

Contents lists available at [ScienceDirect](http://www.sciencedirect.com/science/journal/00221139)

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Evaluation of carbon dioxide equivalent values for greenhouse gases: CEWN as a new indicator replacing GWP

Akira Sekiya *, Sayuri Okamoto

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

ARTICLE INFO

ABSTRACT

Article history: Received 2 November 2009 Accepted 21 November 2009 Available online 1 December 2009

Keywords: Global warming GWP (Global Warming Potential) Warming indicator CEWN (Carbon Dioxide Equivalent Warming Number) Carbon equivalent Kyoto Protocol

A new indicator, the CEWN (Carbon Dioxide Equivalent Warming Number), is proposed as an alternative to the GWP (Global Warming Potential). CEWN is a metric where the global warming by the emission of gases is compared unifying the removal rate of each gas from the atmosphere, using carbon dioxide as a reference. To comply with the basket system of the Kyoto Protocol, GWP is used with a 100-year time horizon, making it unsatisfactory for the evaluation of long-lived compounds. As the removal rate from the atmosphere depends on the lifetime, the CEWN presents a fair assessment of the relative global warming.

 \odot 2009 Elsevier B.V. All rights reserved.

1. Introduction

Since the rise in the global surface temperature is attributed to the release of greenhouse gases caused by the economic activities of humankind, restraints on the release of the greenhouse gases are imperatively required to preserve the global environment. The relation between the amount of greenhouse gas emissions and the global surface temperature rise is a crucial assessment factor. The UNFCCC (United Nations Framework Convention on Climate Change) aims at the stabilization of atmospheric concentrations of greenhouse gases. The IPCC (Intergovernmental Panel on Climate Change) estimated changes in carbon dioxide emissions and its concentration in the atmosphere, and issued a guideline for reduction of carbon dioxide emissions in the future. In evaluation of the warming effect of an industrial technology, the author has introduced simplified methods that present graphically the total intensity of warming effect of released amounts of diverse greenhouse gases over time.

These methods indicated by radiative forcing (W) [\[1\]](#page-4-0) and a global surface temperature rise (ΔT) [\[2\]](#page-4-0) are called TWPG (Total Warming Prediction Graph) [\[3\]](#page-4-0) and TTPG (Total Temperature Prediction Graph) [\[4\]](#page-4-0), respectively, and have been developed and used for selecting suitable industrial technologies that emit various greenhouse gases [\[5\].](#page-4-0)

On the other hand, the Kyoto Protocol adopts the basket system, in which the assessment value is the total sum of the emission of each gas multiplied by its respective 100-year GWP. In this system, the intensity of the warming effect of each gas is evaluated using a single value as the carbon equivalent or carbon dioxide equivalent. This system is the favored method for the evaluation of industrial technologies by LCA (Life Cycle Assessment) or LCCP (Life Cycle Climate Performance).

The evaluation using 100-year GWP values has been widely accepted, because of the simplicity of its design and the lack of an adequate alternative method. However, from the point of view of reducing global warming, its consistency with the scenario of the stabilization of greenhouse gas concentrations predicted along the time axis, the mitigation of climate change, and the evaluation results of TWPG and TTPG, is ambiguous. Specifically, in the case of long-lived gases, although they are still present in the atmosphere and have warming effects even 100 years after their emission, evaluation using 100-year GWP excludes warming effects for a period much longer than 100 years, and thus their warming effects are underestimated. In contrast, in the case of short-lived gases, even though they are not present in the atmosphere 100 years after their emission, their warming effects are evaluated for the entire period of 100 years and the transition of their warming effects during that period is ignored.

Whereas it is difficult for evaluation along the time axis to assign a single warming value applicable to the basket system of the Kyoto Protocol to each greenhouse gas, the evaluation using

^{*} Corresponding author. E-mail address: akira-sekiya@aist.go.jp (A. Sekiya).

^{0022-1139/\$ –} see front matter © 2009 Elsevier B.V. All rights reserved. doi:[10.1016/j.jfluchem.2009.11.020](http://dx.doi.org/10.1016/j.jfluchem.2009.11.020)

GWP that assigns a single value to each gas brings ambiguity over the results.

Shine et al. have pointed out that the GWP does not represent the relationship between climate impacts and the emission of greenhouse gases adequately, and have proposed GTP_P (Global Temperature Change Potential) that is presented by global-mean surface temperature change instead of time-integrated radiative forcing with the view to represent the relation with the actual climate impacts and the emission clearly $[2]$. However, GTP_P shows merely the temperature rise at a given period after a pulse emission for each gas, and does not reflect the transition during that period and the effects after that period. GTP_S, proposed at the same time, makes the evaluation adding to the GTP_P concept a scenario in which 1 kg of gas is emitted every year, and it cannot be applied to the basket system of the Kyoto Protocol as the emission scenario is different.

In this report, a new GWP-alternative indicator, CEWN (Carbon Dioxide Equivalent Warming Number), is proposed for the global warming values of individual gases that are applicable to the basket system of the Kyoto Protocol. The CEWN is a metric that allows the comparisons of warming effects of gases from a scientific and fair point of view by assigning a single warming value incorporating a time-dependent evaluation based on the atmospheric lifetime of gas to each greenhouse gas.

2. Experimental

2.1. Calculation of removal rates from the atmosphere

The CEWN(X) of gas A is derived by dividing the cumulative global-mean radiative forcing of gas A from when 1 kg of gas A is emitted into the atmosphere to when X% of the emission is removed from the atmosphere $(ACEWN(X)_{A})$ by that of the reference gas, carbon dioxide $(ACEWN(X)_{CO₂}).$

The calculation of removal rate from the atmosphere of the carbon dioxide was carried out using both the coefficients of concentration response function quoted from the IPCC report and that from Shine's report, and the two calculations were compared. In principle, the same response function is used in both cases, but the function of IPCC is a trinomial and based on a revised version of the Bern Carbon Cycle model [\[6,1\],](#page-4-0) whereas Shine's function is a quadrinomial and the coefficients used are calculated by Joos (personal communication between Joos and Shine, 2003) using the Bern Carbon Cycle model [\[7,2\]](#page-4-0). The quantity of gas A remaining in the atmosphere following the emission was calculated using the lifetime of gas A according to the common concentration response function. These equations are shown below. The lifetimes of greenhouse gases were quoted from IPCC 2007 (personal communication between Joos and Shine, 2003).

The concentration response of carbon dioxide at time t following a 1-kg pulse emission at time $t = 0$, $R(t)_{\text{C}}$, is given by

$$
R(t)_{\rm C} = a_0 + \sum_i a_i \exp\left(\frac{-t}{\alpha_i}\right) \tag{1}
$$

where t is in years, and the coefficients for the equation used in IPCC 2007 are as follows:

 $a_0 = 0.217$, $a_1 = 0.259$, $a_2 = 0.338$, $a_3 = 0.186$, $\alpha_1 = 172.9$ years, $\alpha_2 = 18.51$ years, $\alpha_3 = 1.186$ years

and the coefficients for the above equation used in Ref. [\[2\]](#page-4-0) are as follows:

[Fig. 2](#page-2-0)(a) and (b) presents the concentration response curves of carbon dioxide. The removal rate of carbon dioxide, X_c , is given by

$$
X_{\rm C} \left[\% \right] = (1 - R(t)_{\rm C}) \times 100 \tag{2}
$$

For the majority of greenhouse gases, the concentration response at time t following a 1-kg pulse emission at time $t = 0$, $R(t)_{A}$, is given by

$$
R(t)_{A} = \exp\left(\frac{-t}{\alpha_{A}}\right) \tag{3}
$$

where α_A is the lifetime of the gas A and both α_A and t are in years. The removal rate of greenhouse gas A, X_A , is given by

$$
X_{A} [\%] = (1 - R(t)_{A}) \times 100
$$
 (4)

2.2. Calculation of CEWN

The $CEWN(X)$ value relative to carbon dioxide was derived by dividing the time-integrated global-mean radiative forcing of gas A, which was yielded by integrating the values obtained by multiplying its quantity remaining in the atmosphere by its radiative efficiency over the period between the emission of gas A and the time when X% of the emission is removed from the atmosphere, by the timeintegrated forcing of carbon dioxide calculated in a similar way. For both cases, IPCC and Shine, the radiative efficiency per kilogram of carbon dioxide used was 1.805×10^{-15} W m⁻² kg⁻¹ which was obtained from the radiative efficiency calculated by IPCC based on the background CO $_2$ mixing ratio of 378 ppm, 0.01413 W m $^{-2}$ ppm $^{-1}$ [\[1\],](#page-4-0) the mean molecular weight of air, 28.96 kg kmol⁻¹, and the total mass of atmosphere, 5.15×10^{18} kg [\[2\].](#page-4-0) For the radiative efficiency of greenhouse gases, the values of IPCC 2007 were used. The equation used for the calculation of CEWN is as follows.

When the elapsed years, after 1 kg of gas A and 1 kg of carbon dioxide are emitted at the beginning until X% of their emission is removed from the atmosphere denoted by t_{X_A} and t_{X_C} , respectively, $CEWN(X)$ of gas A is given by

$$
ACEWN(X)
$$

$$
CEWN(X) = \frac{ACEWN(X)_A}{ACEWN(X)_C}
$$

=
$$
\frac{\int_0^{t_{X_A}} A_A R(t)_A dt'}{\int_0^{t_{X_C}} A_C R(t)_C dt'}
$$

=
$$
\frac{A_A \alpha_A [1 - \exp(-t_{X_A}/\alpha_A)]}{A_C [a_0 t_{X_C} + \sum_i a_i \alpha_i (1 - \exp(-t_{X_C}/\alpha_i))]}
$$
(5)

where A_A and A_C is the radiative efficiency due to 1 kg increase in atmospheric abundance of gas A and carbon dioxide, respectively, and the coefficients, a_0 , a_i and α_i are the same as in Eq. (1). Partial results are shown in [Fig. 1,](#page-2-0) and [Tables 1 and 2](#page-2-0).

2.3. Calculation of CEWN₂

The $CEWN(X)$ of gas A including the warming effect of carbon dioxide, which is a decay product of gas A, was calculated and denoted by $CEWN₂(X)$. When every carbon atom included in gas A decomposed is assumed to change into carbon dioxide, as the CEWN is the value relative to carbon dioxide, the CEWN attributable to the decay product, $CO₂$, is simply derived from the carbon number of gas A and the ratio of molecular weights of carbon dioxide to that of gas A, and the $CEWN₂$ is given by

$$
CEWN2(X) = CEWN(X) + CA \times \frac{M_C}{M_A} \times \frac{X}{100}
$$
 (6)

where C_A is the carbon number of gas A, and M_C and M_A are molecular weights of carbon dioxide and gas A, respectively.

$$
\begin{array}{ll} a_0=0.1756, & a_1=0.1375, & a_2=0.1858, \, a_3=0.2423, & a_4=0.2589, \\ \alpha_1=421.093 \, \text{years}, & \alpha_2=70.5965 \, \text{years}, & \alpha_3=21.4216 \, \text{years}, & \alpha_4=3.4154 \, \text{years} \end{array}
$$

Fig. 1. (a) Values of CEWN at the given removal rate in the case where coefficients for concentration response function of $CO₂$ are the same as Shine [\[2\]](#page-4-0). (b) As (a) but in the case where the coefficients are the same as IPCC 2007. The radiative efficiency of CO₂ used for the calculation is 1.805×10^{-15} W m⁻² kg⁻¹.

3. Results and discussion

3.1. Calculation of CEWN

The CEWN (X) of compound A is a value obtained by dividing the accumulated warming effects due to pulse emission of 1 kg of compound A until X% of A is removed from the atmosphere by that of 1 kg of the reference gas, carbon dioxide, until $X\$ [%] of $CO₂$ is removed. Eq. [\(5\)](#page-1-0) shows this calculation.

As the behavior in the atmosphere differs from gas to gas, the time required for the removal of $X\$ [%] of compound A, t_{X_0} , is obviously different from the time required for the removal of the reference, carbon dioxide, t_{X_C} , in Eq. [\(5\)](#page-1-0).

Fig. 1(a) shows the relations between the value of CEWN and the removal rate from the atmosphere for CFC-11, HFC-134a, and NF₃ calculated using the coefficients for concentration response function of Shine [\[2\].](#page-4-0) Fig. 1(b) shows a graph calculated in the same way as Fig. 1(a) but using coefficients quoted from IPCC 2007 [\[1\].](#page-4-0)

In these figures, as the decay of greenhouse gases in the atmosphere is given by Eq. [\(3\)](#page-1-0), when the concentration response function of carbon dioxide is the same, those gases should show homothetic curves. Therefore, the ratio of the years until individual greenhouse gas decreases by the given removal rate to the lifetime of each gas becomes the same when the removal rate is fixed. These

Fig. 2. (a) Concentration response of long-lived gases and carbon dioxide in the case where coefficients for concentration response function of $CO₂$ are the same as Shine [\[2\]](#page-4-0). (b) As (a) but in the case where the coefficients are the same as IPCC 2007. The radiative efficiency of CO₂ used for the calculation is 1.805×10^{-15} W m⁻² kg⁻¹.

values that depend on the removal rate are shown in Tables 1 and 2. For carbon dioxide, as its behavior in the atmosphere is different from other gases, the years until $CO₂$ decreases by the given removal rate are shown in Tables 1 and 2.

Comparing Fig. 1(a) and (b), at low removal rates, the CEWN value calculated using the IPCC coefficients is almost twice the value of the CEWN by the Shine's coefficients. This is because up to a removal rate of 6%, carbon dioxide decreases more rapidly from the atmosphere in the case of using the IPCC coefficients than that of Shine's coefficients. When the removal rate is low, the time required to reach the same removal rate differs by coefficients used by nearly half the time, then the warming effects of carbon dioxide calculated as the integration value during that time differs by half, and consequently results are obtained of a difference of almost twice the CEWN value that takes this integration value as the denominator. The CEWN calculated using IPCC coefficients shows an L-shaped curve against the removal rate. This is attributed to the inversion of the decrease rate of carbon dioxide in the vicinity of 6% of removal rate between the case of using IPCC coefficients and that of Shine's coefficients. At low removal rates, the IPCC value does not correspond to the Shine value well.

Moreover, as warming at the early stage is overestimated at low removal rates, the fairness of the comparison is poor. When comparing greenhouse gases by CEWN in which carbon dioxide is

Table 1(a)

The radiative efficiency of CO₂ used for the calculation is 1.805×10^{-15} W m⁻² kg⁻¹.

Ouoted from IPCC 2007.

b The CEWN values for methane have been multiplied by 1.4 to account for the indirect forcing following GWP for methane in IPCC 2007.

Table 1(b)

Carbon dioxide Equivalent Warming Numbers for some GHGs in the case where the coefficients for concentration response function of CO2 are the same as Shine [\[2\].](#page-4-0)

The radiative efficiency of CO₂ used for the calculation is 1.805×10^{-15} W m $^{-2}$ kg $^{-1}$.

Quoted from IPCC 2007.

^b The CEWN values for methane have been multiplied by 1.4 to account for the indirect forcing following GWP for methane in IPCC 2007.

used as a reference, we recommend comparing at high removal rates.

[Fig. 2](#page-2-0) shows concentration response to a pulse emission for long-lived gases such as CF_4 , C_2F_6 , C_3F_8 , and carbon dioxide. Results for carbon dioxide according to the IPCC function are shown in [Fig. 2](#page-2-0)(a), and those for Shine's function are shown in [Fig. 2\(](#page-2-0)b).

As shown in these figures, carbon dioxide due to a pulse emission decreases to a certain removal rate, and then shows no further changes. This means that the concentration response function can hardly express the removal of carbon dioxide from the atmosphere after a certain period of time. Therefore, if the removal rate is set at too high a value, the scientific basis related to the removal of carbon dioxide from the atmosphere becomes poor. The period of the years elapsed for the carbon dioxide concentration response used for CEWN calculation is assumed to be limited to between 700 and 1000 years according to the IPCC function, and from 1400 to 2000 years according to Shine's function. These limits shown in terms of removal rate result in slightly over 78% in the case of IPCC function and slightly over 82% in the case of Shine's function, as shown in [Fig. 2](#page-2-0).

Table 2

 $CEWN(82)$ and $GWP₁₀₀$ for major GHGs.

The radiative efficiency of CO₂ used for the calculation is 1.805×10^{-15} W m⁻² kg⁻¹. The coefficients for concentration response function of CO₂ are the same as Shine [\[2\].](#page-4-0)
^a Quoted from IPCC 2007.

b The CEWN value for methane has been multiplied by 1.4 to account for the indirect forcing following GWP for methane in IPCC 2007.

The radiative efficiency of CO₂ used for the calculation is 1.805×10^{-15} W m $^{-2}$ kg $^{-1}$ ^a Quoted from IPCC 2007 except for the values of ethane, propane and pentane which are calculated in accordance with the procedure for calculating GWP in IPCC 2007 using lifetimes quoted from IPCC/TEAP 2005 [8].

[Table 1](#page-2-0) shows CEWN values in three removal rates for some greenhouse gases. [Table 1\(a\)](#page-2-0) corresponds to those for the case of the IPCC function, whereas [Table 1\(b\)](#page-3-0) corresponds to those for the case of Shine's function.

From analyses of data in [Table 1](#page-2-0) and the concentration response function of carbon dioxide, it was thought that a high degree of scientific fairness in CEWN values could be achieved, when the removal rate in the case of IPCC is 78% and that in the case of Shine is 82%. The optimal point set for the removal rate is higher in the case of Shine than IPCC, and consequently it is possible to calculate the decrease of carbon dioxide according to Shine's function for a longer period of time. As a higher removal rate is desirable, the CEWN(82) value calculated using the Shine's concentration response curve for carbon dioxide is considered to be the optimal CEWN value. [Table 2](#page-3-0) shows those values.

3.2. Calculation of CEWN₂

The CEWN₂ (X) of gas A is the value that adds the warming effect of a decay product of gas A, carbon dioxide, to $CEWN(X)$. Eq. [\(6\)](#page-1-0) shows this calculation. $CEWN₂$ values for some greenhouse gases are shown in Table 3.

4. Conclusions

The CEWN presents the following feature compared to the GWP.

(1) Comparison between greenhouse gases are carried out at equal quantities.

In the case of GWP₁₀₀, although the emission of gas is 1 kg as CEWN, the warming effect caused by gas remaining after 100 years is ignored. That is, for a gas 50% of which has been removed from the atmosphere by 100 years later, the warming effect of the remaining 0.5 kg is not taken into account, therefore it cannot be said that the effect of 1 kg of the gas was evaluated. Of course, for a gas that has been 100% removed for up to 100 years, the evaluation covers the whole 1 kg. Therefore, it is not an equivalent quantity evaluation. On the other hand, in the case of CEWN, as the quantity of the gas to be evaluated is always equivalent by unifying the removal rate from the atmosphere, the scientific fairness is higher than in the case of GWP.

(2) The concept of atmospheric lifetime has been introduced.

The 100-year GWP value conventionally used represents the warming effect uniformly during a period of 100 years following the emission, whereas the CEWN equalizes the removal rates of gases to be compared, and the short-lived gas is evaluated during a short period of time, and the long-lived gas is evaluated during a long period of time. Therefore, the CEWN has actuality and higher fairness.

(3) As prolonged evaluation as possible may be carried out by CEWN within the range where the behavior of carbon dioxide in the atmosphere is unambiguous by setting an upper limit on the removal rate of carbon dioxide from the atmosphere as shown in [Fig. 2.](#page-2-0) The behavior of carbon dioxide in the atmosphere over long periods is still not well understood. However, a comparison including extremely long-lived gases such as PFCs will not be accomplished unless a quite long-term evaluation is carried out. In the case of GWP₁₀₀, the long-term evaluation for these gases is impossible. On the other hand, in the case of CEWN, which employs the evaluation at the same removal rate, the longterm evaluation for extremely long-lived gases, in which their respective lifetimes are reflected, is possible within the range where the removal rate of carbon dioxide is clear, thus the CEWN is a fairer metric.

The CEWN presents the following characteristics compared to the GTP.

- (1) While the GTP_P represents the global-mean surface temperature change and its relation with the climate impact is clear, the relation between the CEWN and climate change is harder to understand, as the CEWN gives great importance to the fairness of the comparison of warming effects. However, the CEWN has an advantage in the comparison of the total global warming effects.
- (2) The GTP_P corresponds to a value after a given period of time has elapsed, whereas the CEWN corresponds to an integrated value until a given removal rate has been reached. Accordingly, when applying to the evaluation by the basket system, the CEWN is a more adequate indicator for the evaluation of warming effects with reference to carbon dioxide.
- (3) As GTP_S carries its own emission scenario, it does not comply with the prediction of warming effects based on other scenarios. Meanwhile, as the CEWN has no own emission scenario, it is a possible alternative to the GWP.

References

- [1] P. Forster, et al. in: S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor, H.L. Miller (Eds.), Climate Change 2007: The Physical Science Basis, Cambridge University Press, Cambridge, UK/New York, USA, 2007 , pp. 129–234.
- [2] K.P. Shine, J.S. Fuglestvedt, K. Hailemariam, N. Stuber, Clim. Change 68 (2005) 281–302.
- [3] A. Sekiya, J. Fluorine Chem. 128 (2007) 1137–1142.
- [4] A. Sekiya, ACS Winter Fluorine Conf., Florida, USA, January, 2009.
- A. Sekiya, et al. in: A. Tressaud (Ed.), Fluorine and the Environment: Atmospheric Chemistry, Emissions & Lithosphere, vol. 1, Elsevier, 2006, pp. 33–87.
- [6] F. Joos, I.C. Prentice, S. Sitch, R. Meyer, G. Hooss, G.-K. Plattner, S. Gerber, K. Hasselmann, Glob. Biogeochem. Cycles 15 (2001) 891–908.
- F. Joos, M. Bruno, R. Fink, U. Siegenthaler, T.F. Stocker, C. Le Quéré, J.L. Sarmiento, Tellus 48B (1996) 397–417.
- G.J.M. Velders, et al. in: B. Metz, et al. (Eds.), IPCC/TEAP Special Report: Safeguarding the Ozone Layer and the Global Climate System, Cambridge University Press, Cambridge, UK, 2005, pp. 133–180.

Table 3