TFA are broader than those of R-1234YF and CF₃C(O)F, respectively. This phenomenon reflects a “reaction cascade,” which began from R-1234YF via CF₃C(O)F to TFA. Although the concentration distribution of TFA was broad, the maximum concentration was on land and not on sea, as shown in Fig.2. Hence, the concentrations of TFA in dry and wet depositions can be predicted to be maximum on land.

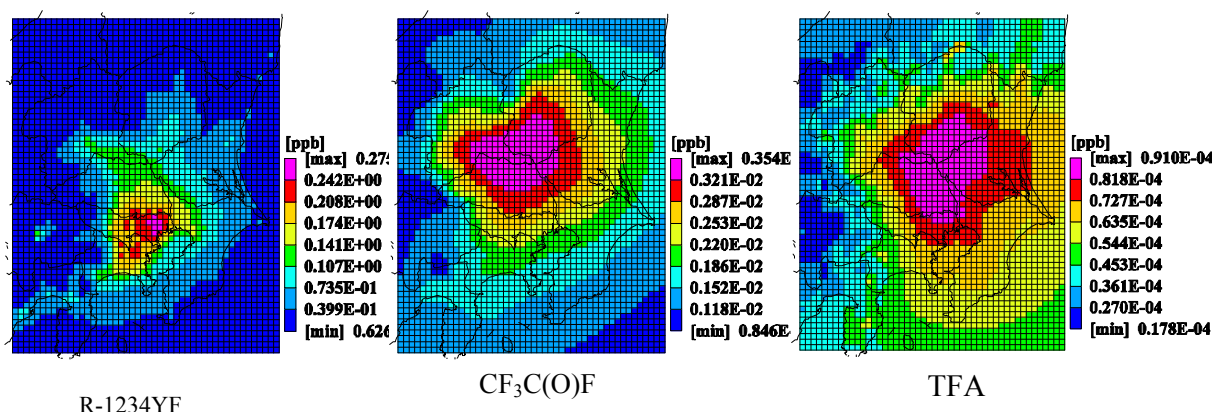


Fig.2 Estimated concentration distributions of R-1234YF, CF₃C(O)F, and TFA in atmosphere in Kanto

The estimated dry and wet deposition fluxes and the concentrations of TFA in environmental water are shown in Table 4. It was found that the dry and wet deposition fluxes of TFA are comparable. The estimated maximum concentrations of TFA in rainwater and surface water were 0.45 and 1.3 μg/L, respectively. The average estimated concentration of TFA in surface water in Kanto was approximately twice that in rainwater, which was 0.04~0.08 μg/L [10].

Aquatic ecotoxicity studies have shown that the most sensitive algae species was the algae *Selenastrum capricornutum* with an NOAEL of 0.10 mg/L (0.12 mg/L for the sodium salt NaTFA)[11]. The estimated maximum concentration of TFA in surface water was approximately 80 times smaller than that of the NOAEL for aquatic ecotoxicity. However, TFA is known to be extremely stable in environment. Considering the TFA concentration variations caused by seasonal precipitation patterns and the possibility that TFA will accumulate in some closed aquatic systems after deposition[12], the ratio between the estimated concentration in surface water and NOAEL for aquatic ecotoxicity appears not to be sufficiently large.

Validations of the numerical simulation model remains a future task; in particular, the reproducibility of precipitation, the accuracy of the hydrolysis rate of the reaction intermediate $\text{CF}_3\text{C}(\text{O})\text{H}$, and the role of the background concentrations of TFA must be studied. Further, behavior in aquatic environments including the accumulation of TFA on land after dry and wet depositions needs to be evaluated.

Table 4 Estimated dry and wet deposition fluxes and concentrations of TFA in environmental water

	Dry deposition flux [g/m ² /year]	Wet deposition flux [g/m ² /year]	Concentration in rain water [μg/L]	Concentration in surface water [μg/L]
Max.	2.0×10^{-4}	2.2×10^{-4}	0.45	1.3
Min.	1.1×10^{-5}	1.5×10^{-6}	0.002	0.028
Average	8.7×10^{-5}	3.8×10^{-5}	0.12	0.41

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