Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 1137–1142
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

The evaluation of time variation global warming effects, TWPA and CWP, for CFC alternatives

Akira Sekiya

National Institute of Advanced Industrial Science and Technology (AIST) 5-2.1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received 30 March 2007; received in revised form 18 April 2007; accepted 18 April 2007
Available online 24 April 2007

Abstract

Evaluations methods of global warming are presented by considering the direct warming effect of chemical compounds and of decomposed compounds, warming effect due to the formation of troposphere ozone, and the cooling effect due to the decomposition of stratosphere ozone. It is easy to take account the stabilization of global warming gases concentration in the atmosphere, as those methods can conduct the time variations analysis. The methods are named Total Warming Prediction Analysis (TWPA) and Composite Warming Potential (CWP). The evaluation of Mobile Air Conditioning refrigerant is presented as an example of application of our method.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Global warming; Evaluation method; CFC, HCFC, HFC, CO_2, HC; TWPG, CWP; Time analysis; LCA, LCCP; Refrigerant

1. Introduction

Global warming is the most pressing environmental problem affecting human beings [1]. To solve this problem, it would be necessary to achieve stabilization of the concentration in the atmosphere of warming compounds. In Intergovernmental Panel on Climate Change (IPCC) 2001 [2], a stabilization scenario for concentration of carbon dioxide is discussed based on atmospheric model calculations, but atmospheric model calculations are complex and difficult to apply to industrial activities with diverse characteristics. On the other hand, in the quest to achieve the reduction of global warming, it is common to use the GWP (global warming potential, 100 years value) of warming compounds to calculate the warming effect of industrial activities [3]. In order to determine the stabilization of the concentration in the atmosphere it is necessary to carry out an analysis of the time variation of the concentration of warming compound, but the GWP (100 years value) cannot be used because it uses a fixed value for 100 years. It could be possible to analyze the time variation using a GWP (x years value) [4], but as the warming effect of carbon dioxide, which is used as the standard value, depends on the time, simultaneous time variation of both the GWP value and the warming effect makes it difficult to establish any comparison. In the case of a compound with a long atmospheric life like CF_4, assessment of the global warming effect using GWP (100 years value) gives a result for 100 years although its atmospheric lifetime is 50,000 years. In the same way, although carbon dioxide is known to be the cause of global warming and its atmospheric life [5] is long, current assessments for only 100 years seem to be too small. In the case of compounds with long atmospheric life, it is still more necessary to assess the stabilization of concentration in the atmosphere in the time [1].

The present report introduces total warming prediction analysis (TWPA) and composite warming potential (CWP) as methods for assessment of time variation of global warming effect. These methods are the first to incorporate four warming effects. An example of application of the methods developed is presented.

2. Results and discussion

2.1. Calculation of TWPA and CWP

TWPA indicates the changes with time of the remaining amount of a compound that has decomposed after being released into the atmosphere. There are two ways to record this variation, TWPA (kg) which indicates the weight of the

E-mail address: akira-sekiya@aist.go.jp.

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.04.024

chemical compound remained in the atmosphere, and TWPA (W m^{-2}) which indicates the amount of chemical compound remained in the atmosphere in terms of warming amount (W m^{-2}). TWPA results can be presented using TWPG (total warming prediction graph), which displays the results from TWPA in form of graph, and TWPT (total warming prediction table) which displays the results from TWPA in a table. TWPG and CWP assume that the current atmosphere conditions will continue under the premise of a sustained development society.

The most important element in the study of the behavior of a warming gas present in the atmosphere is the speed at which a given compound decomposes and decreases in the atmosphere. TWPA (kg) represents this value. For 1 kg of a compound that is released into the atmosphere, TWPA (kg) represents how much of this compound will remain in the atmosphere some years later. The graphic representation of the relationship between time and remaining amount constitutes the TWPG (kg). The table representing this relationship is the TWPT (kg). Fig. 1 shows the TWPG (kg) for CO_2 and HFC-134a and the contrast with the time variation of GWP.

Next, the variation with the time of the warming effect of 1 kg of gas released into the atmosphere is presented.

The warming effect in the atmosphere of a single compound, gas A, is complex. In order to achieve an accurate evaluation, the present report attempts to combine the essential elements involved in warming, evaluating the following four effects [6]:

(1) Direct warming effect (DWE)
The warming effect of compound A itself.

(2) Warming effect of decomposed compounds (WEDC)
The warming effect of decomposition of compound A into warming gases is calculated. For example, compound A decomposes into carbon dioxide, the time of A to decompose to carbon dioxide is also taken into account to assess warming effect.
In the case of HFC-134a, it is well known that HFC-134a is decomposed in the atmosphere yielding around 7–30% of trifluoroacetic acid (TFA) [7,8]. Although the balance of natural TFA amount has still not been explained clearly [9], the calculation of WEDC uses the balance that 80% of HFC-134a is decomposed into carbon dioxide and 20% of HFC-134a is converted to TFA.

(3) Warming effect of created ozone (WECO)
If compound A is cause of the formation of troposphere ozone, this warming effect is calculated in time. For example, in the case of a compound A with short atmospheric life, NOx promotes formation of troposphere ozone [10] through its decomposition in the atmosphere. Troposphere ozone oxidant is not only the cause of photochemical smog, but also has an effect as warming compound. This warming effect is calculated in time.

(4) Cooling effect of ozone layer destruction (CEOLD)
The cooling effect caused by destruction of the ozone layer [11] by compound A is calculated in time. For example, if compound A contains chlorine, which causes decomposition of the stratosphere ozone, cooling of the troposphere caused by this decomposition is estimated in time.

The results of combining the above (1)–(4) are expressed as TWPA (W m^{-2}) in the form of graph and table.

Table 1 corresponds to the TWPT (W m^{-2}) for 1 kg of compound A released. Fig. 2 shows the TWPG (W m^{-2}) for the release of 1 kg per year of a warming gas. Assuming sustainability of the industry, it is possible to observe how the concentration in the atmosphere changes if the same amount is released each year.

As observed in Fig. 2, carbon dioxide accumulates in the atmosphere, whereas concentration of HFC-134a stabilizes and stops increasing. For short atmospheric life, the amount released into the atmosphere is equivalent to the amount that decomposes in the atmosphere, and the concentration in atmosphere stabilizes.

Table 1 shows TWPT (kg) and TWPT (W m^{-2}) corresponding to 1 kg of several chemical compounds that have elapsed at 1, 100, 500 and 1000 years after releasing.

CWP shows the warming effect brought by 1 kg of a chemical compound A released into the atmosphere until

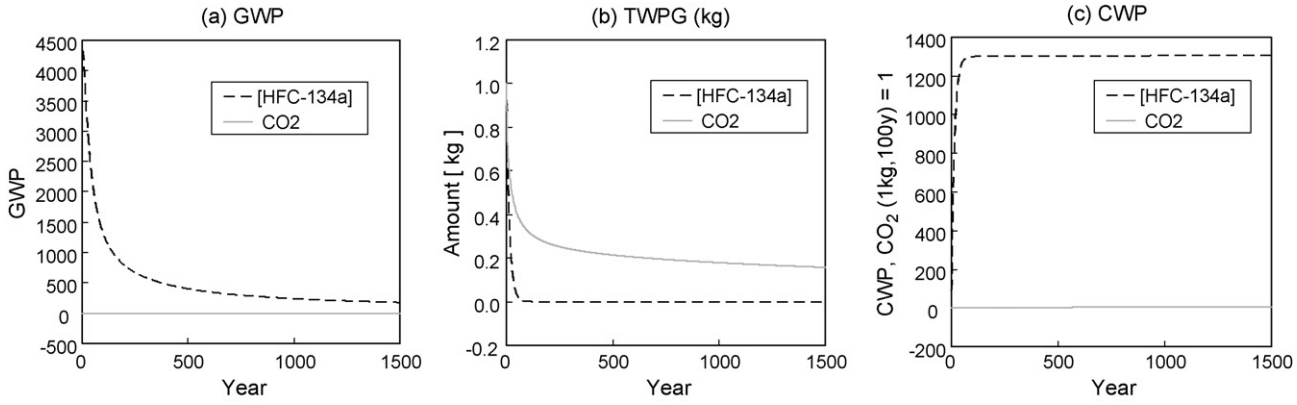

Fig. 1. GWP, TWPG (kg) and CWP evaluation for 1 kg release of HFC-134a and CO_2. (a) The relative direct warming effect values of HFC-134a and CO_2 by GWP evaluation. (b) The residual amount of HFC-134a and CO_2 in the atmosphere for 1500 years by TWPG (kg) analysis. (c) The relative integrated warming effect, TWPG (W m^{-2}), of HFC-134a and CO_2 by CWP evaluation.

Table 1
Example of TWPT (kg), TWPT (W m^{-2}) and CWP

Year	Carbon dioxide (CO_2)	HFC-134a[a] (CF_3CFH_2)	HFC-245fa ($CF_3CH_2CF_2H$)	PFC-14 (CF_4)	PFC-116 (C_2F_6)	Nitrogen trifluoride (NF_3)	Propane (C_3H_8)	Carbonyl fluoride (COF_2)	Methane (CH_4)
TWPT (kg)									
0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
100	3.24×10^{-1}	7.13×10^{-4}	9.29×10^{-7}	9.98×10^{-1}	9.90×10^{-1}	8.74×10^{-1}	0	0	2.40×10^{-4}
500	2.15×10^{-1}	1.84×10^{-16}	6.93×10^{-31}	9.90×10^{-1}	9.51×10^{-1}	5.09×10^{-1}	0	0	8.02×10^{-19}
1000	1.79×10^{-1}	3.38×10^{-32}	4.80×10^{-61}	9.80×10^{-1}	9.05×10^{-1}	2.59×10^{-1}	0	0	6.44×10^{-37}
TWPT (W m^{-2})									
0	2.10×10^{-15}	9.40×10^{-12}	1.25×10^{-11}	5.50×10^{-12}	1.10×10^{-13}	1.10×10^{-11}	3.80×10^{-12}	1.40×10^{-15}	1.71×10^{-13}
100	6.81×10^{-16}	6.69×10^{-15}	6.99×10^{-16}	5.43×10^{-12}	1.12×10^{-11}	9.58×10^{-12}	2.04×10^{-15}	4.54×10^{-16}	1.99×10^{-15}
500	4.51×10^{-16}	3.13×10^{-16}	4.45×10^{-16}	5.39×10^{-12}	1.07×10^{-11}	5.58×10^{-12}	1.35×10^{-15}	3.01×10^{-16}	1.24×10^{-15}
1000	3.77×10^{-16}	2.61×10^{-16}	3.72×10^{-16}	5.34×10^{-12}	1.02×10^{-11}	2.84×10^{-12}	1.13×10^{-15}	2.51×10^{-16}	1.04×10^{-15}
CWP									
0	0.000	0	0	0	0	0	0.0	0.0	0.0
100	1.000	1,301	951	5,700	10,000	10,800	5.1	0.67	25.5
500	3.219	1,303	953	28,386	47,017	41,968	11.7	2.1	31.7
1000	5.388	1,304	955	56,490	87,233	63,322	18.2	3.6	37.7

1 kg of each compound is compared.
[a] Degradation effects of HFC-134a is included in TWPT(W m^{-2}) and CWP calculation. 80% of HFC-134a is decomposed into carbon dioxide and 20% is decomposed into trifluoroacetic acid.

reaching a given time. This concept is equivalent to the concept for GWP, except for the following points.

(1) GWP is based on the warming effect of carbon dioxide for a given evaluation period, whereas CWP is based on the warming effect of carbon dioxide for a period of 100 years, and it does not changes with the evaluation time, making it possible to carry out an evaluation changing the period of time. The difference between CWP and GWP can be observed in equations of Fig. 3.
(2) GWP estimates the direct effect of the chemical compound, whereas CWP consider the four combined warming effects. It also leaves open the possibility of incorporating new evaluation criteria in the future.

Table 2 presents the calculated values for HCFC-141b by classifying the four effects.

Fig. 1 shows curves for CWP of carbon dioxide and HFC-134a. Table 1 shows the value for CWP and TWPT.

2.2. Evaluation of warming effect of automobile air conditioning using TWPA and CWP

Evaluation of warming effect of automobile air conditioning based on the Life Cycle Climate Performance (LCCP [12]) data of Japan Automobile Manufacturers Association (JAMA) [13] was carried out using TWPA and CWP. For calculation purposes, this assessment considers production time, use time, leakage disposal time and leakage due to accidents as direct effect of the HFC-134a refrigerant, and energy consumption during use as indirect effect. A period of use of 10 years for each automobile is assumed. TWPG evaluation is presented in terms of one automobile produced each year for 50 years and each automobile is disposed after 10 years use. In the same way, CWP analysis is presented for the case of one unit produced each year for 1500 years and of one unit disposed after 10 years use. Based on this evaluation, Fig. 4 shows the results from TWPG analysis in the case of collection and no collection of the refrigerant.

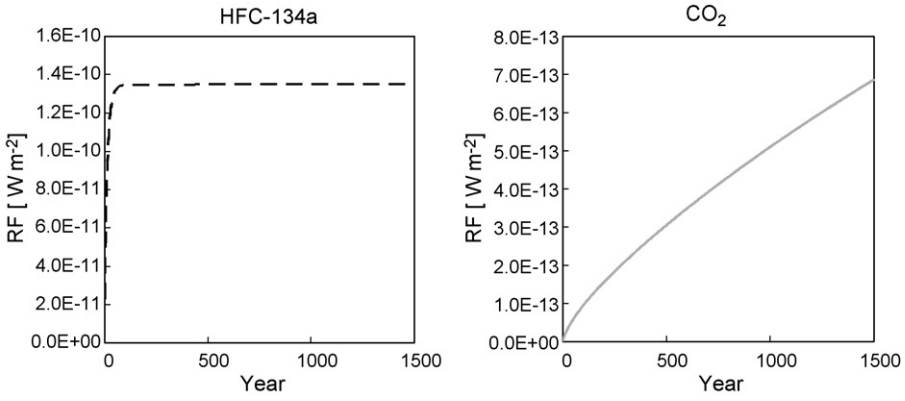

Fig. 2. TWPG (W m^{-2}) analyses. The warming effect by TWPG(W m^{-2}) analyses when 1 kg of HFC-134a or CO_2 is released every year for 1500 years.

$$CWP_X(ITH) = DWE + WEDC + WECO + CEOLD$$

$$= \frac{\int_0^{ITH} R_X(t)C_X(t)\,dt}{\int_0^{100} R_{CO_2}(t)C_{CO_2}(t)\,dt} + WEDC + WECO + CEOLD$$

$$GWP_X(ITH) = DWE = \frac{\int_0^{ITH} R_X(t)C_X(t)\,dt}{\int_0^{ITH} R_{CO_2}(t)C_{CO_2}(t)\,dt}$$

R_X : *Radiative Forcing of Compound X*

C_X : *Concentration of Compound X*

Fig. 3. Difference between CWP and GWP. CWP: composite warming potential, DWE: direct warming effect, WEDC: warming effect of decomposed compounds, WECO: warming effect of created ozone, CEOLD: cooling effect of ozone layer destruction.

As shown in Fig. 4, HFC-134a, a refrigerant with a high warming index of GWP (100 years) but a high-energy efficiency, is more effective than carbon dioxide with poor energy efficiency as refrigerant in reducing the warming effect. The HFC-134a, which has short atmospheric life, does not accumulate in atmosphere, whereas because of its low efficiency carbon dioxide is released in large amounts and accumulates in the atmosphere, resulting in a large warming effect. As HFC-134a does not accumulate in the atmosphere after use, it does not have a large effect on the warming, even though it is not recovered as refrigerant. For one automobile analysis in time span of 1500 years in Tokyo, use of 0.5 kg of HFC-134a as refrigerant results in a 10,000 fold reduction of the warming effect compared to the use of carbon dioxide for a time span of 100 years.

Table 2
Composite warming potential (CWP) of HCFC-141b

ITH [y]	100	500	1000	1500	∞	GWP
DWE[a]	700.000	700.015	700.015	700.015	700.000	700
WEDC[b]	0.700	2.388	4.026	5.434	42.001	
WECO[c]	0.005	0.005	0.005	0.005	0.005	
CEOLD[d]	−493.000	−493.011	−493.011	−493.011	−493.011	
CWP	207.705	209.398	211.035	212.444	248.995	

CWP = DWE + WEDC + WECO + CEOLD

[a] Direct warming effect.

[b] Warming effect of decomposed compounds.

[c] Warming effect of created ozone.

[d] Cooling effect of ozone layer destruction.

3. Experimental

3.1. Calculation of TWPA

3.1.1. Calculation of TWPA (kg)

For 1 kg of a compound that is released into the atmosphere, TWPA (kg) indicates how much of this compound will remain in the atmosphere a number of years later. The graphic representation of the relationship between time and remaining amount constitutes the TWPG (kg). The table representing this relationship is the TWPT (kg). For the TWPG (kg) of carbon dioxide, the equation for remaining amount in the atmosphere from the carbon cycle model WMO 1998 [14] was directly used. For HFC and similar compounds, the value was calculated based on the atmospheric life calculated from the reaction rate constant of the compound with OH radicals present in the atmosphere. From their theoretical reaction speeds, there is

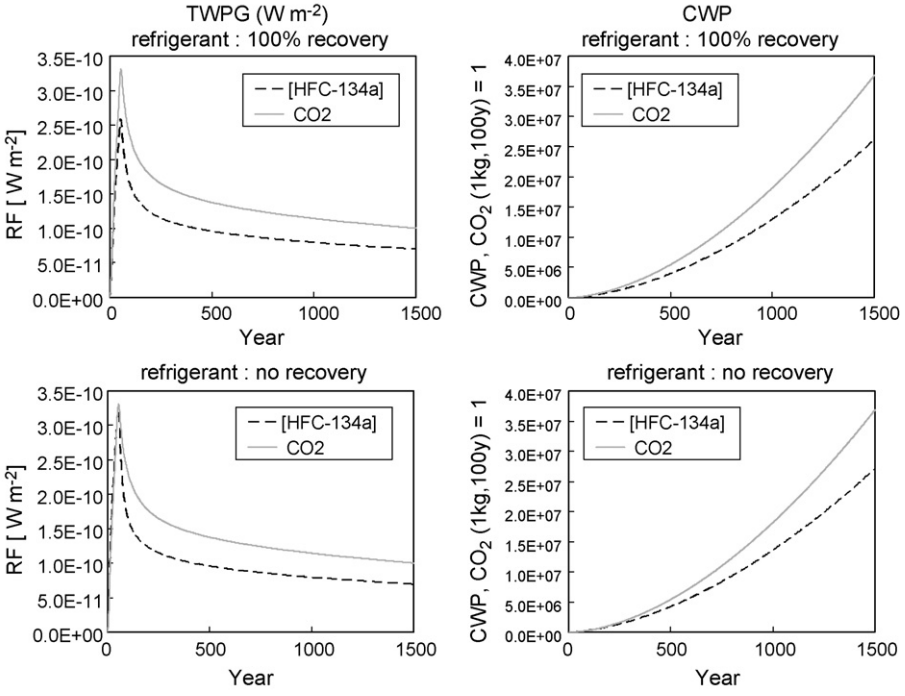

Fig. 4. Comparison between HFC-134a and CO_2. TWPG (W m^{-2}) analyses and CWP of mobile air conditioning refrigerant in Tokyo. Production and the use of the refrigerant are the same every year for the first 50 years.

relative decomposition of HC and HFC in the atmosphere. Partial results are shown in Fig. 1 and Table 1.

3.1.2. Calculation of TWPA ($W\,m^{-2}$)

TWPA ($W\,m^{-2}$) was calculated adding the four warming effects described below.

3.1.2.1. Calculation of the direct warming effect (DWE). This calculation represents the greenhouse effect of 1 kg of a chemical compound released into the atmosphere and the decrease with time of this greenhouse effect. radiative forcing (RF) calculated according to the atmospheric model is converted to weight units and multiplied by TWPA (kg) to calculate TWPA ($W\,m^{-2}$). The RF value used was the value established by IPCC [15].

3.1.2.2. Calculation of the warming effect of decomposed compound (WEDC). There are several warming substances produced from decomposition of a compound A in the atmosphere, and not all of them can be identified. Carbon dioxide, which is the most common compound formed when carbon-containing compounds react with the OH radicals in the atmosphere, was used for the calculations. How many kilograms of carbon dioxide are produced from compound A (1 kg) was estimated from chemical stoichiometric equations, and this value was used to calculate the gradual release of carbon dioxide as the chemical compound A decomposes in the atmosphere. Taking into account the release and decrease of carbon dioxide in the atmosphere, the TWPA ($W\,m^{-2}$) of decomposed compounds was established.

In the case of HFC-134a, the theoretical amount of released carbon dioxide by decomposition of HFC-134a in the atmosphere over time is assumed to be 0.8 of its stoichiometric amount, as 20% of HFC-134a is converted to TFA [7,8].

3.1.2.3. Calculation of the warming effect of created ozone (WECO). The value for RF of troposphere ozone was 0.34 W/m^2 as reported in several works [5]. For the total world amount of troposphere ozone, 250 Tg (1998) was used for the calculation, which gives a RF value for ozone of 1.36×10^{-12} W/m^2kg. On the other hand, the amount of troposphere ozone produced by a compound A was calculated using the Carter Equation [16,17]. In other words, the amount in kg of ozone produced from compound A (1 kg) was calculated from the UMIR (upper limit maximum incremental reactivities). For TWPG ($W\,m^{-2}$) related to the formation of troposphere ozone, this RF is used and an atmospheric life of 20 days is assumed to calculate the time variation of the remaining amount in the atmosphere.

3.1.2.4. Calculation of the cooling effect of ozone layer destruction (CEOLD). It is well known that the destruction of ozone layer has affected the cooling of the troposphere [18]. In the case of these chemical compounds, this effect is estimated as net-GWP. As the difference between the upper and lower limits of the cooling effect is large, in the case of chemical compounds that have been reported in the literature [11], RF of the cooling effect is calculated using the average value of the upper and lower limits. On the other hand, for chemical compounds that are not reported, the RF of the cooling effect was calculated based on the estimation of the net-GWP from the graphs of the cooling effect of a set value of released chlorine and their atmospheric life. The amount of chlorine released during decomposition of chlorine containing chemical compound A (1 kg) was calculated. It was assumed that the cooling effect is proportional to the extent of depletion of the ozone layer, which is proportional to the amount of chlorine that reaches the stratosphere, which is proportional to the amount of chlorine released by decomposition of compound A. For a set of calculations, time variation of the cooling effect ($W\,m^{-2}$) was calculated according to the TWPA (kg) in atmosphere of chemical compound A.

3.1.2.5. Calculation of TWPA ($W\,m^{-2}$). The four effects calculated (DWE, WEDC, WECO, and CEOLD) were added in the time to complete TWPA ($W\,m^{-2}$). A part of the results is presented in Table 1.

3.2. Calculation of CWP

CWP corresponds to the value of integration of TWPG ($W\,m^{-2}$), which incorporates the four effects. Integration time horizon (ITH) of the warming effect becomes the total sum of these effects.

In actual calculation, after integrating each four effects separately, the obtained values were added to calculate CWP. Table 2 shows an example of HCFC-141b for each of the four effects. Table 1 presents some values for CWP.

3.3. Evaluation of mobile air conditioning by TWPG and CWP

The Japan Automobile Manufacturers Association (JAMA) presents [13] the LCCP evaluation of automobile air conditioning. The data is converted to TWPG and CWP shown in Fig. 4. Evaluation was based on the combination of the warming gases released during the use of automobile air conditioning and analyses of the TWPG and CWP for 1 kg of the previously calculated compound such as carbon dioxide and HFC-134a.

4. Conclusion

The most important objective for global warming strategies is the stabilization of the warming gases present in the atmosphere. This objective has been incorporated into the Framework Convention on Climate Change (FCCC). The present evaluation methods, TWPA and CWP are considered to be effective to achieve this objective. It was also possible to incorporate the four warming effects into a general index. These evaluation results can be applied to a large number of guidelines for strategies to stop global warming.

References

[1] A. Sekiya, M. Yamabe, K. Tokuhashi, Y. Hibino, R. Imasu, H. Okamoto, Fluorine and the Environment, vol. 1, Elsevier Science, 2006 (Chapter 2), pp. 33–87, ISSN 1872-0358.

[2] IPCC, Climate Change The Scientific Base, IPCC, 2001, p. 223.
[3] H. Onishi, 15th Annual Earth Technical Forum and Mobile Air Conditioning Summit, Washington, DC, USA, 2004.
[4] IPCC, Climate Change The Scientific Base, IPCC, 2001, p. 385.
[5] IPCC, Climate Change The Scientific Base, IPCC, 2001 (Chapter 3), p. 183.
[6] Collins, et al. Climate Change, 52, 2002, pp. 435–479.
[7] 7–20% is reported T.J. Wallington, et al. J. Phys. Chem. 100 (1996) 18116–18122.
[8] 30% is reported O.-J. Nielsen, et al. in: Proceedings of the Workshop on the Atmospheric Degradation of HCFCs and HFCs. AFEAS (Alternative Fluorocarbons Environmental Acceptability Study), 1993, pp. 2–74.
[9] H. Frank, et al. Environ. Sci. Technol 36 (2002) 12–15.
[10] IPCC, Climate Change The Scientific Base, IPCC, 2001, p. 260.
[11] (a) J.M. Calm, Proceeding of the Fourth International Symposium NCGG-4, 2005, ISBN 90 5966 043 9;
(b) A. Sekiya, Investigation on the global warming index for chlorofluorocompounds, in: 18th International Symposium on Fluorine Chemistry, APPL 013, Bremen, Germany, 2006.
[12] (a) A. Sekiya, Automotive Airconditioning Reporter (AAR), vol. 49, October–November 2005, pp. 6–10;
(b) S. Papasavva, W.H. Hill, MAC Summit, New Delhi, India, 2005;
(c) R.W. Johnson, The Earth Technologies Forum and Exhibition, Washington D.C., USA, 2003;
(d) A.D. Little, AFEAS, Ref. 46342, Cambridge, MA, USA, 1994;
(e) A. Sekiya, JSAE Automotive Air-Conditioning Conference, Tokyo, 2007;
(f) A. Sekiya, 18th Winter Fluorine Conference, 2007.
[13] T. Ikegami, JSAE Automotive Air-Conditioning Conference, Tokyo, 2007.
[14] Scientific Assessment of Ozone Depletion, WMO, 1998, pp. 10.21.
[15] IPCC, Climate Change The Scientific Base, IPCC, 2001 Table 6.7–8, p. 388.
[16] W.P.L. Carter, Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment, Final Report to California Air Resources Board Contract Nos. 92-329, 95-308, May 2000.
[17] L. Chen, S. Kutsuna, K. Tokuhashi, T. Uchimaru, A. Sekiya, Kinetics of the gas-phase reaction of $CF_2{=}CF{-}CF{=}CF_2$ with O_3 and NO_3 radicals, Chem. Phys. Lett. 416 (2005) 187–191.
[18] IPCC, Climate Change The Scientific Base, Summary for policymakers, IPCC, 2001, p. 8.