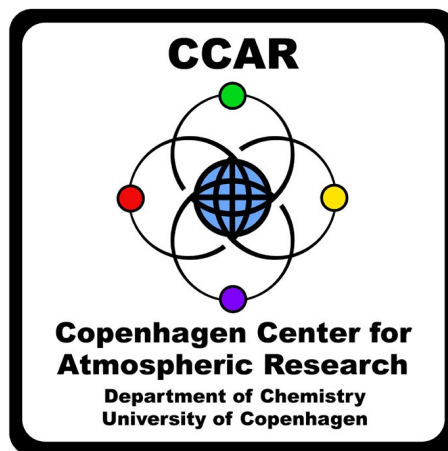


Halogenated Compounds in Near-term Strategies for Slowing Warming in the Arctic



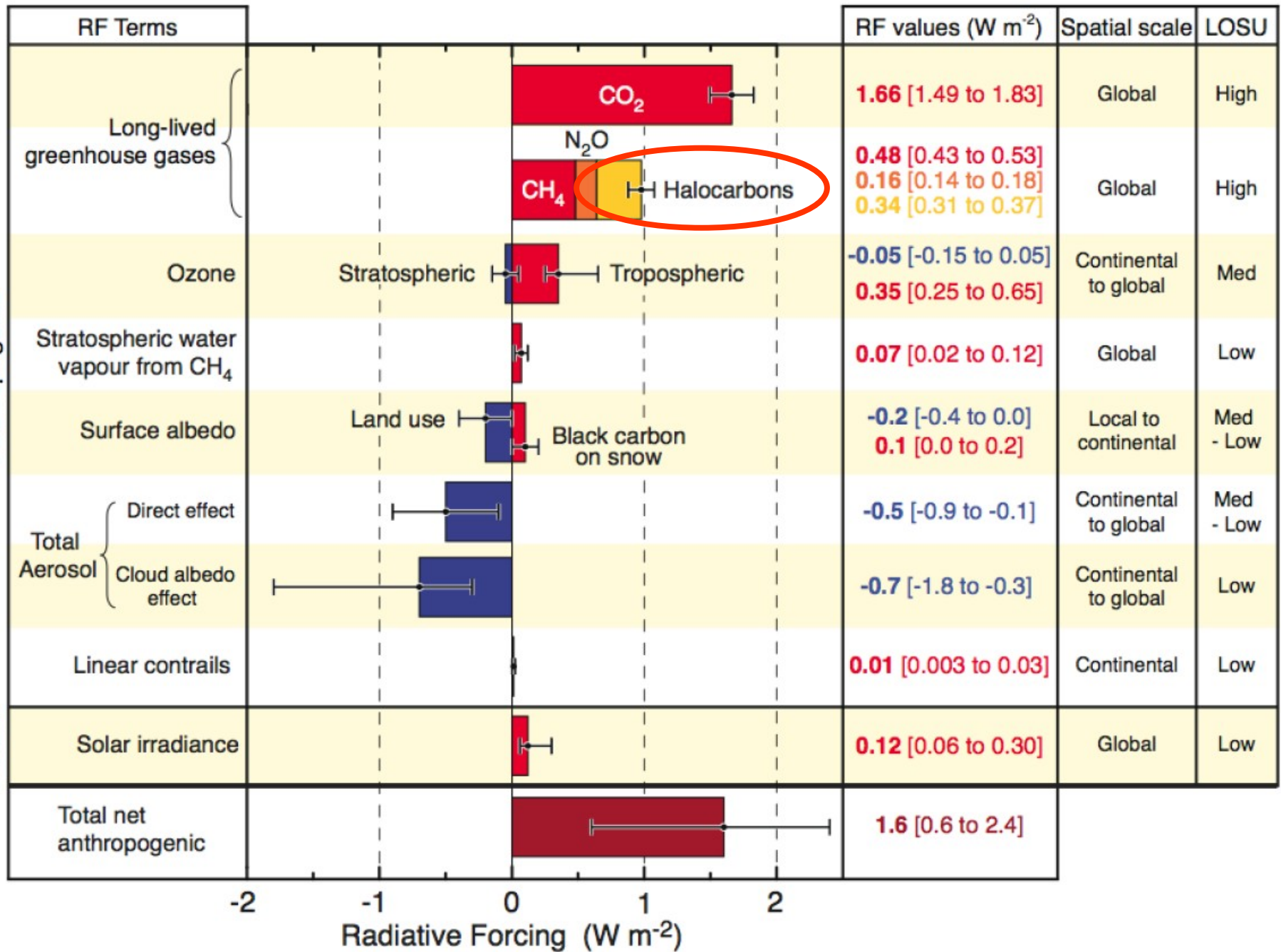
Ole John Nielsen

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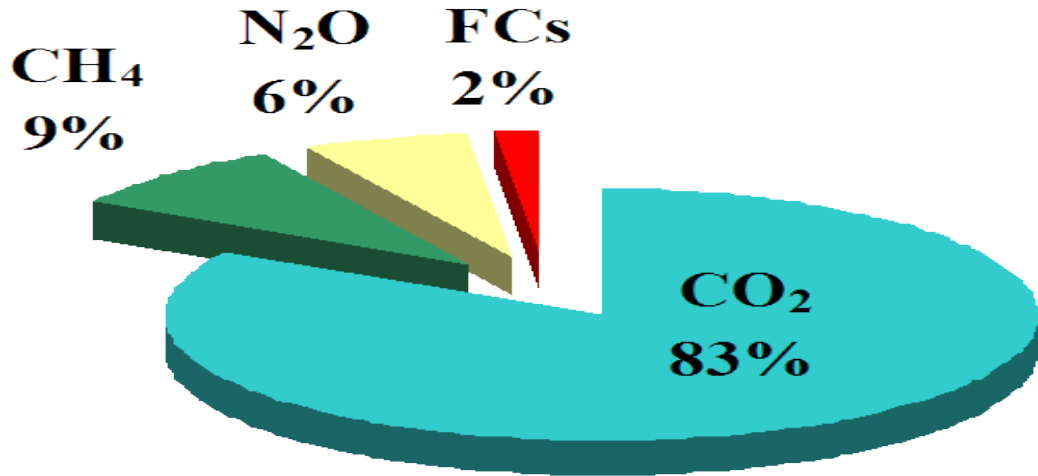
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Radiative Forcing Components



Why should we be interested in halo(F)carbons?

2005 Global Greenhouse Gas Emissions % Contribution on CO₂ Basis



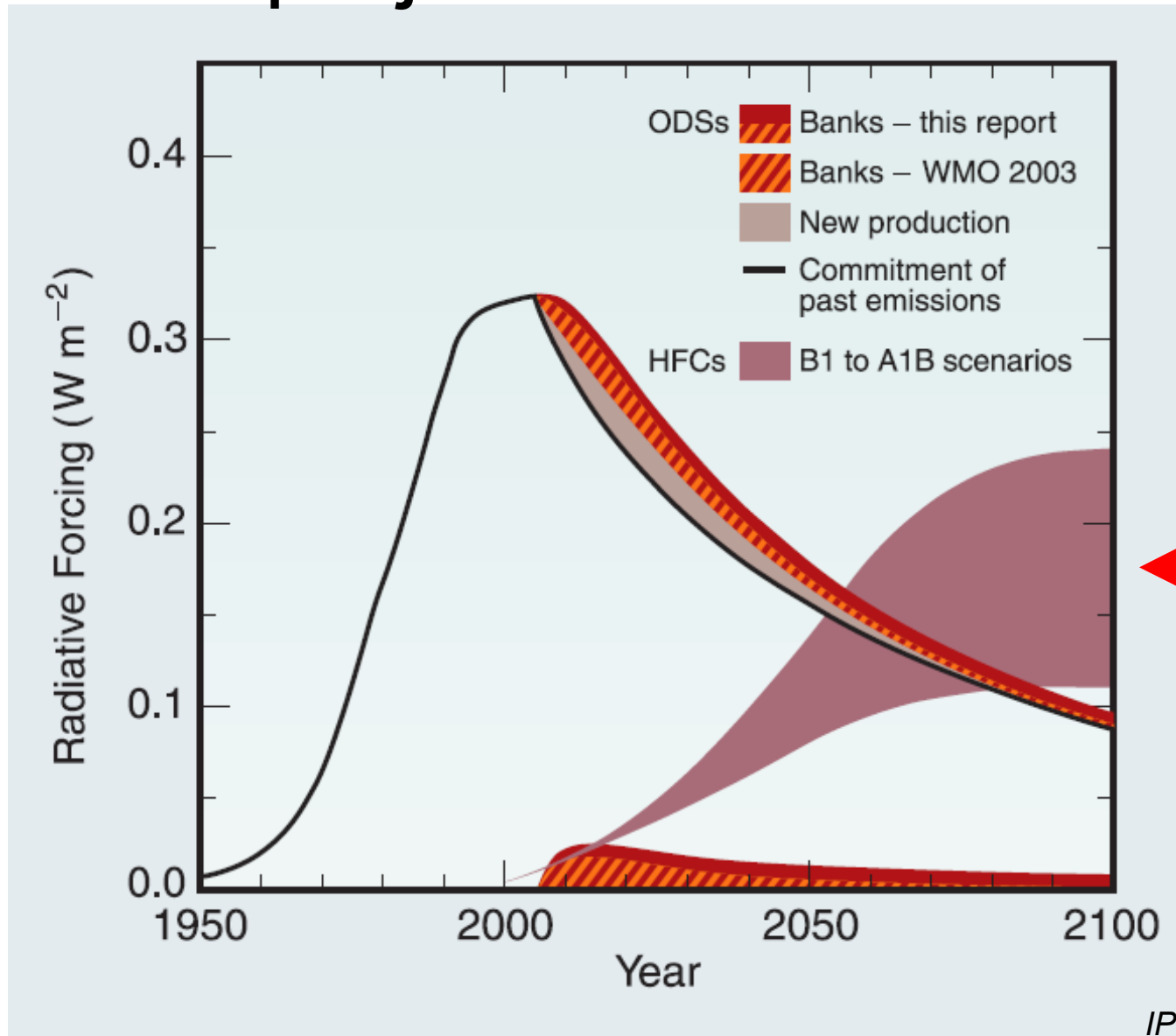
Change since 1990

CO ₂	+1.6%
CH ₄	-18%
N ₂ O	-20%
FCs	+19%

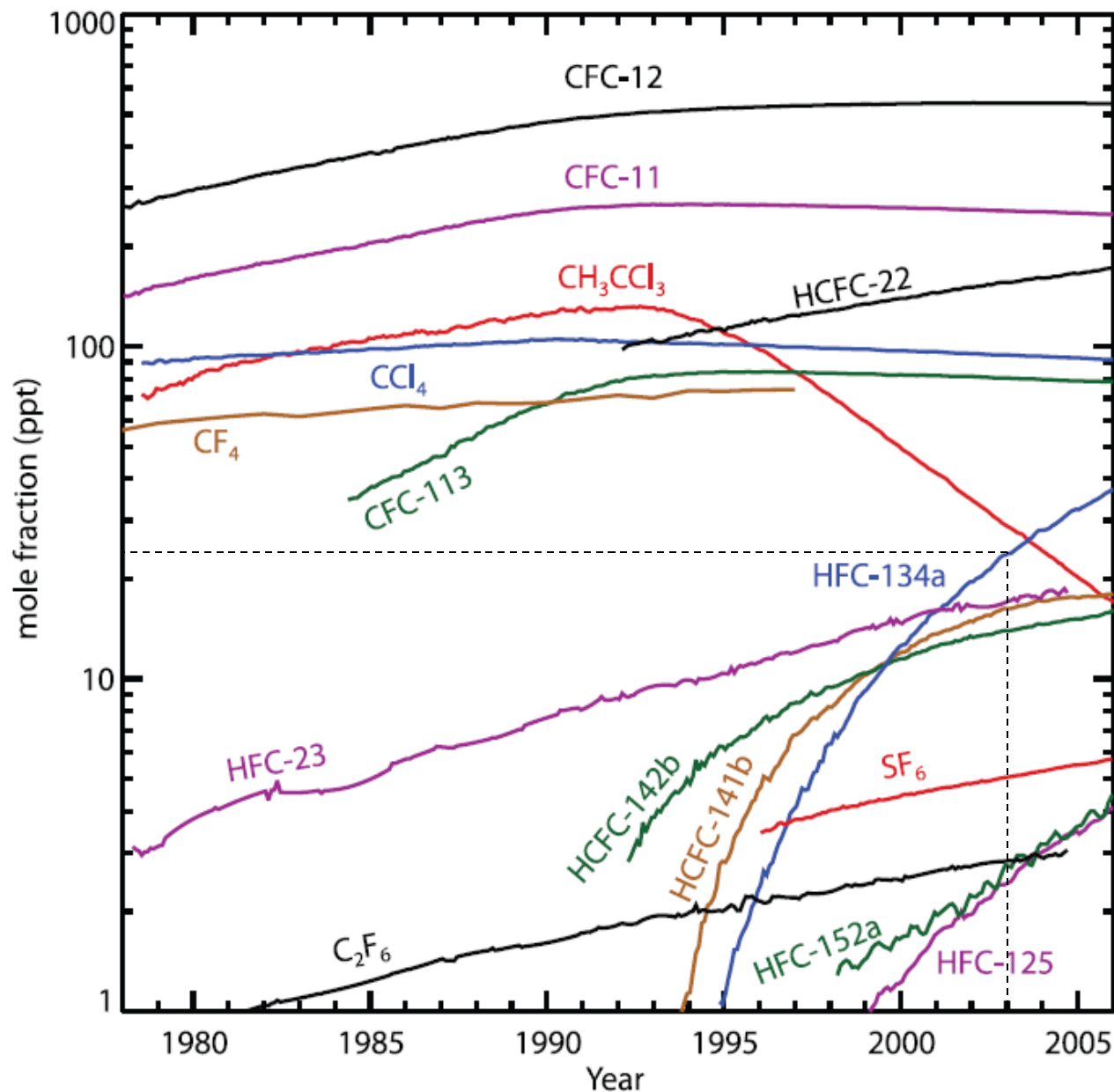
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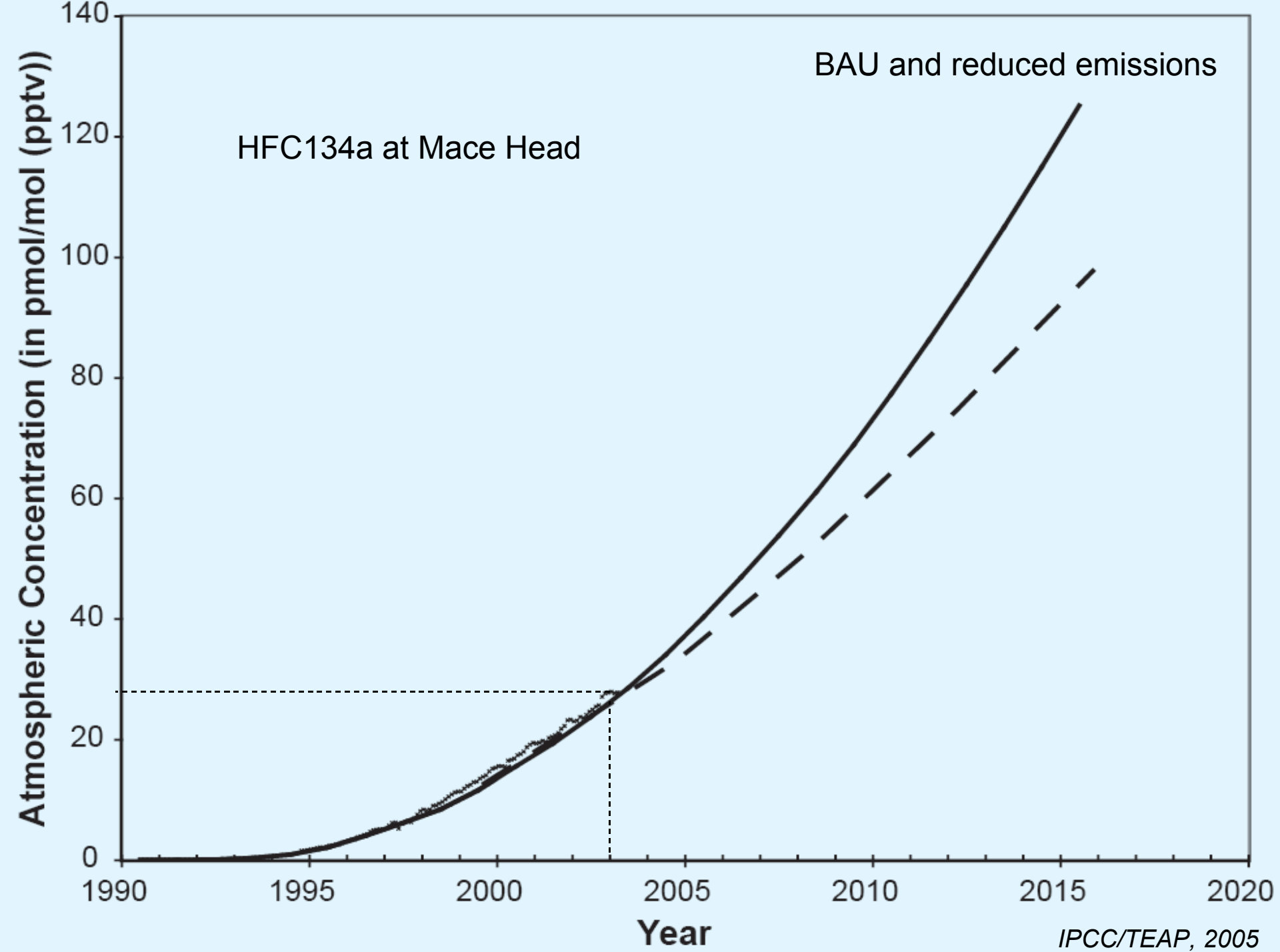
HFCs	+154%
PFCs	-45%
SF ₆	-62%

Direct radiative forcing of all ODS and projections for HFCs



Halogenated Compounds in the Atmosphere





What determines the importance of a GHG?

1. The intensity and position of infrared absorption
2. The atmospheric lifetime (near term)
3. The amount released

EU law will be: $GWP_{100y} < 150$

What can we do something about for the halogenated compounds?

Atmospheric Lifetime of Halogenated Compounds

- Do not undergo photolysis in lower atmosphere
(λ_{max} typically ≤ 200 nm)
- Not expected to be removed by wet or dry deposition
(non-polar with water solubility in ppmw)
- Principal removal mechanism for the alternative halocarbons is reaction with OH



Replacement of Ozone-Depleting Compounds with hydrofluorocarbons (HFCs) – no Cl!

CFC-11 CCl_3F CFC-115 $\text{CF}_3\text{CF}_2\text{Cl}$

CFC-12 CCl_2F_2 halon 1301 CF_3Br

CFC-113 $\text{CCl}_2\text{FCClF}_2$ halon 1211 CBrClF_2

Also GHG


HFC-23 CF_3H HFC-227ea $\text{CF}_3\text{CFHCF}_3$

HFC-125 $\text{CF}_3\text{CF}_2\text{H}$ HFC-236fa $\text{CF}_3\text{CH}_2\text{CF}_3$

HFC-134a $\text{CF}_3\text{CF}_2\text{H}$ HFC-365mfc $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$

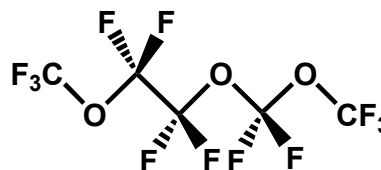
Lifetime and GWP of Fluoroalkanes

<u>Compound</u>	<u>Atm. Lifetime (yrs)</u>	<u>GWP (IPCC2007) (100 yr)</u>	
CF ₄ (PFC-14)	50000	7,390	
CHF ₃ (HFC-23)	270	14,800	CH ₂ F ₂
(HFC-32)	4.9	675	CH ₃ F
(HFC-41)	3.7	140	
CF ₃ CF ₃ (PFC-116)	10000	12,200	
CF ₃ CHF ₂ (HFC-125)	29	3,500	
<u>CF₃CH₂F (HFC-134a)</u>	14	1,430	
CF ₃ CH ₃ (HFC-143a)	52	4,470	
CHF ₂ CH ₃ (HFC-152a)	1.4	124	
CH ₂ FCH ₃ (HFC-161)	0.25	10	
CF ₃ CHF ₂ CF ₃ (HFC-227ea)	34.2	3,220	
CH ₂ FCF ₂ CHF ₂ (HFC-245ca)	6.6	720	
CF ₃ CH ₂ CF ₂ CH ₃ (HFC-365mfc)	8.6	794	
CF ₃ CHFCHFC ₂ F ₅ (HFC-43-10mee)	15.9	1,640	

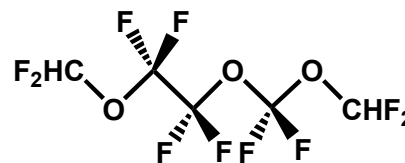
Different Fluorinated Ethers

Potential replacements for CFCs and perfluorocarbons.

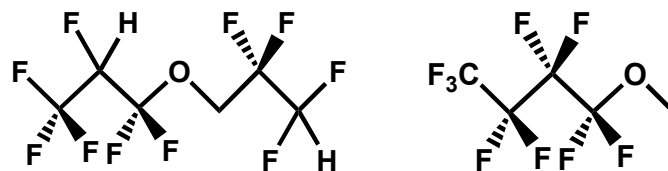
Perfluoropolyether (**PFPE**)



Hydrofluoropolyether (**HFPE**)



Hydrofluoroether (**HFE**)

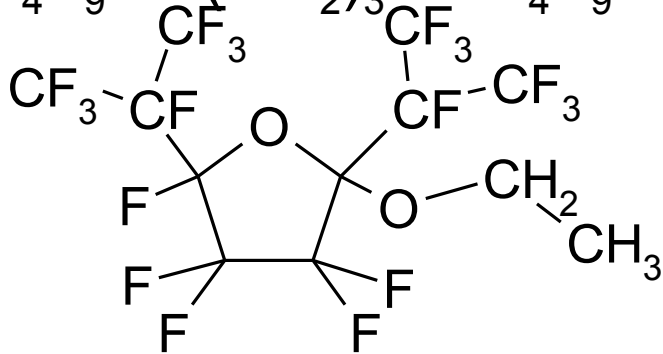


Effect of Ether Oxygen on Atmospheric Lifetime

<u>Compound</u>	<u>Atm. Lifetime (yrs)</u>	<u>GWP (100 Yr ITH)</u>	
CH_3CF_3 (HFC-143a)	52	4,470	alkane
CH_3OCF_3 (HFE-143a)	4.3	756	ether
$\text{CF}_3\text{CFHCF}_3$ (HFC-227ea)	34.2	3,220	
$\text{CF}_3\text{CFHO CF}_3$ (HFE-227ea)	11	1,500	
$\text{CF}_3\text{CH}_2\text{CF}_3$ (HFC-236fa)	240	9,810	
$\text{CF}_3\text{CH}_2\text{OCF}_3$ (HFE-236fa)	3.7	470	
$\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa)	7.6	1,030	
$\text{CF}_3\text{CH}_2\text{OCHF}_2$ (HFE-245fa2)	4.9	659	

GWP still too high!

Atmospheric Lifetimes of *Segregated* HFEs

$R_f - O - R_h$	k_{OH} ($\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$)	τ (GWP) (years)
n-C ₄ F ₉ - OCH ₃	1.20 x 10 ⁻¹⁴	4.7 (~404)
i-C ₄ F ₉ - OCH ₃	1.54 x 10 ⁻¹⁴	3.7 (~404)
n-C ₄ F ₉ - OC ₂ H ₅	6.4 x 10 ⁻¹⁴	0.9 (~ 57)
i-C ₄ F ₉ - OC ₂ H ₅	7.7 x 10 ⁻¹⁴	0.7 (~ 57)
C ₄ F ₉ -O-(CH ₂) ₃ -O-C ₄ F ₉	1.44 x 10 ⁻¹³	0.4 (n.d.)
	5.93 x 10 ⁻¹⁴	1.0 (55)

Other ways of lowering the atmospheric lifetime

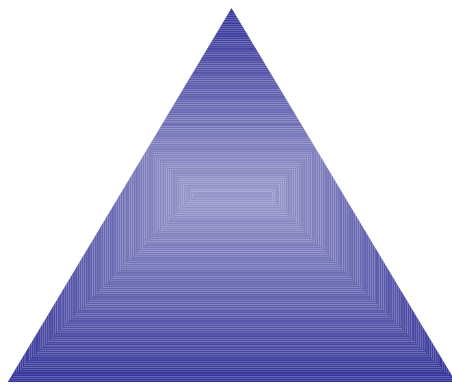
Insert a double bond

Compound	k_{Cl}	k_{OH}	k_{O_3}	τ	GWP
$\text{CF}_3\text{CF}=\text{CF}_2$ Mads	$(2.7 \pm 0.3) \times 10^{-11}$	$(2.4 \pm 0.2) \times 10^{-12}$	$< 3 \times 10^{-21}$	18 d	6
$\text{CF}_3\text{CH}=\text{CFH}$ Roar	$(4.7 \pm 0.2) \times 10^{-11}$	$(9.3 \pm 0.5) \times 10^{-13}$	$(2.8 \pm) \times 10^{-21}$	14 d	6
$\text{CF}_3\text{CF}=\text{CH}_2$ Meshkat	$(6.9 \pm) \times 10^{-11}$	$(1.06 \pm) \times 10^{-12}$	$(6.6 \pm) \times 10^{-20}$	11 d	4
$\text{CF}_3\text{CH}=\text{CH}_2$ Anne	$(9.0 \pm 1.1) \times 10^{-11}$	$(1.4 \pm 0.3) \times 10^{-12}$	$(3.5 \pm 0.3) \times 10^{-19}$	8.5 d	n.d.
$\text{CH}_3\text{CH}=\text{CH}_2$ <i>everybody</i>	2.4×10^{-10}	2.6×10^{-11}	1.0×10^{-17}	10 h	n.d.?

Design of New Chemical Technology

Safety

low toxicity
nonflammable



Environmental

non-ozone depleting
short atmospheric lifetime
low global warming potential

Performance

stability
compatibility
boiling/freezing point

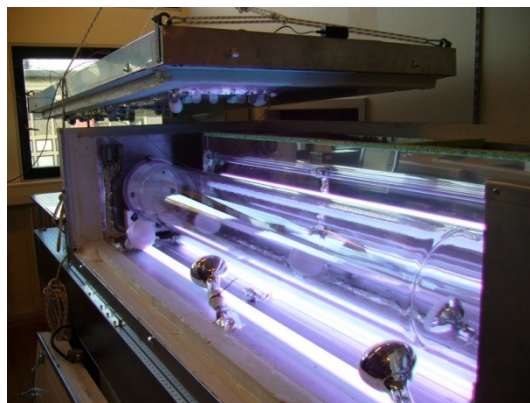
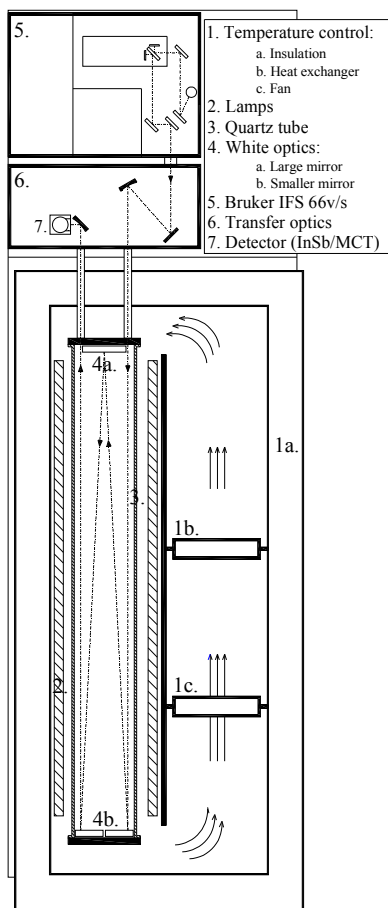
Conclusions

- Atmospheric lifetimes and GWPs of halocarbons cover very wide range
- Possible to create some alternatives with much lower GWPs
- In many applications significant (and easy) radiation forcing reductions can be obtained using lower GWP materials
- Article 5 countries are going to need a lot of alternatives
- Cost ? Not prohibitive. Often a small part of a larger item.

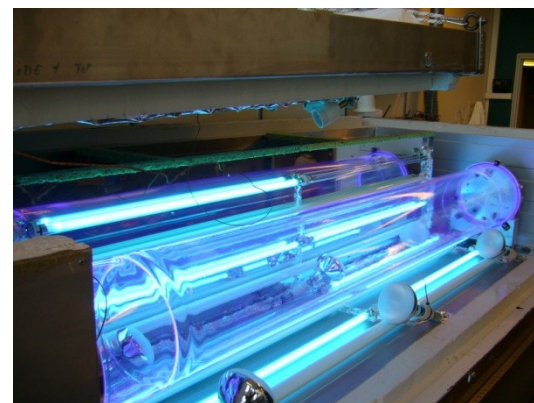
Extra Slides

The Photochemical Reactor

for reaction rates, product distributions
and infrared absorption



UV-A



UV-C



Sun lamps

Other ways of lowering the atmospheric lifetime

Insert a double bond

Compound	k_{Cl}	k_{OH}	k_{O_3}
$\text{CF}_3\text{CF}=\text{CF}_2$ Mads	$(2.7 \pm 0.3) \times 10^{-11}$	$(2.4 \pm 0.2) \times 10^{-12}$	$< 3 \times 10^{-21}$
$\text{CF}_3\text{CH}=\text{CFH}$ Roar	$(4.7 \pm 0.2) \times 10^{-11}$	$(9.3 \pm 0.5) \times 10^{-13}$	$(2.8 \pm) \times 10^{-21}$
$\text{CF}_3\text{CF}=\text{CH}_2$ Meshkat	$(6.9 \pm) \times 10^{-11}$	$(1.06 \pm) \times 10^{-12}$	$(6.6 \pm) \times 10^{-20}$
$\text{CF}_3\text{CH}=\text{CH}_2$ Anne	$(9.0 \pm 1.1) \times 10^{-11}$	$(1.4 \pm 0.3) \times 10^{-12}$	$(3.5 \pm 0.3) \times 10^{-19}$
$\text{CH}_3\text{CH}=\text{CH}_2$ everybody	2.4×10^{-10}	2.6×10^{-11}	1.0×10^{-17}

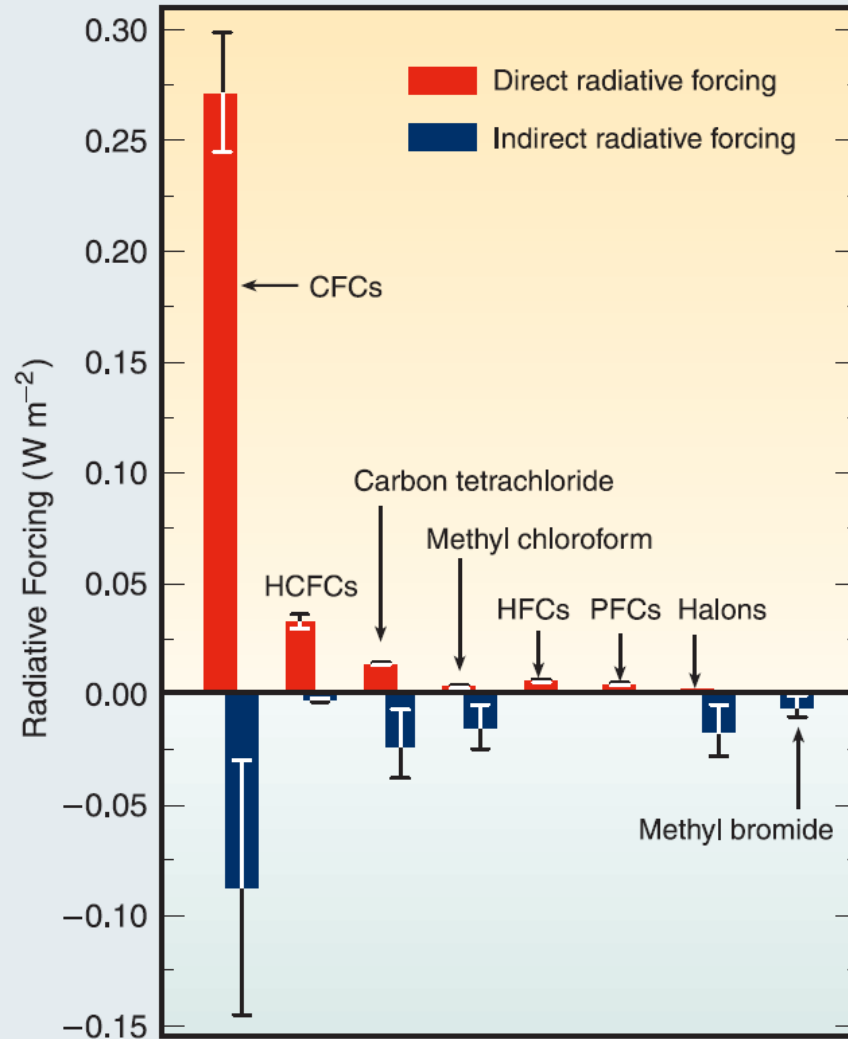
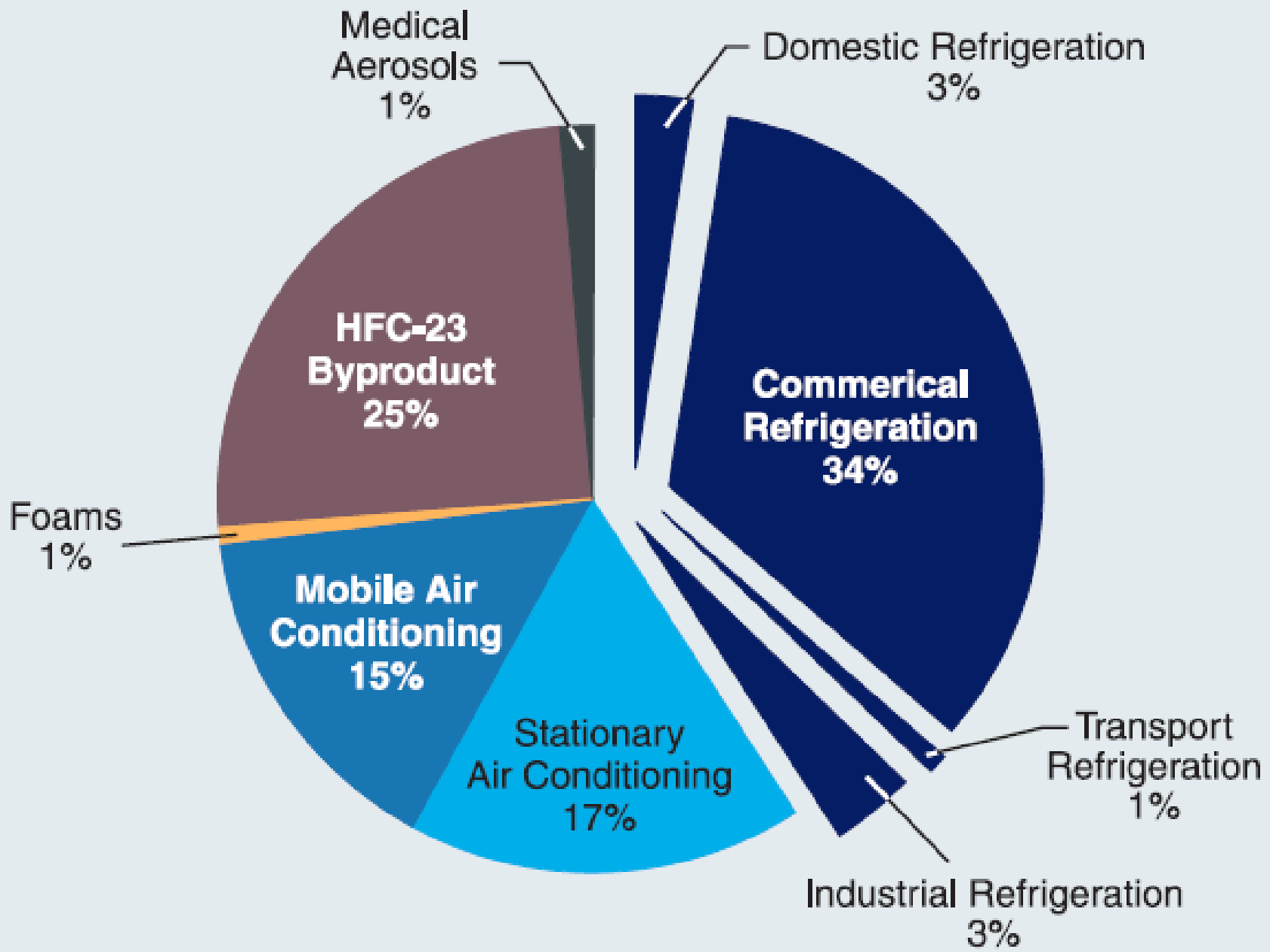
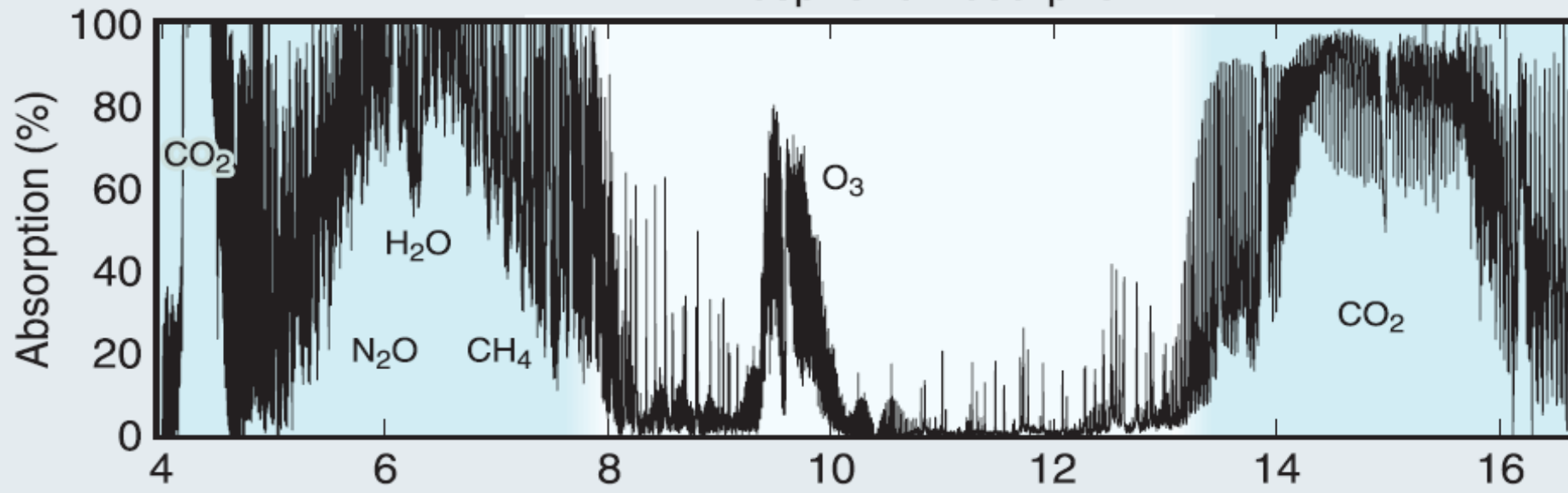


Figure SPM-2. Direct and indirect radiative forcing (RF) due to changes in halocarbons from 1750 to 2000.⁹ Error bars denote ± 2 standard-deviation uncertainties. [Based on Table 1.1]

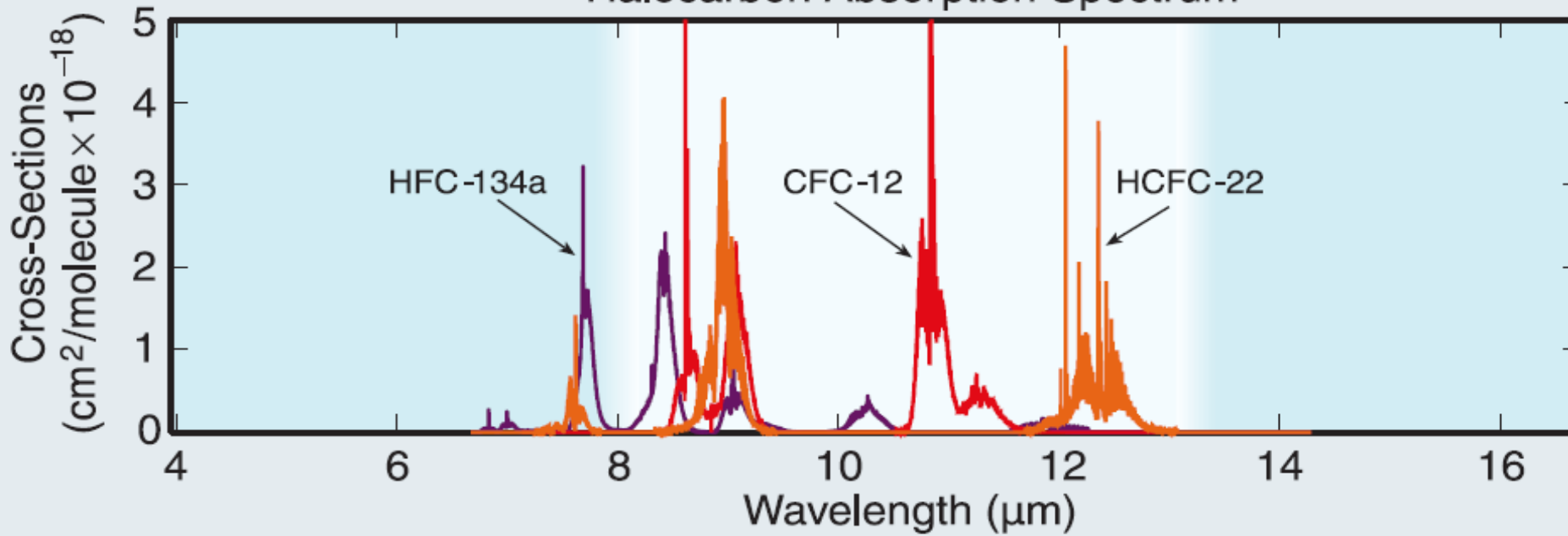


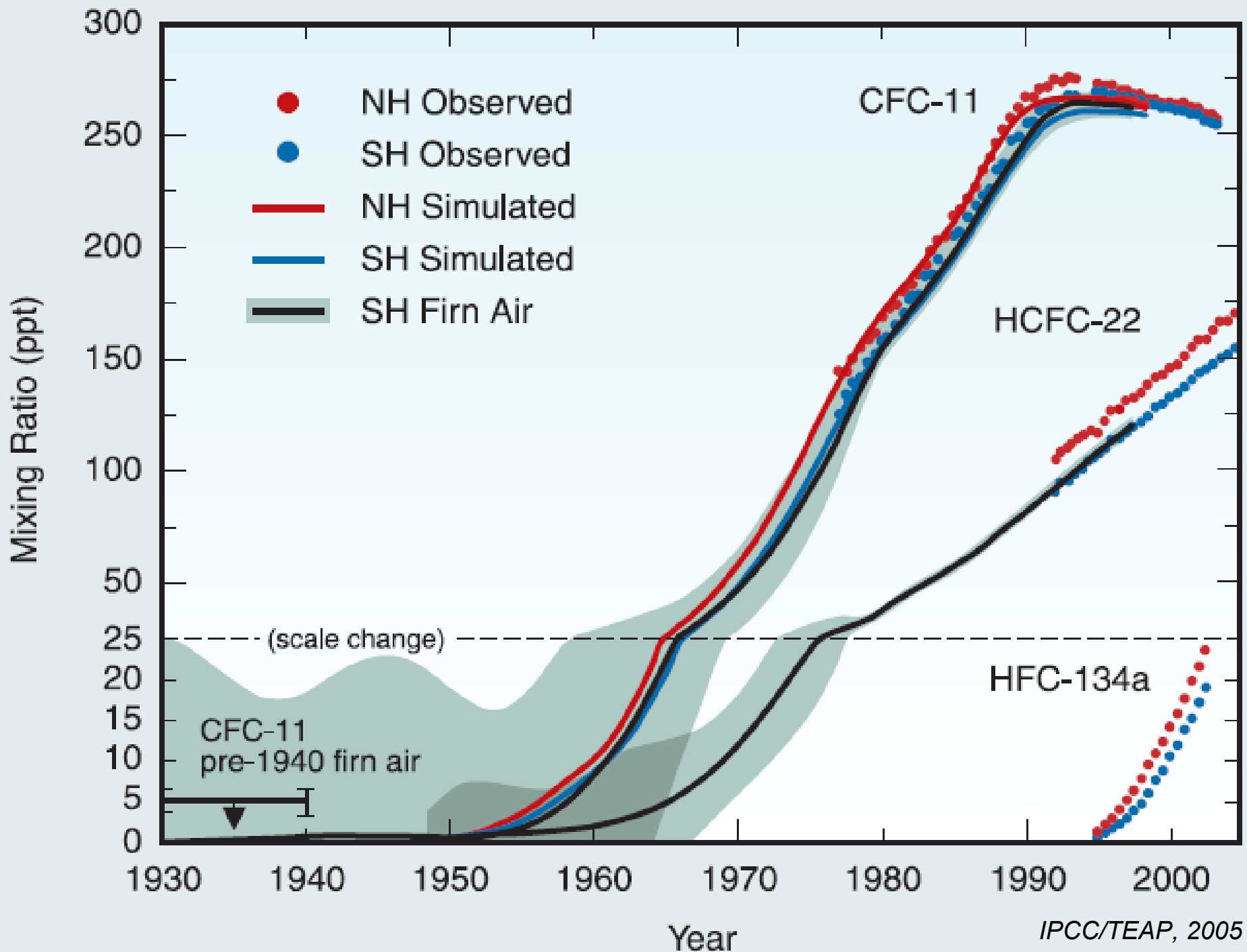
Sectoral Emission Reduction Potentials 2015

Atmospheric Absorption



Halocarbon Absorption Spectrum





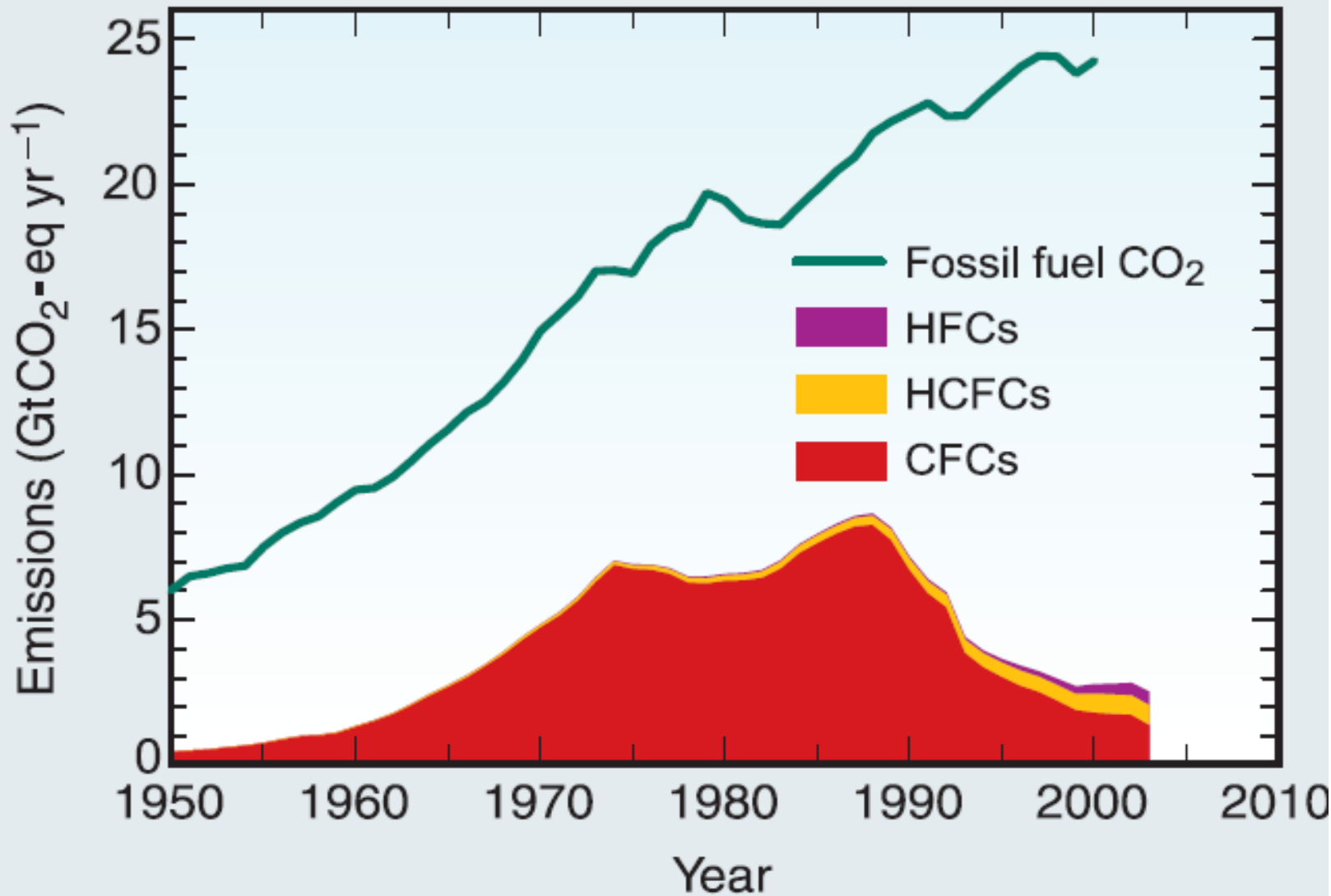


Figure TS-9. Direct GWP-weighted emissions (100-yr time horizon) for CFCs and HCFCs and HFCs compared with total CO₂ emissions due to fossil fuel combustion and cement production.

Direct radiative forcing of all ODS and projections for HFCs

