

新規フッ素系温室効果ガスの種類と特性、評価

Environmentally Accepted Fluorinated Gases

産業技術総合研究所

関屋 章

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2008年11月26日、ホテル機山館

The steps for acceptance of new technologies

Select Useful Alternative Technologies

What is Target

Technology Level

Sustainability
Efficiency

How to evaluate environment

What is benefit:

- Environment
- Resources

What is contribution to society

Environment analyses

Evaluated by $GWP \times t$

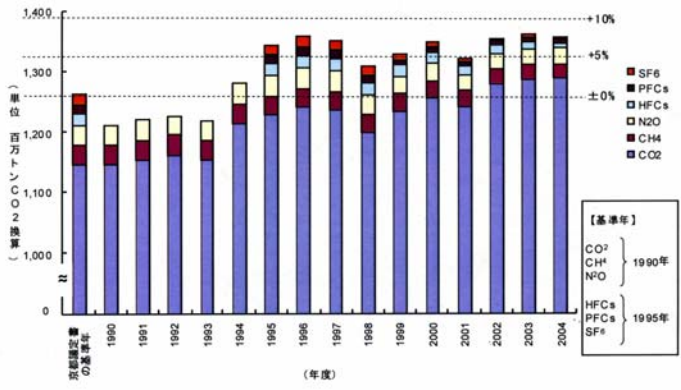


図 1 温室効果ガス総排出量の推移

National Greenhouse Gas Inventory Report of Japan 2006 ver.2

Mole fraction (ppt) of GHGs by IPCC 2007

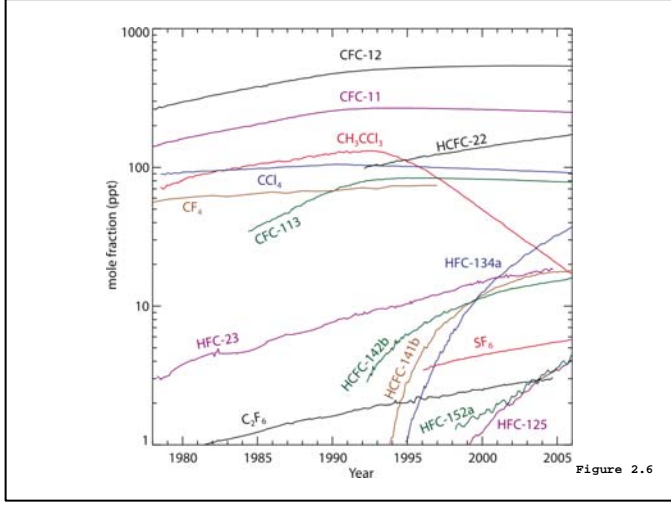
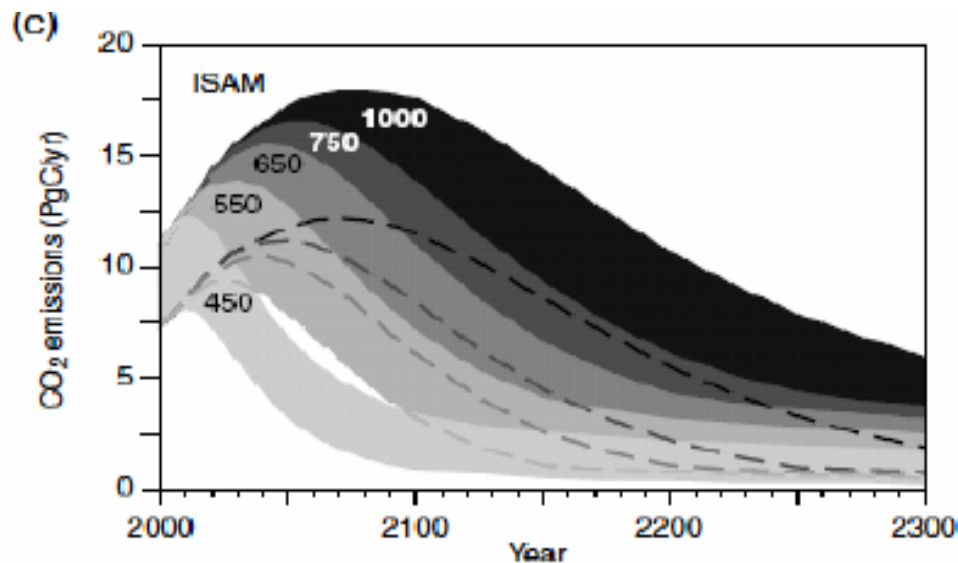


Figure 2.6

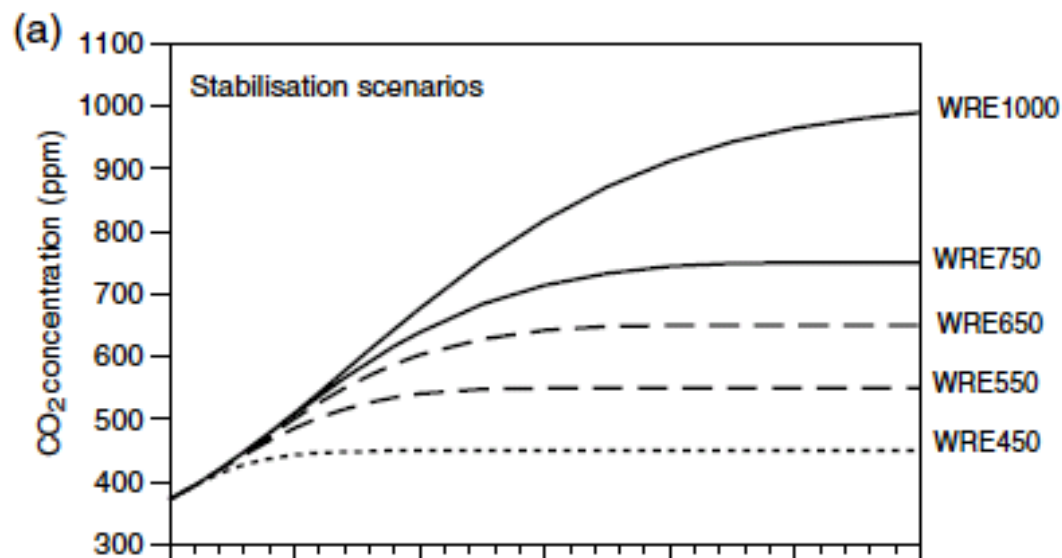
- GWP
 - Easy to look trend of GHGs emissions.
 - Random ITH value
 - Difficult to image future environment.
 - Selection of Technologies
 - Successful to chose better technology
 - Weak relation to atmosphere

Which do you chose by LCCP analysis?
 Tech. 1: $1000(GWP, Short LT) \times 1kg = 10000$
 Tech. 2: $1(GWP, Long LT) \times 1000kg = 10000$

IPCC 2001



**Reduction schedule of
GHGs is considered
with ppm analyses**



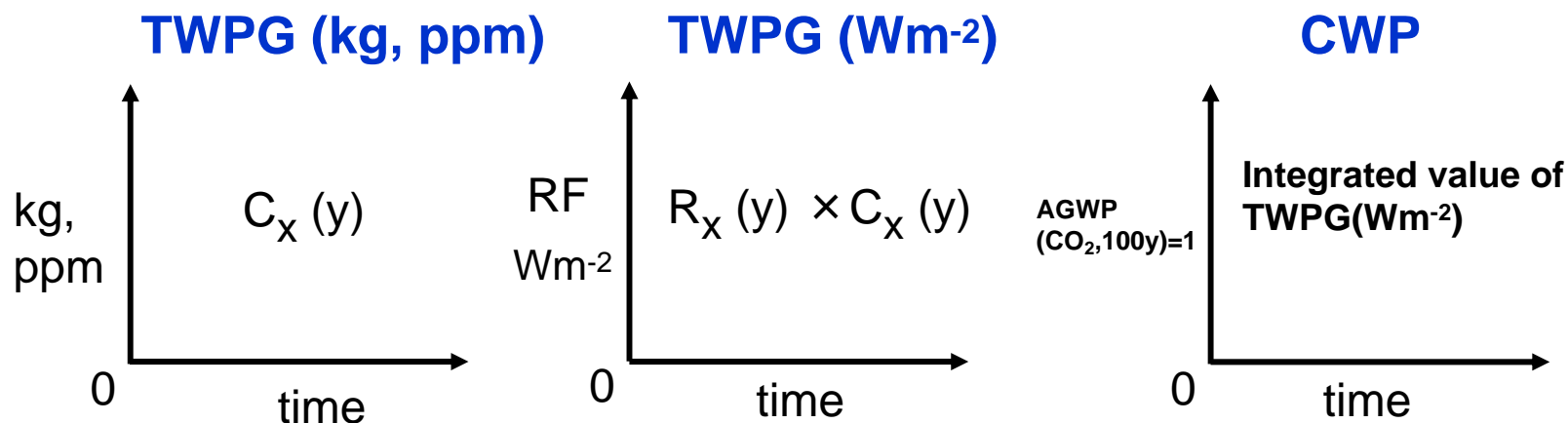
**UNFCCC:
Target is stabilize
GHGs atmospheric
concentrations**

Analysis Methods of Global Warming

Current analyses: **GWP**

(LCCP, LCA, LCCO₂, Carbon Offset, CDM, Carbon Footprint, Ecological Footprint, Carbon Neutral, Carbon Positive, Eco-point, -----)

Analyses by time



TWPG: Total Warming Prediction Graph

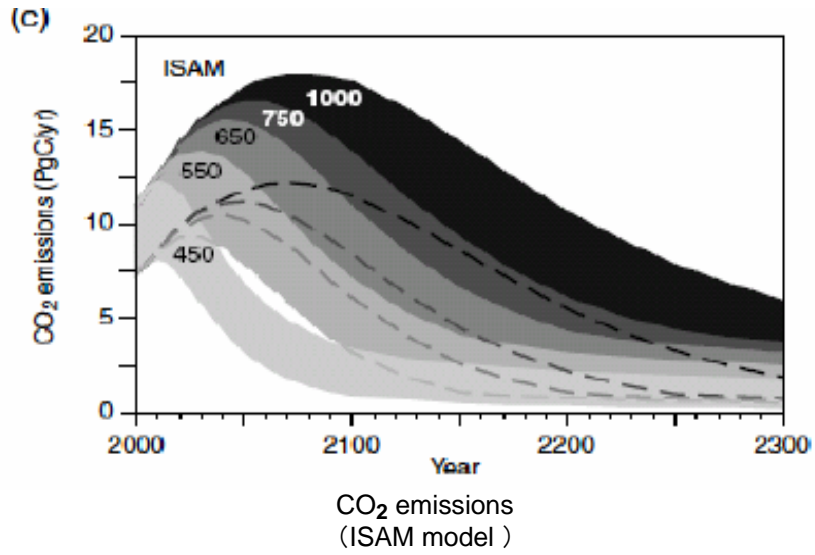
CWP: Composite Warming Effect

Calculated on the assumption that the same atmosphere is kept in the future.

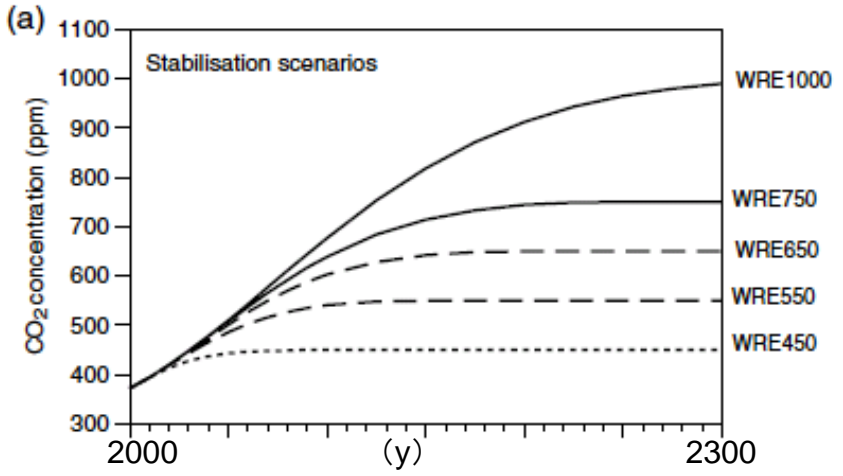
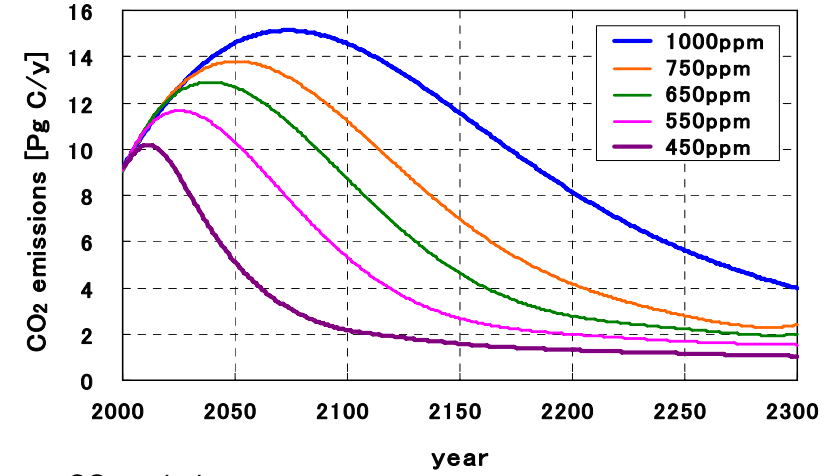
(According to "Sustainable Development" Concept)

A.Sekiya, Journal of Fluorine Chemistry 128 (2007) 1137–1142

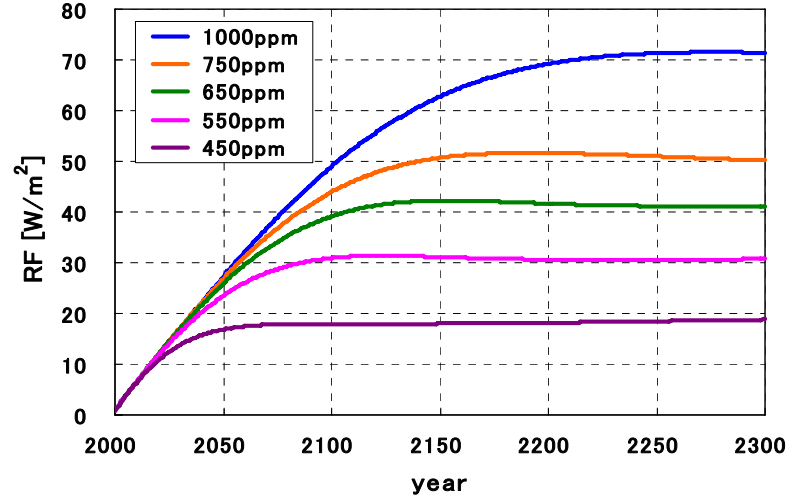
Scenarios of CO₂ emissions by TWPG and CWP



Simulation in IPCC 2001



TWPG



Ref. IPCC 2001

Similar to IPCC

Our Method

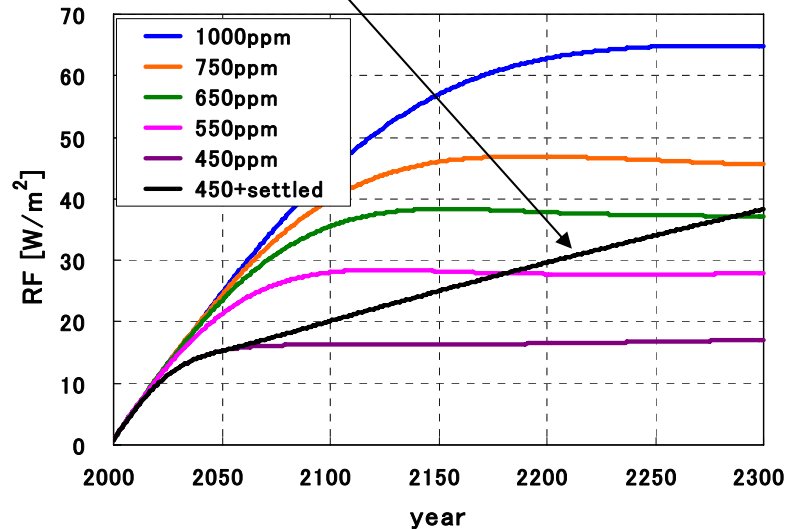
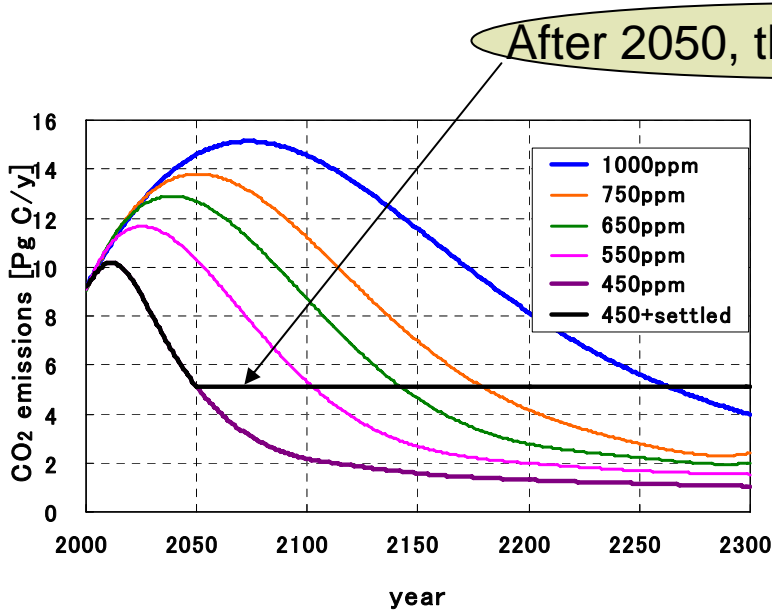
TWPG and CWP Analyses

Scenarios of CO₂ Emissions

TWPG

1) Scenario of IPCC 2001

2) 450 ppm scenario before 2050 + the same emissions after 2050

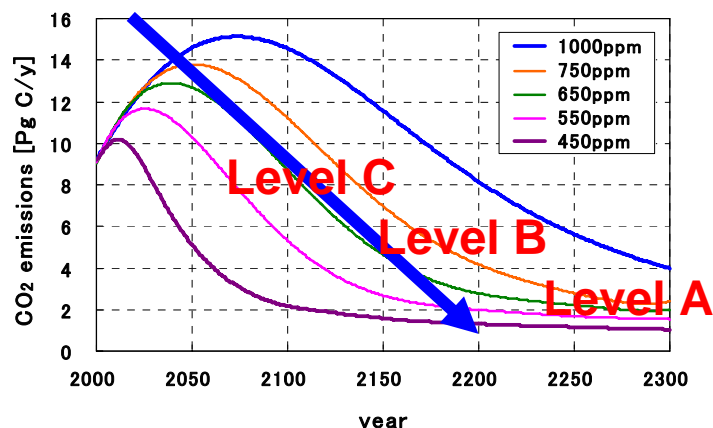


Continuous reduction of CO₂ emission is necessary

- 1) The energy related to carbon emissions must be phased out in the near future.
- 2) New non-carbon energy has to be developed urgently.

Setting Technology level is Important

Level of technologies



1) Continuous reduction of CO₂ emission is necessary

Level set is necessary

2) Technologies have to chose by high level setting

Level C: 6%(Japan) reduction, but no effect for more reductions

Level B: 50% (World) reduction, but no effect for more reductions

Level A: Sustainable technologies

-Backcasting (Level A)

- 1) What technology will be accepted in Level A technologies ?
- 2) Develop Level A technologies urgently.

-Forecasting (Level C, B, A)

- 1)New technologies which could reduce GHG emissions are under development.
- 2) Even if reduction amount of GHGs is small, quite high cost must be paid.

Current Alternative Technologies

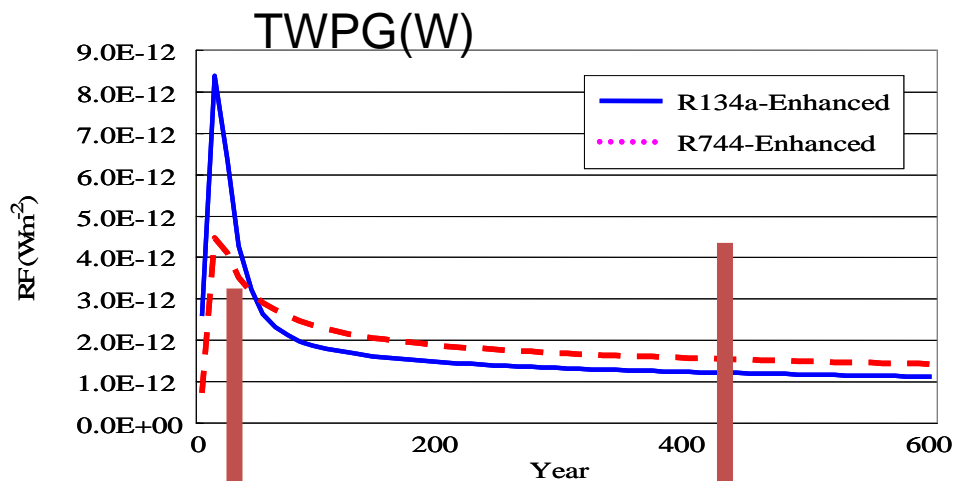
Example

Refrigerant
Foam Blowing Agent
Solvent

Semiconductor ?

• PFCs

• **NF₃**



Short Lifetime
Low GWP ?

High Performance

LCCP analysis

LCCP analysis shows total warming but doesn't shows the difference of two

Gases **HFO ↓** , HFC,

PFC ↑ , SF6 ↑ , NF3 ↑

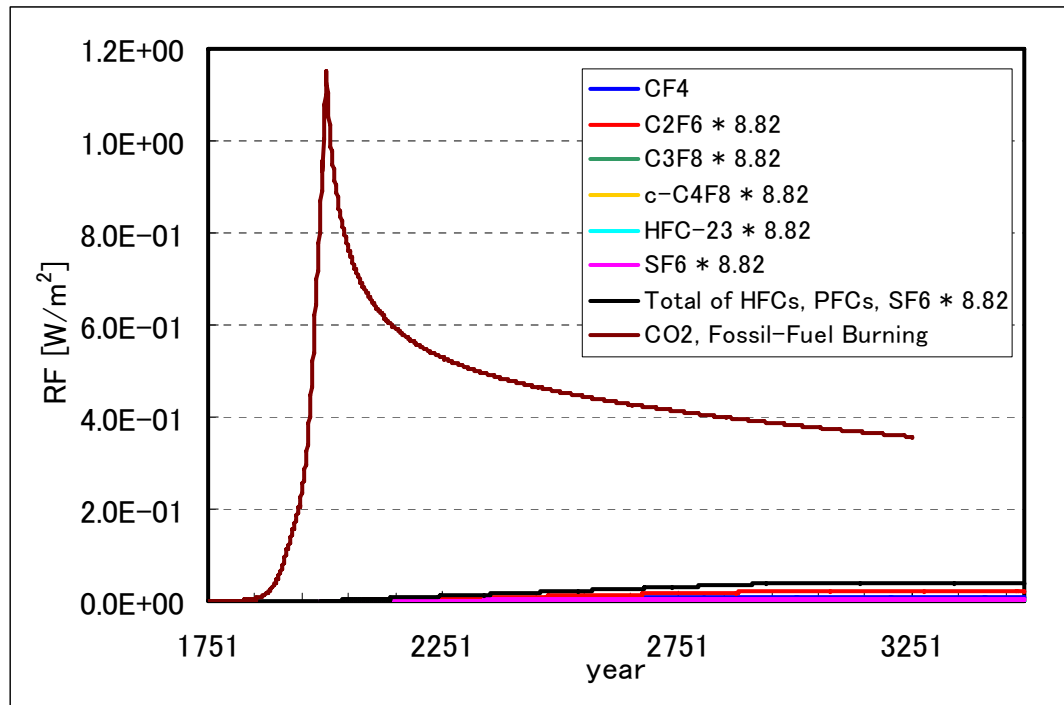
Energy

CO2 ↑

Semiconductor

TWPG (RF) of predicted emissions of PFCs

TWPG on the assumption that the same amount of 2001-2006 is emitted continuously until 3000.



Emissions and predicted emissions of PFCs from semiconductor manufacture in US

The graph shows the comparison between RF of PFCs' continuous use and of CO₂ emissions until 2004.

Continuous emissions of PFCs bring the large RF in the future.

Environmental Impacts of Semiconductor Gases

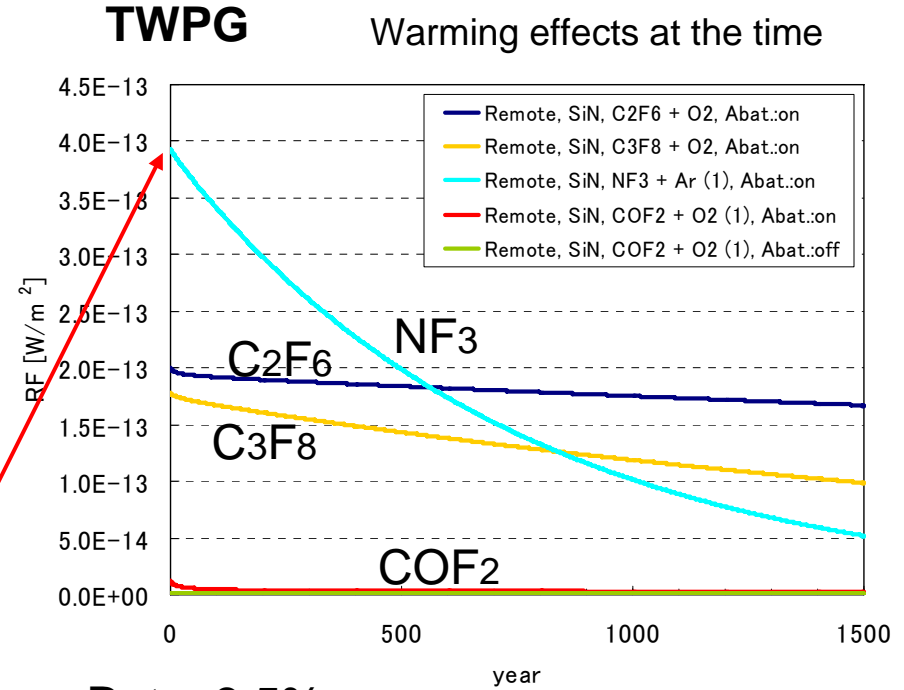
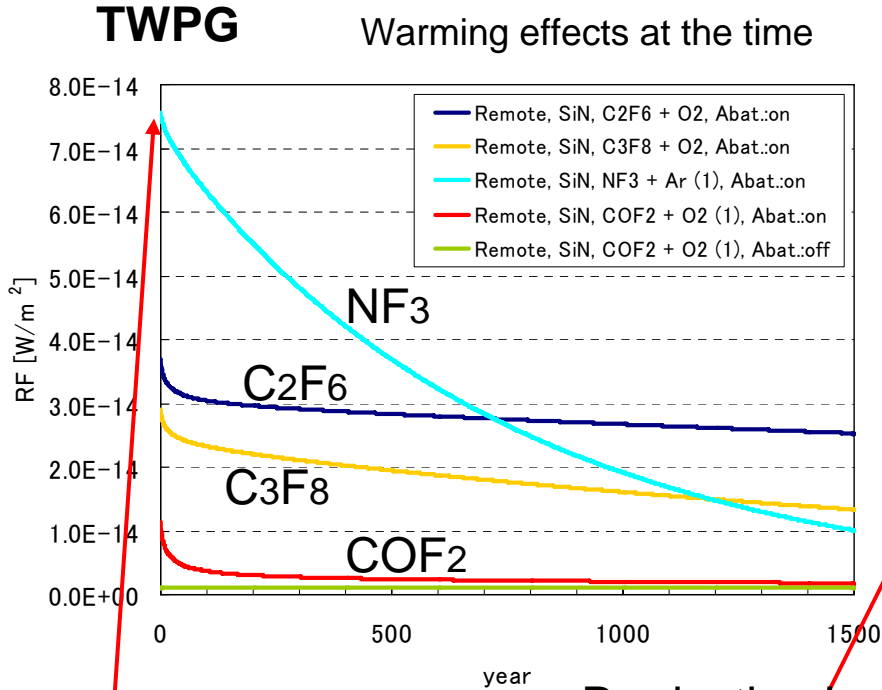
1kg analysis based on IPCC 2007

	Comp.	Lifetime [year]	CWP				GWP
			100 y	500 y	1000 y	1500y	100 y
↑ Unsustainable	CF ₄	50,000	7,390	36,802	73,239	109,313	7,390
	C ₂ F ₆	10,000	12,200	59,798	116,680	170,787	12,200
	C ₃ F ₈	2,600	8,830	40,941	74,721	102,591	8,830
	SF ₆	3,200	22,800	107,197	198,888	277,316	22,800
	NF ₃	740	17,200	66,837	100,797	118,149	17,200
↓ Sustainable	C ₄ F ₆	0.016	6.5	8.9	11.2	70.3	0.027
	c-C ₅ F ₈	0.98	91	93	96	152	90
	COF ₂	~0	0.7	2.1	3.6	40.0	0
	F ₂	0	0	0	0	0	0

•CWP includes the decomposed products and CO₂.

TWPG analyses of Semiconductor Cleaning system

- Tier 3
 - Remote
 - SiN
 - Abate. on/off
- (Incineration, City Gas)



Production Leakage Rate: 3.5%

Destruction Efficiency Parameters for Abatement (Equipment Specific)

PFCs, NF₃ = 0.99 → 0

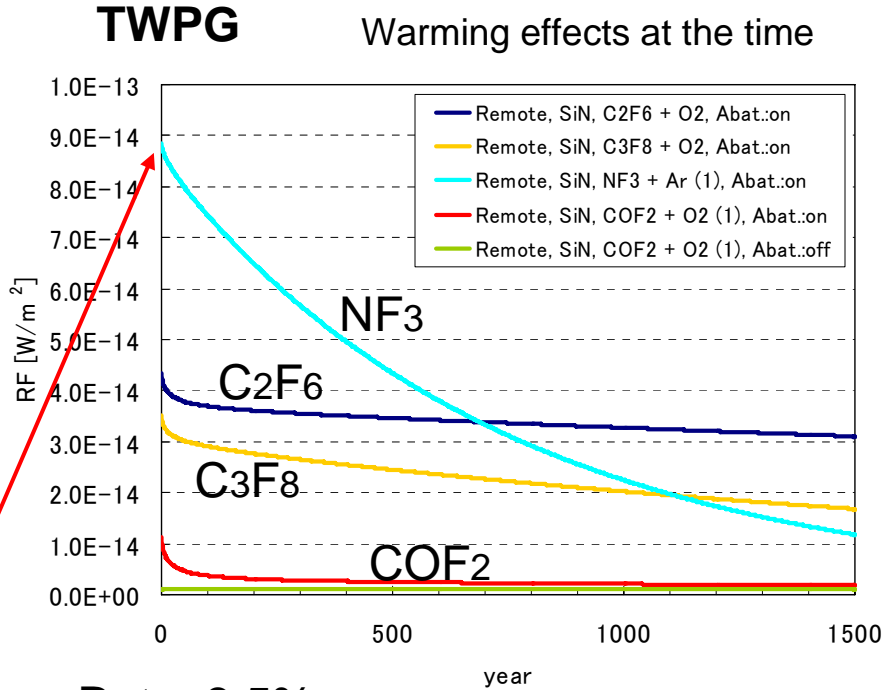
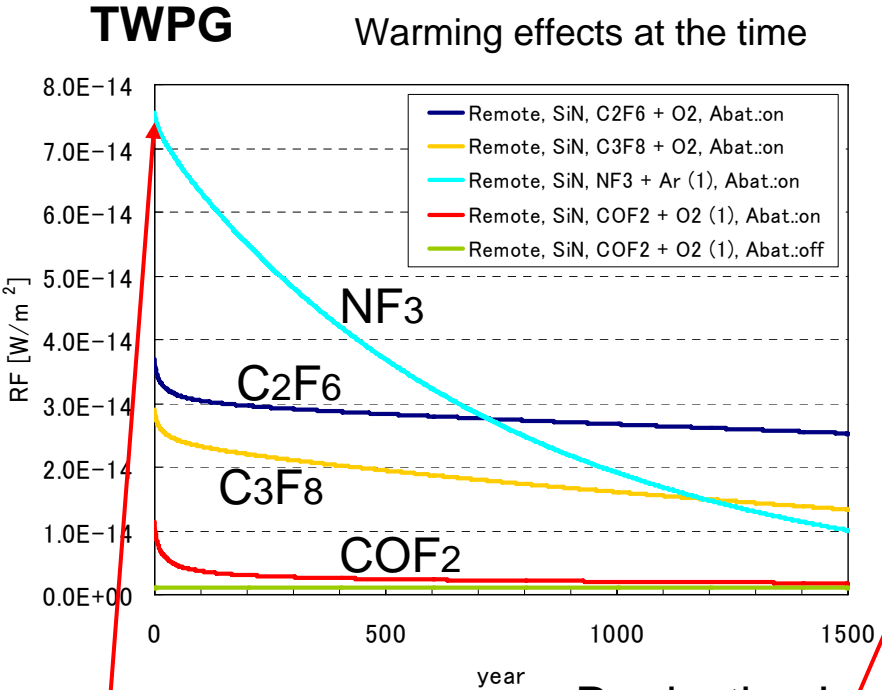
7.6×10^{-14} → 3.9×10^{-13}
(5.2 times larger)

TWPG(RF) becomes 5.2 times larger
CWP increases similarly.

TWPG analyses of Semiconductor Cleaning system

- Tier 3
- Remote
- SiN
- Abate. on/off

(Incineration, City Gas)



Production Leakage Rate: 3.5%

Destruction Efficiency Parameters for Abatement (Equipment Specific)

PFCs, NF₃ = 0.99 → 0.95

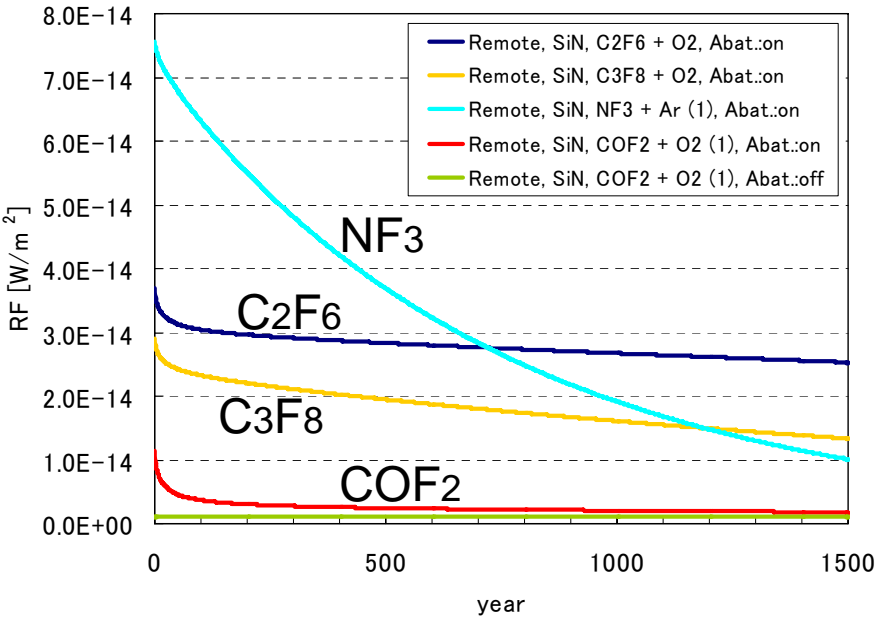
7.6×10^{-14} → 8.9×10^{-14}
(17% larger)

TWPG(RF) becomes 17% larger
CWP also becomes 17% larger

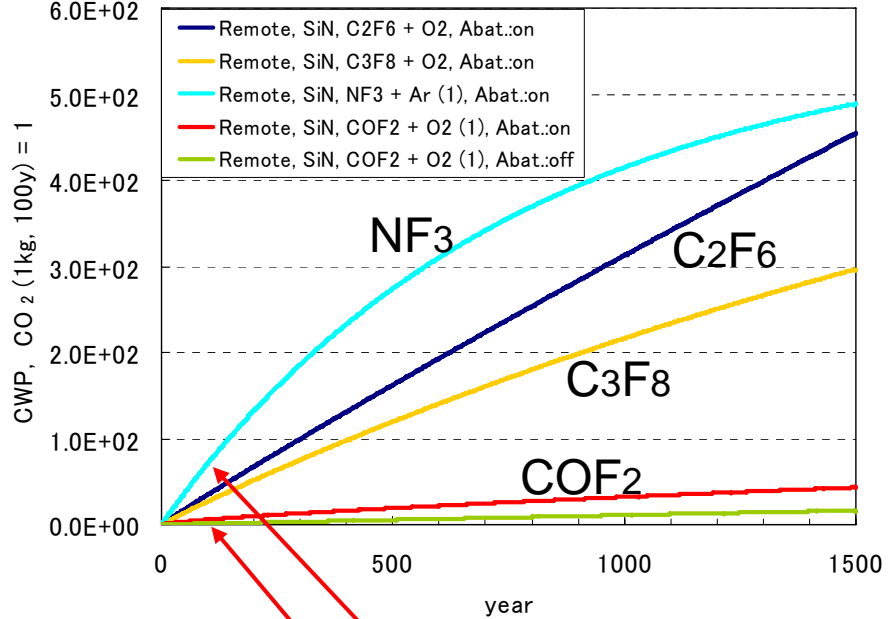
- Tier 3
 - Remote
 - SiN
 - Abate. on/off
- (Incineration, City Gas)

TWPG and CWP analyses of Semiconductor Cleaning system

TWPG(W) Warming effects at the time



CWP Integrated warming effects



Production Leakage Rate: 3.5%

Destruction Efficiency Parameters for Abatement (Equipment Specific)

PFCs, NF3 = 0.99

Integrated warming effect ... COF2 vs. NF3 = 1 : 62 (100y)

COF2(1.14) vs. NF3(71.05) = 1 : 62.3

Comparison of NF_3 and COF_2 as semiconductor cleaning gases

Remote system, SiN

		Reduction (W)		
NF_3	→	COF_2	62 → 1	Level A
Destruction ratio (No abatement system)				
0	→	0.99	5.2 → 1	Level B
Destruction ratio				
0.95	→	0.99	1.2 → 1	Level C

**Alternative technologies is the best choice.
It is much better than abatement system**

Scientific analyses guide the high level technologies

About GTP

Keith P. Shine, Jan S. Fuglestvedt, Kinfe Hailemariam, Nicola Stuber, *Climatic Change*, 68, pp.281-302, 2005.
"Alternatives to the Global Warming Potential for Comparing Climate Impacts of Emissions of Greenhouse Gases"

Abstract (part)

The Global Warming Potential (GWP) is used within the Kyoto Protocol to the United Nations Framework Convention on Climate Change as a metric for weighting the climatic impact of emissions of different greenhouse gases. **The GWP has been subjected to many criticisms** because of its formulation, but nevertheless it has retained some favor because of the simplicity of its design and application, and its transparency compared to proposed alternatives. Here, two new metrics are proposed, which are based on a simple analytical climate model. The first metric is called the **Global Temperature Change Potential** and represents the temperature change at a given time due to a pulse emission of a gas (**GTP_P**); the second is similar but represents the effect of a sustained emission change (hence **GTP_S**). Both GTP_P and GTP_S are presented as relative to the temperature change due to a similar emission change of a reference gas, here taken to be carbon dioxide.

- **There are uncertainties between the GWP metric and the environment change.**
- **The global warming is figured out using the metric based on the surface temperature change.**

GTP is also described in IPCC 2007 and UN.

Characteristics of GTP, GWP and TWPG

GWP: time-integrated radiative forcing after a pulse emission over normally a 100-year time horizon ($\text{CO}_2 = 1$)

The contribution of the past RF remains over 100 years. A 100-year makes little sense.

TWPG (AGWP): radiative forcing (W) after a pulse emission

A time-based value. After disappear from atmosphere, the radiative forcing is not counted. The value does not employ CO_2 as a reference.

AGT_P: global mean surface temperature change after a pulse emission

A time-based value. A gradual recovery of the heat from the sea is counted. The value does not employ CO_2 as a reference.

GTP_S: global mean surface temperature change due to sustained emission change

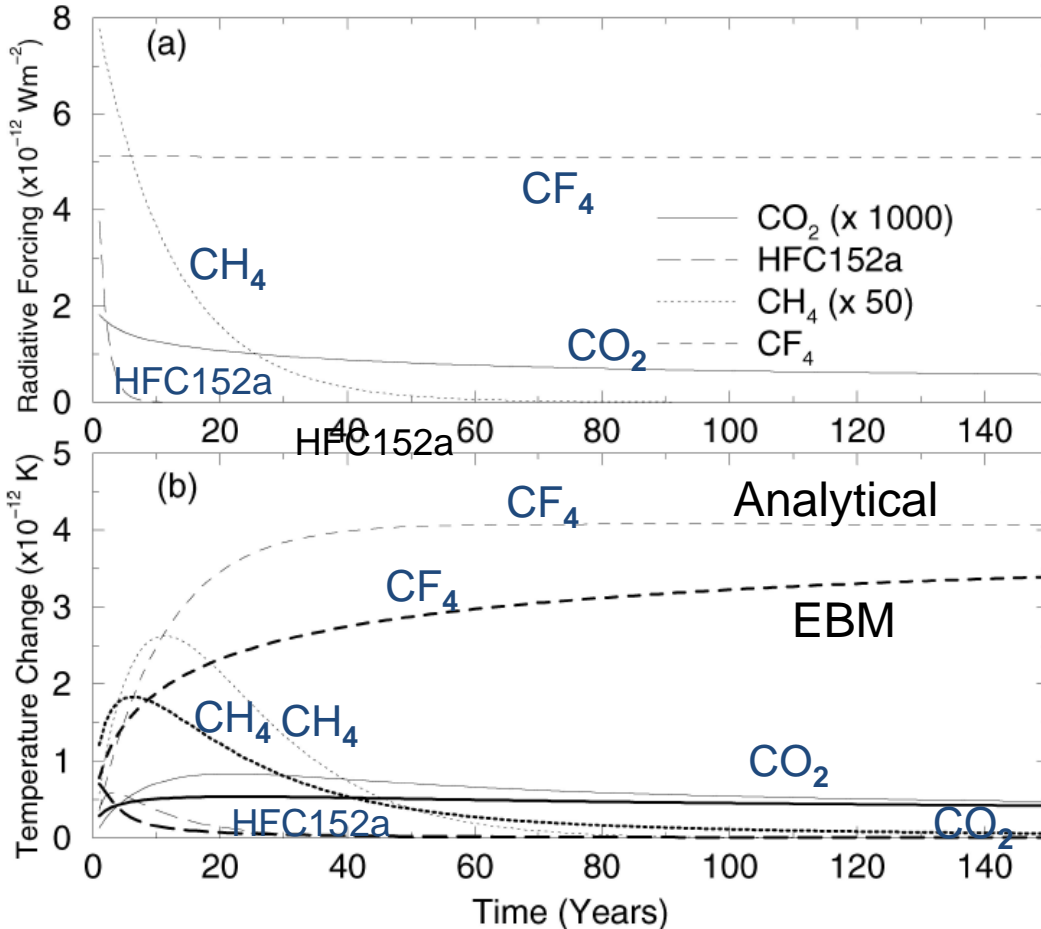
A sustained emission change is similar into the integrated value and **is not a practical case. This value employs CO_2 as a reference.**

Comparison among GTP, GWP and TWPG

metrics		value	unit	reference
GWP	atmosphere	<i>Integrated</i> RF of <i>pulse</i> emission	dimensionless (ratio)	CO₂
TWPG (AGWP)	atmosphere	RF change of <i>pulse</i> emission	Watt	stand-alone
analytical -GTP_P	atmosphere & sea	Temp. change of <i>pulse</i> emission	dimensionless (ratio)	CO₂
analytical -AGTP_P	atmosphere & sea	Temp. change of <i>pulse</i> emission	K (temperature)	stand-alone
GTP_S	atmosphere & sea	Temp. change of sustained emission change	K year (temperature)	CO₂

The results of GTP_P evaluation

KEITH. P. SHINE ET AL.



Radiative forcing after 1 kg release

- The same as TWPG
- The time-integrated this value is equal to AGWP.

The temperature change corresponding to RF in figure (a)

- **thin lines** : Analytical AGTP_P
- **thick lines** : AGTP_P based on EBM
- During the first a few years, EBM is higher.
- Analytical AGTP_P both overestimates the peak response and underestimates the recovery from the pulse.

Figure 1. (a) Radiative forcing due to a 1-kg pulse emission of greenhouse gases with a range of lifetimes (see Table A1). The AGWP is the integral under these curves to a given time horizon. (b) Temperature response using the analytical AGTP_P (thin lines) and the Energy Balance Model (thick lines) to the radiative forcing shown in (a).

TABLE I
AGWP (in $10^{-14} \text{ W m}^{-2} \text{ kg}^{-1} \text{ year}$) and AGTP_P (in $10^{-16} \text{ K kg}^{-1}$) from both the analytical equations and the energy balance model (EBM) for carbon dioxide, and the GWP and GTP_P for five other greenhouse gases at time horizons of 20, 100 and 500 yr

	GWP			Analytical GTP _P			EBM GTP _P		
	20	100	500	20	100	500	20	100	500
Absolute CO ₂	2.66	9.05	29.1	8.34	5.46	3.47	5.38	4.55	3.38
HFC152a	400	120	37	170	0.15	0	135	22	4.0
CH ₄	62	22	7	52	0.35	0	46	5	0.8
HFC134a	3290	1260	390	2840	34	0	2550	300	44
N ₂ O	270	290	150	290	270	13	290	270	35
CF ₄	3850	5650	8730	4150	7490	11700	4320	7090	11200

Note. The values for methane include the indirect forcing. The analytical GTP values are calculated with a climate sensitivity of $0.8 \text{ K (W m}^{-2})^{-1}$ and a mixed layer with a depth of 100 m. The EBM GTP_P values are derived using the same climate sensitivity, with other parameters given in Appendix B.

TABLE II

AGWP (in $10^{-14} \text{ W m}^{-2} \text{ kg}^{-1} \text{ year}$) and AGTP_S (in $10^{-14} \text{ K (kg year}^{-1})^{-1}$) from both the analytical equations and the energy balance model (EBM) for carbon dioxide and GWP and GTP_S for five other greenhouse gases at time horizons of 20, 100 and 500 yr

	GWP			Analytical GTP _S			EBM GTP _S		
	20	100	500	20	100	500	20	100	500
Absolute CO ₂	2.66	9.05	29.1	1.24	6.67	23.0	0.95	4.94	20.0
HFC152a	400	120	37	570	130	40	500	140	40
CH ₄	62	22	7	69	24	7	66	25	8
HFC134a	3290	1260	390	3590	1370	400	3470	1420	430
N ₂ O	270	290	150	260	290	160	270	290	160
CF ₄	3850	5650	8730	3610	5480	8690	3700	5430	8520

Note. The values for methane include the indirect forcing. The analytical GTP values are calculated with a climate sensitivity of $0.8 \text{ K (W m}^{-2})^{-1}$ and a mixed layer with a depth of 100 m. The EBM GTP_S values are derived using the same climate sensitivity, with other parameters given in Appendix B.



Framework Convention on Climate Change

Distr.
GENERAL

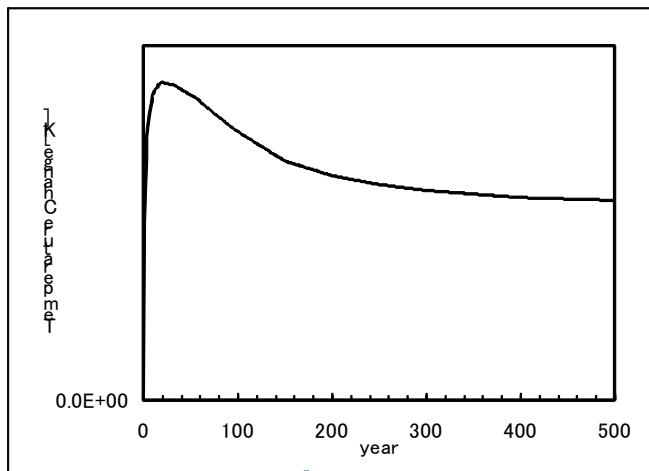
FCCC/TP/2008/2
6 August 2008

Table. Global warming potentials and global temperature potentials

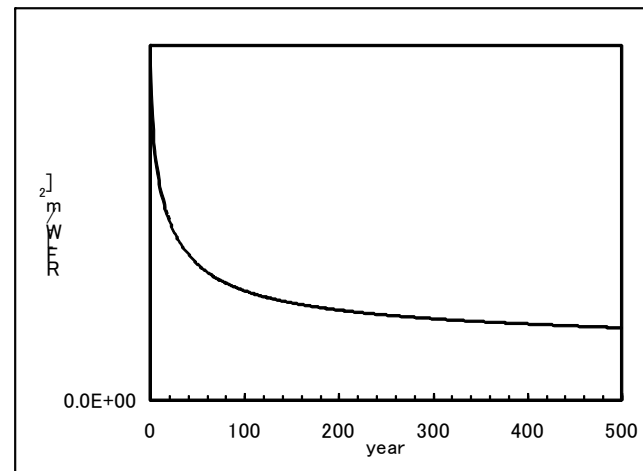
Species	Chemical formula	Covered by Kyoto Protocol	Covered by Montreal Protocol	Estimation method in 2006 Guidelines	IPCC 1995			IPCC 2001			IPCC 2007			Shine et al 2005										
					Global Warming Potential			Global Warming Potential			Global Warming Potential			Analytical GTP _p			EBM GTP _p							
					20 years	100 year	500 years	20 years	100 year	500 years	20 years	100 year	500 years	20	100	500	20	100	500					
Carbon dioxide	CO ₂	x		x	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Methane	CH ₄	x		x	56	21	6.5	62	23	7	72	26	7.6	62	0.35	0	46	6	0.8					
Nitrous oxide	N ₂ O	x		x	290	310	170	275	296	156	289	298	153	290	270	13	290	270	36					
<i>Substances controlled by the Montreal Protocol</i>																								
CFC-11	CCl ₃ F		x					6300	4500	1600	6730	4750	1620											
CFC-12	CCl ₂ F ₂		x					10200	10600	6200	11000	10900	6200											
CFC-13	CClF ₃		x					10000	14000	16300	10600	14400	16400											
CFC-113	CCl ₂ FCClF ₂		x					6100	6000	2700	6540	6130	2700											
CFC-114	CClF ₂ CClF ₂		x					7500	9800	8700	8040	10000	8730											
CFC-115	CClF ₂ CF ₃		x					4900	7200	9900	5310	7370	9990											
Halon-1301	CBrF ₃		x					7900	6900	2700	8480	7140	2760											
Halon-1211	CBrClF ₂		x					3600	1300	390	4760	1890	675											
Halon-2402	CBrF ₂ CBBrF ₂		x								3680	1640	503											
Carbon tetrachloride	CCl ₄		x					2700	1800	580	2700	1400	435											
Methyl bromide	CH ₃ Br		x					16	5	1	17	5	1											
HCFC-21	CHCl ₂ F		x					700	210	65														
HCFC-22	CHClF ₂		x					4800	1700	540	5160	1810	649											
HCFC-123	CHCl ₂ CF ₃		x					390	120	36	273	77	24											
HCFC-124	CHClF ₂ CF ₃		x					2000	620	190	2070	609	185											
HCFC-141b	CH ₃ CCl ₂ F		x					2100	700	220	2260	726	220											
HCFC-142b	CH ₃ CClF ₂		x					5200	2400	740	5490	2310	705											
HCFC-225ca	CHCl ₂ CF ₂ CF ₃		x					590	180	55	429	122	37											
HCFC-225cb	CHClF ₂ CF ₂ CF ₂		x					2000	620	190	2030	595	161											
<i>Hydrofluorocarbons</i>																								
HFC-23	CHF ₃	x		x	9100	11700	9600	9400	12000	10000	12000	14900	12200											
HFC-32	CH ₂ F ₂	x		x	2100	650	200	1800	550	170	2330	675	205											
HFC-41	CHF ₃	x		x	490	150	45	330	97	30														
HFC-125	C ₂ H ₂ F ₅	x		x	4600	2900	500	5900	3400	1100	6350	3500	1100											
HFC-134	C ₂ H ₂ F ₄	x		x	2900	1000	310	3200	1100	330														
HFC-134a	CH ₂ FCF ₃	x		x	3400	1300	420	330	1300	400	3630	1430	435	2840	34	0	2560	300	44					
HFC-143	C ₂ H ₃ F ₃	x		x	1000	300	94	110	330	100														
HFC-143a	C ₂ H ₃ F ₃	x		x	5000	3800	1400	5500	4300	1600	6880	4470	1690											
HFC-152	CH ₂ FCH ₂ F			x				140	43	13														
HFC-152a	CH ₃ CHF ₂	x		x	460	140	42	410	120	37	437	124	58	170	0.15	0	135	22	4					
HFC-161	CH ₃ CH ₂ F			x				40	12	4														
HFC-227ea	C ₃ H ₇ F	x		x	4300	2900	950	5500	3500	1100	5310	3220	1040											
HFC-236fa	CF ₃ CH ₂ CF ₃			x	5100	6300	4700	7500	9400	7100	8100	9810	7660											
HFC-236cb	CH ₂ FCF ₂ CF ₃			x				3300	1300	390														
HFC-236ea	CF ₃ CHF ₂ CF ₃			x				360	1200	390														
HFC-245ca	C ₃ H ₃ F ₅	x		x	1800	580	170	2100	640	200														
HFC-245fa	CHF ₂ CH ₂ CF ₃			x				3000	950	300	3360	1030	314											
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃			x				2600	890	280	2620	794	241											
HFC-43-10mee	CF ₃ CHF ₂ CF ₂ CF ₃			x	3000	1300	400	3700	1500	470	4140	1640	600											

AGTP-EBM and TWPG

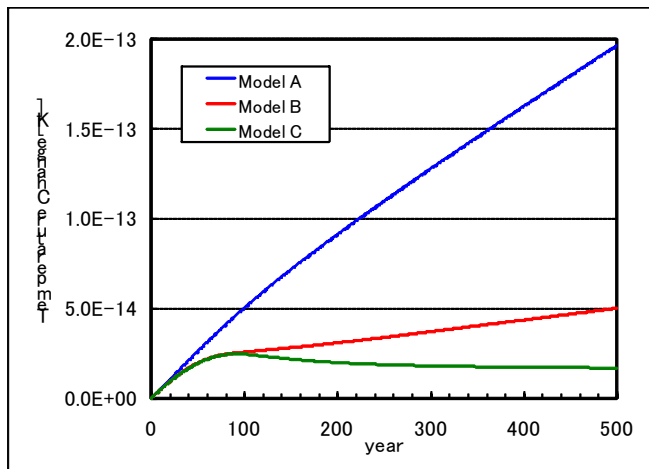
AGTPP – EBM due to 1kg pulse emission



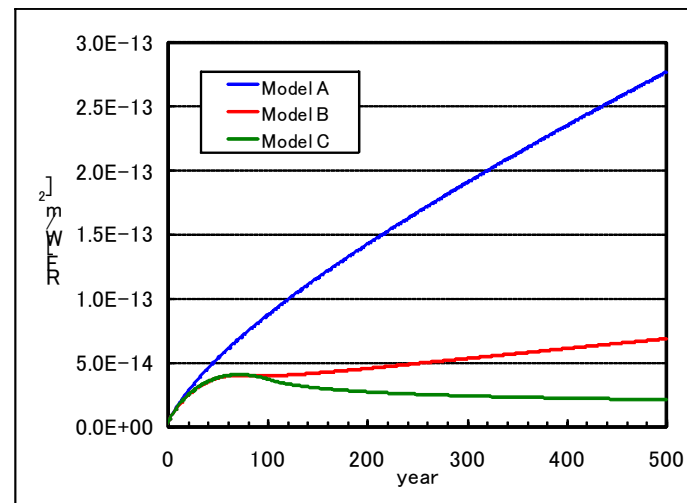
TWPG(W) due to 1kg pulse emission



AGTPP – EBM due to emissions based on the model cases



TWPG(W) due to emissions based on the model cases



Model A: Every year 1 kg for 500 years

Model B: First year: 1kg, 2-80 years: 1% reduction, 81-: 0.2kg for every year

Model C: First year: 1kg, 2-100 years: 1% reduction, 101-: no emission for every year

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	GWP			Analytical GTP _P			EBM GTP _P			TWPG _P *		
	20	100	500	20	100	500	20	100	500	20	100	500
Absolute CO ₂	2.66	9.05	29.1	8.34	5.46	3.47	5.38	4.55	3.38	10	6.2	4.1
HFC152a	400	120	37	170	0.15	0	135	22	4.0	1.5	1.47	1.46
CH ₄	62	22	7	52	0.35	0	46	5	0.8	29	3.2	2.9
HFC134a	3290	1260	390	2840	34	0	2550	300	44	2300	12.9	0.95
N ₂ O	270	290	150	290	270	13	290	270	35	350	274	12.4
CF ₄	3850	5650	8730	4150	7490	11700	4320	7090	11200	6800	11000	16000

Note. The values for methane include the indirect forcing. The analytical GTP values are calculated with a climate sensitivity of $0.8 \text{ K (W m}^{-2}\text{)}^{-1}$ and a mixed layer with a depth of 100 m. The EBM GTP_P values are derived using the same climate sensitivity, with other parameters given in Appendix B.

*) TWPGをCO₂基準に変形し、TWPG_P*とした。
A.Sekiya

	Climate	Atmos.	Energy Sea	Dec. Prod.	VOC O ₃	Ozon Layer Cooling
GWP	×	○	×	×	×	△
Anal-GTP _P	○	○	○	×	×	×
EBM-GTP _P	○	○	○	×	×	×
TWPG _P *	○	○	×	○	○	○

Needed data for calculations:
RF, Lifetime

Values
GWP ≙ GTP_S、 Similar
TWPG ≙ AGTP_P

Conclusion

Level A Technologies

How to find

How to introduce

All technologies

Reductions by Kyoto

Scientific evaluations
Future estimations

AGTP_p
TWPG

(GWP is using now)

GWP

Selections of level A technologies

GWP use ?
Replace GWP?

**Factors
etc.**

Push Level A Tech.

Sustainable Society

Thank you for the attention