Atmospheric Chemistry

Lecture 12

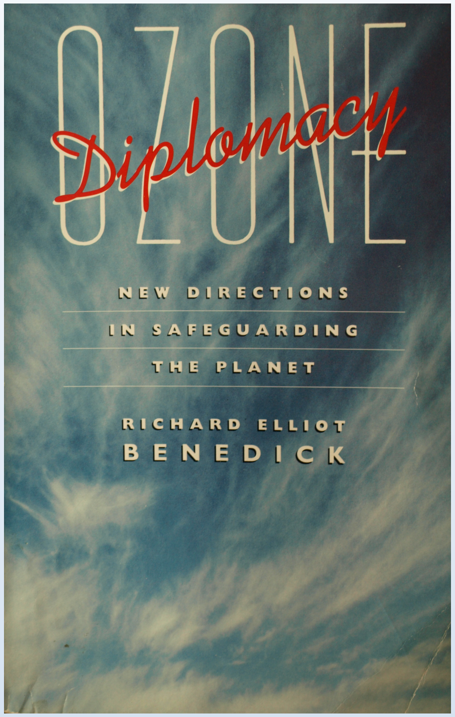
The Vienna Convention and the Montreal Protocol: What are they?

- The ***Vienna Convention for the Protection of the Ozone Layer (1985)*** **is a multilateral environmental agreement. It is a framework for efforts to protect the ozone layer, but no binding actions.**
  - **Recognized the need to protect the ozone layer**
  - **Established a Secretariat & regular meeting for ozone layer issues**
  - **Established a framework for science research**

- The ***Montreal Protocol on Substances That Deplete the Ozone Layer (1987)*** **is an agreement which supplements the Vienna Convention.**
  - **Regulates the production and consumption of specific substances that modify the ozone layer.**
  - **Multi-Lateral Fund (Article 10), regular reporting of production & consumption (Article 7), re-examination of control measures.**
  - **Assessment process (Article 6), every 4 years, Science Assessment Panel (SAP), Technology and Economics Assessment Panel (TEAP), and Environmental Effects Assessment Panel (EEAP).**

What is significant about the Montreal protocol?

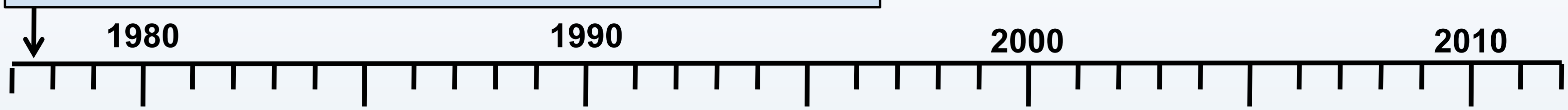
- "Living" protocol: provision for updates
- Fund for developing countries to offset cost of potentially more expensive alternatives
- Participation of scientists, government officials, industry, and environmental organizations
- Based on scientific assessments from 3 panels
  - Scientific Assessment Panel (SAP)
  - Environmental Effects Assessment Panel (EEAP)
  - Technology and Economic Assessment Panel (TEAP)



Richard Benedick was the chief US negotiator for the Protocol

International Ozone Assessments

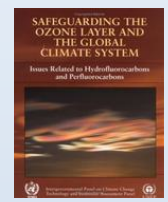
WMO World Plan of Action on the Ozone Layer - 1977



WMO The Stratosphere 1981: Theory and Measurements

Scientific Assessment of Ozone Depletion: 1989, 1991, 1994, 1998, 2002, 2006, 2010 (WMO/UNEP)

WMO Atmospheric Ozone - 1985



Safeguarding the Ozone Layer and the Global Climate System: 2005 (IPCC/TEAP)

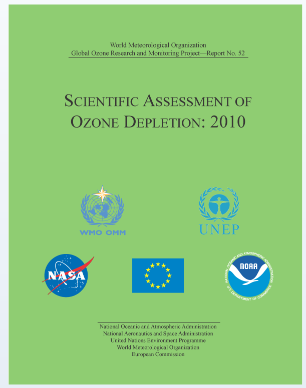
Other NASA and Climatic Impact Assessment Program (CIAP) reports prior to 1981 were primarily performed in the USA

WMO Report of the International Ozone Trends Panel – 1988

Scientific Assessment of Ozone Depletion: 2010

Scientific Assessment Panel of the Montreal Protocol

SAP Co-chairs
Ayité-Lô Ajavon (Togo)
Paul Newman (USA)
John Pyle (UK)
A.R. Ravishankara (USA)



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Ch. 1: Ozone-Depleting Substances (ODSs) and Related Chemical

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Ch. 2: Stratospheric Ozone and Surface Ultraviolet Radiation

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Ch. 3: Future Ozone and Its Impact on Surface UV

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Ch. 4: Stratospheric Changes and Climate

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Ch. 5: A Focus on Information and Options for Policymakers

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20 Questions and Answers

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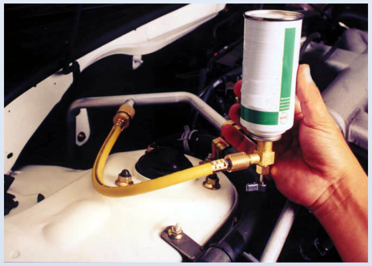
Ozone Depleting Substances (ODSs)

CFC-11	CCl_3F
CFC-12	CCl_2F_2
CFC-113	CCl_2FClF_2
Methyl chloroform	CH_3CCl_3
Carbon tetrachloride	CCl_4
HCFC-22	$CHClF_2$
Halon 1211	$CBrClF_2$
Halon 1301	$CBrF_3$

Solvents, foam blowing agents (cups, insulation), MDI, aerosol propellants, refrigerants, fire extinguisher (Br)





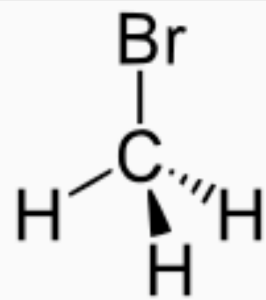




Bromine Compounds

Bromine is 50 to 60 times more efficient at destroying stratospheric ozone than chlorine

Methyl Bromide is used extensively as a fumigant

Bromomethane	
	
IUPAC name	Bromomethane
Other names	Methyl bromide, Monobromomethane, Methyl fume, Halon 1001, Curafume, Embafume, R-40 B1, UN 1062

Digression

- **Why is bromine more effective as a catalytic agent than chlorine?**
- **Why is fluorine unimportant for stratospheric ozone?**

We need to consider reaction energetics to work out the answers

Enthalpy of Formation, ΔH_f^o (heat of formation)

- **Energy required to form one mole of substance from standard states**
- **Standard states are generally naturally occurring states**
  - O_2 $\Delta H_f^o = 0$
  - F_2 $\Delta H_f^o = 0$
  - Cl_2 $\Delta H_f^o = 0$
  - Br_2 $\Delta H_f^o = 0$
  - H_2 $\Delta H_f^o = 0$
- **Enthalpies for atoms are just ½ the dissociation energy of the diatomic molecule**
  - O atom $\Delta H_f^o = 249$ kJ/mole
  - F atom $\Delta H_f^o = 79$ kJ/mole
  - Cl atom $\Delta H_f^o = 121$ kJ/mole
  - Br atom $\Delta H_f^o = 112$ kJ/mole
  - H atom $\Delta H_f^o = 218$ kJ/mole

Enthalpies for Reactions

- Enthalpies for combination of atom with H atoms (to form gaseous anhydrides of acids
  - HF ΔH_f^o = -269 kJ/mole
  - HCl ΔH_f^o = -92 kJ/mole
  - HBr ΔH_f^o = -36 kJ/mole

- Other important enthalpies
  - OH ΔH_f^o = 39 kJ/mole
  - H_2O ΔH_f^o = -242 kJ/mole

- Reaction enthalpies
  - OH + HCl → H_2O + Cl

    39 + (-92) (-242) + 122

    {-53} {-120}

    $\Delta H_f^{reaction}$ = -67 kJ/mole

  - OH + HBr → H_2O + Br

    39 + (-36) (-242) + 112

    {3} {-130}

    $\Delta H_f^{reaction}$ = -133 kJ/mole

  - OH + HF → H_2O + F

    39 + (-269) (-242) + 79

    {-230} {-163}

    $\Delta H_f^{reaction}$ = +67 kJ/mole

We can now answer the questions about catalytic effectiveness of F, Cl, Br

- $OH + HF \rightarrow H_2O + F$ is energetically impossible: once HF is formed by the reaction $F + CH_4 \rightarrow HF + CH_3$, it remains in that form as a stable molecule and does not participate in catalytic cycles.

- HBr is less strongly bound than HCl so that the reaction $OH + HBr \rightarrow H_2O + Br$ occurs more rapidly than the corresponding reaction for HCl. Thus the bromine atom spends less time in the reservoir molecule HBr.

Back to bromine and the Montreal Protocol

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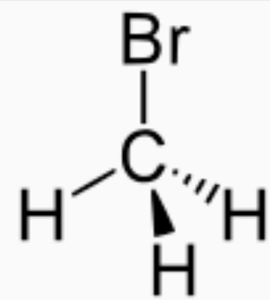
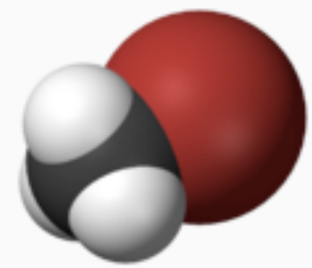
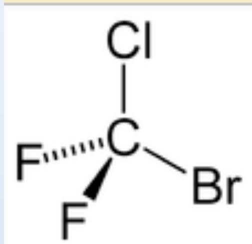
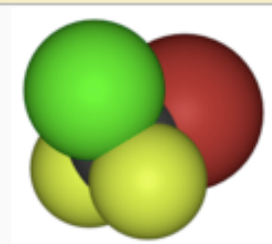
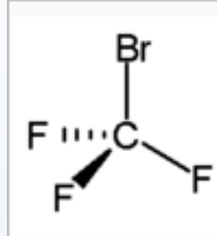
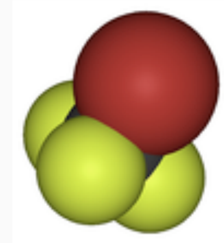
Bromomethane	
	
IUPAC name	Bromomethane
Other names	Methyl bromide, Monobromomethane, Methyl fume, Halon 1001, Curafume, Embafume, R-40 B1, UN 1062

Halons

- Halon 1211 (CF_2ClBr) developed by ICI in UK
- Halon 1301 (CF_3Br) developed at Purdue U. under auspices of US Army

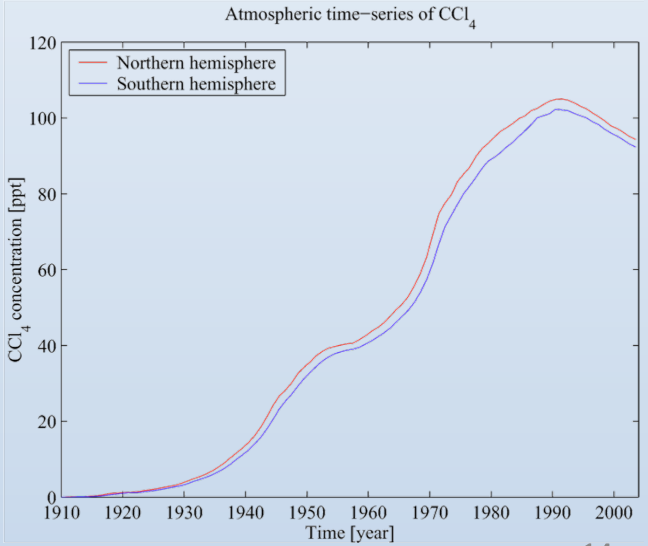
Bromochlorodifluoromethane	
	
IUPAC name	Bromochlorodifluoromethane
Other names	Chlorodifluoromonobromomethane, Halon 1211, Halon 1211 BCF, BCF, Freon 12B1

Bromotrifluoromethane	
	
IUPAC name	Bromotrifluoromethane
Other names	Trifluorobromomethane, Monobromotrifluoromethane, Trifluoromethyl bromide, Bromofluoroform, Carbon monobromide trifluoride, Halon 1301, BTM, Freon 13BI, Freon FE 1301, R 13B1, Halon 1301 BTM, UN 1009

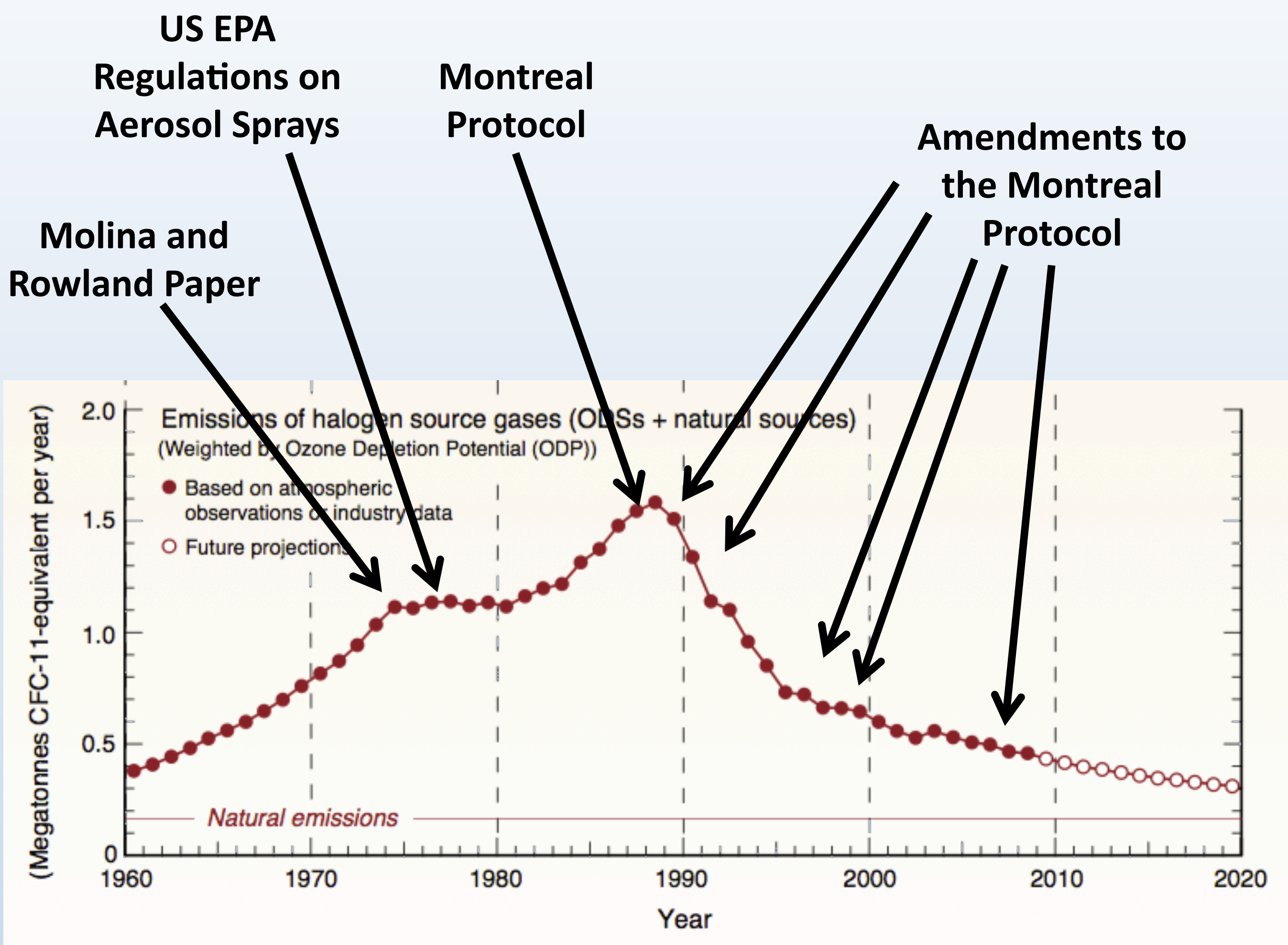
Used in fire suppression at concentrations no higher than 7% v/v in air and can suppress many fires at 2.9% v/v

Electrical Fire Extinguishers

- Early extinguishers for electrical fires used Carbon tetrachloride (CCl_4)
- Carbon tetrachloride originally synthesized by Henri Victor Regnault in 1839.
- "Carbon tetrachloride fire extinguishers" Ind. Eng. Chem., 1923, 15, 1053-1053.
  - Most effective at electrical fires with no shock danger
  - But produces phosgene, chlorine gas, and hydrogen chloride in "quite dangerous concentrations".



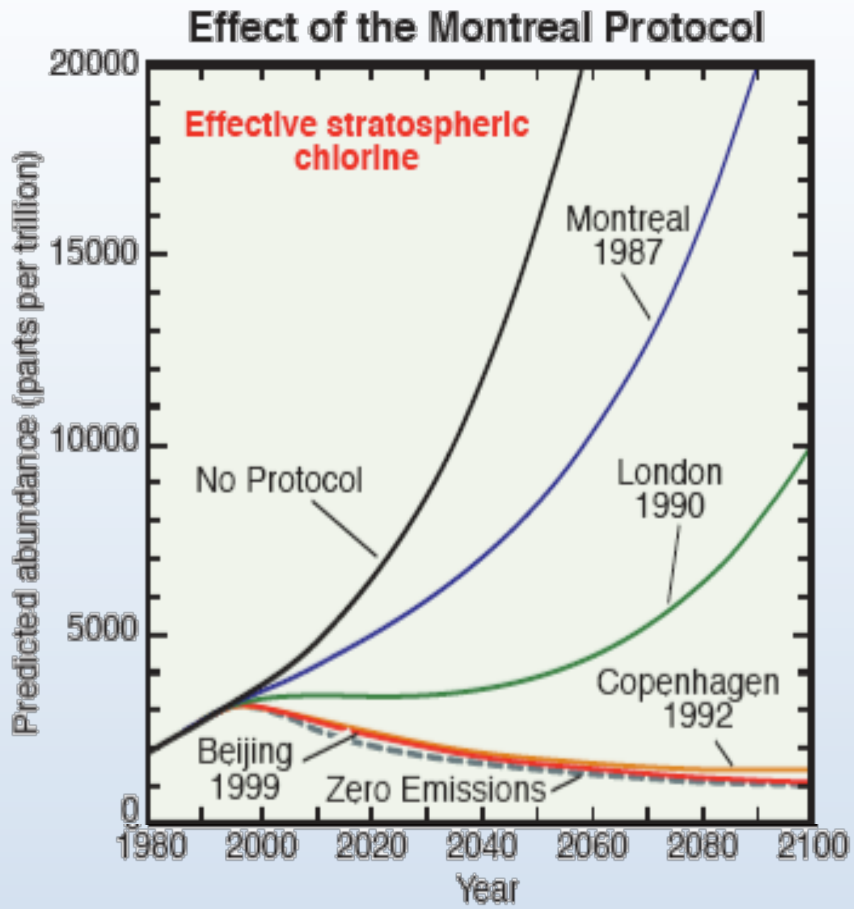
Milestones in Emissions of ODSs



The Montreal Protocol

History

- **March, 1985: Vienna Convention for Protection of the Ozone Layer**
- **Sept 16, 1987: opened for signature**
- **Jan 1, 1989: entered into force**
- **May, 1989: first meeting of the parties**



Revisions or Amendments

- **1990 London**
- **1992 Copenhagen**
- **1997 Montreal**
- **1999 Beijing**
- **2007 Montreal**

COUNTRY	Signature Vienna Convention	Signature Montreal Protocol	Vienna Convention	Montreal Protocol	London Amendment	Copenhagen Amendment	Montreal Amendment	Beijing Amendment
TOTALS	28	46	197	197	196	194	186	173

CFC Lifetimes
(Atmospheric Residence Times)

Industrial Designation or Common Name	Chemical Formula	Lifetime (years)
Halogen-substituted methanes		
HFC-41	CH_3F	2.4
HFC-32	CH_2F_2	4.9
HFC-23	CHF_3	270
FC-14 (Carbon tetrafluoride)	CF_4	50 000
Methyl chloride	CH_3Cl	1.0
Dichloromethane	CH_2Cl_2	*0.38*
Chloroform	$CHCl_3$	*0.41*
Carbon tetrachloride	CCl_4	26
HCFC-31	CH_2ClF	1.3
HCFC-22	$CHClF_2$	12.0
HCFC-21	$CHCl_2F$	1.7
CFC-13	$CClF_3$	640
CFC-12	CCl_2F_2	100
CFC-11	CCl_3F	45

More Fluorine → Longer lifetime (HFC-41, HFC-32, HFC-23, FC-14)

Hydrogen → Shorter lifetime (Methyl chloride, Dichloromethane, Chloroform)

e.g. $CHClF_2 + OH \rightarrow CF_2Cl + H_2O$

Most commonly used in 1980s (CFC-12, CFC-11)

CFC 11 and 12 were increasing at 3-5%/year during 1970s and 1980s

Progression of Chlorine Compounds under the Provisions of the Montreal Protocol

CFCs – fully halogenated hydrocarbons

↓

HCFCs – hydrogen substituted for shorter lifetimes

↓

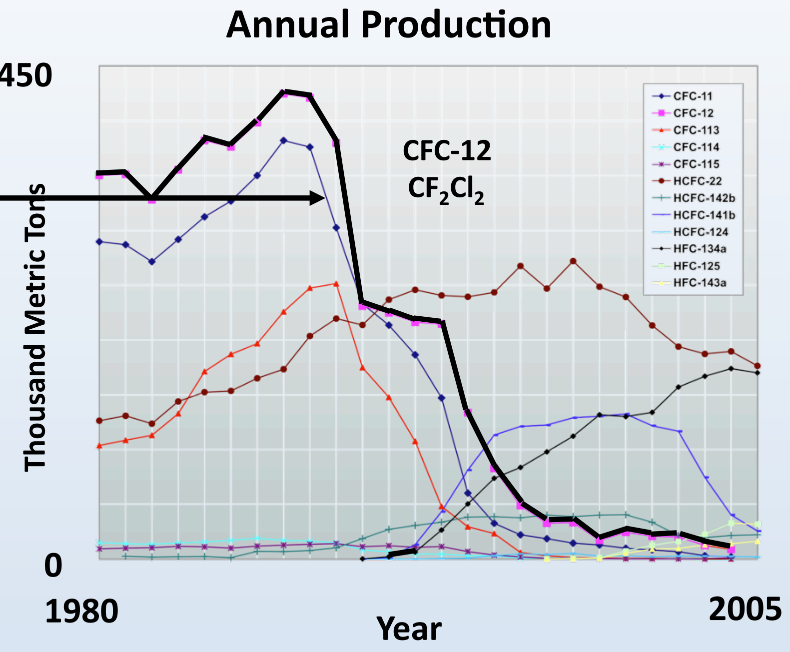
HFCs – no chlorine, no ozone depletion

↓

? What next ?

Production of CFCs 11 and 12 Fell Off Rapidly with Montreal Protocol

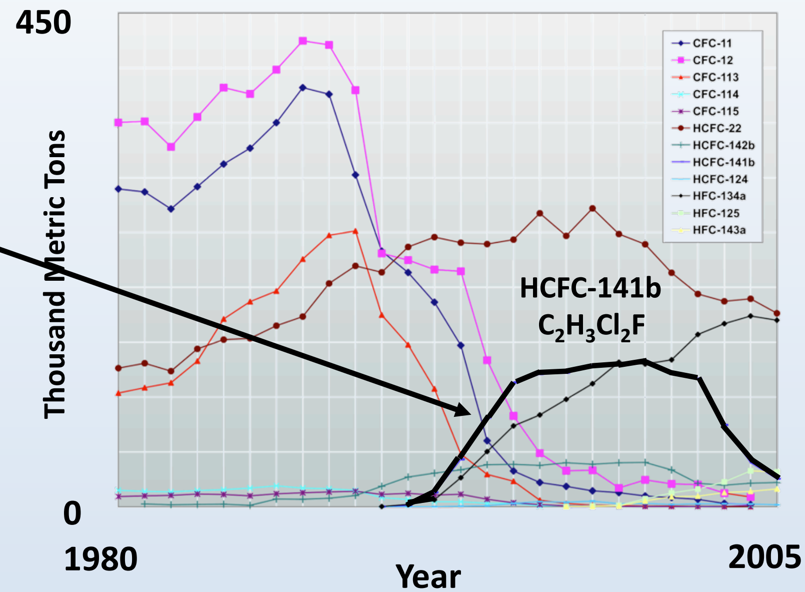
- **Production of fully-halogenated CFCs fell off rapidly**



Replacement HCFCs began to have increased production

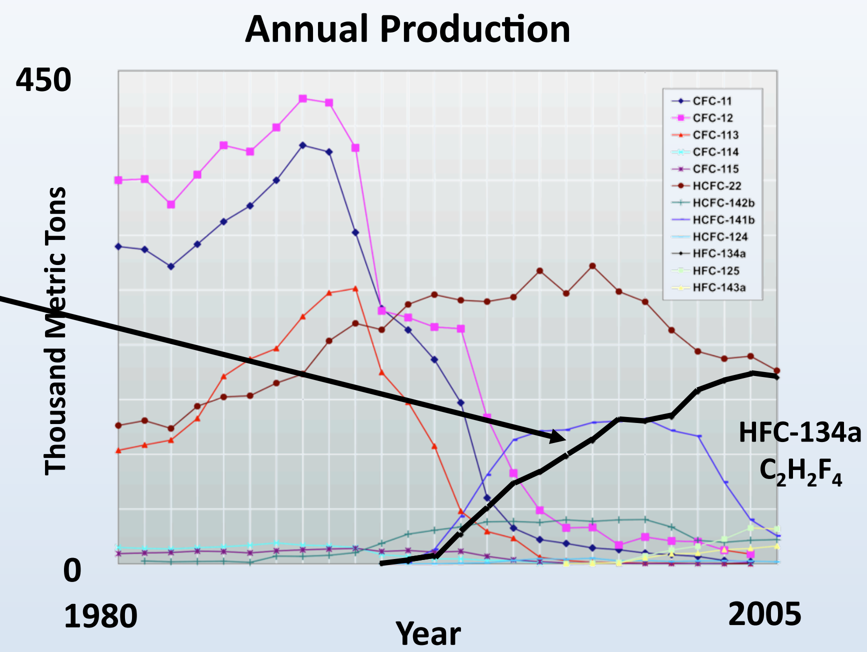
- Replacement HCFCs increased (and some have already begun to decrease)
- HCFCs have shorter lifetime, smaller ozone depletion potential, and small global warming potential than the CFCs they replaced

Annual Production



HCFCs are now beginning to be replaced by HFCs

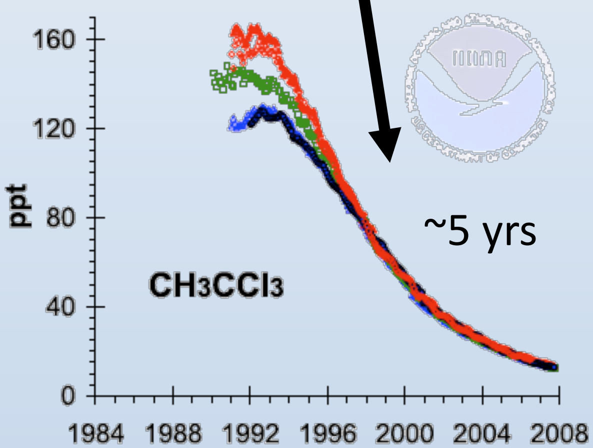
- **HFCs, which contain no chlorine, have already begun to be phased in as replacements for HCFCs**

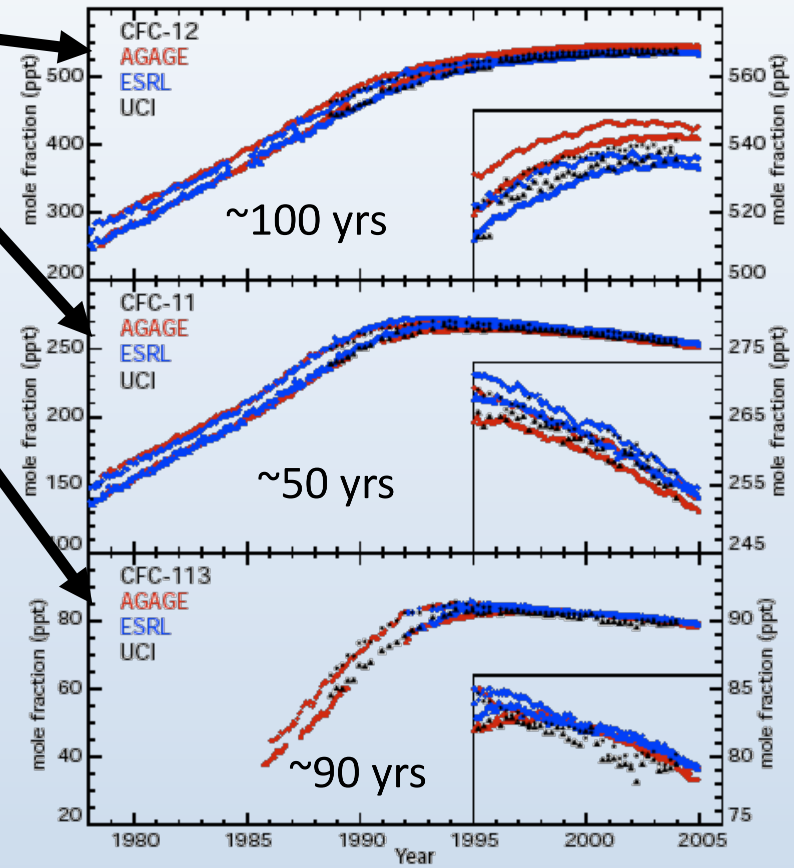


HFCs are still greenhouse gases

Growth Rate of some CFCs from Measurements at Surface Stations

- **Long-lived CFC 12 has leveled off**
- **CFC 11 has begun to decline**
- **CFC 113 (CF_3CCl_3) has also begun to decline**
- **Methyl chloroform has reached near-zero concentration**





Atmospheric Measurements from NOAA Network

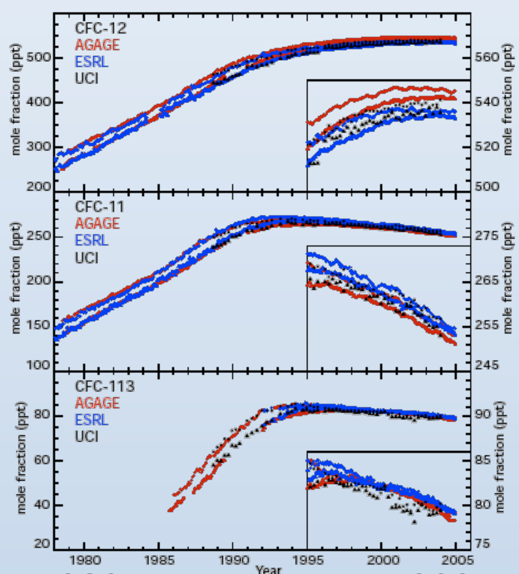
The Protocol is having a real effect!

1. Controlled Substances are leveling off or decreasing

2. Stratospheric chlorine has begun to decrease

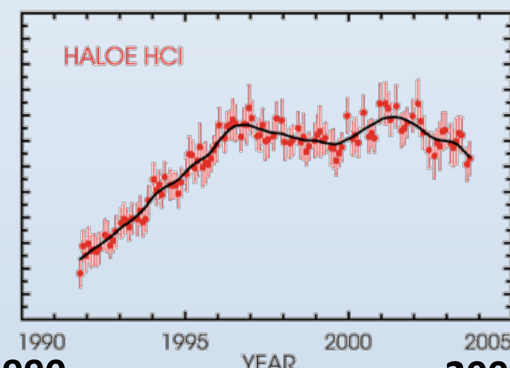
3. Ozone shows signs of responding to the leveling off of chlorine

CFC-11,12,113



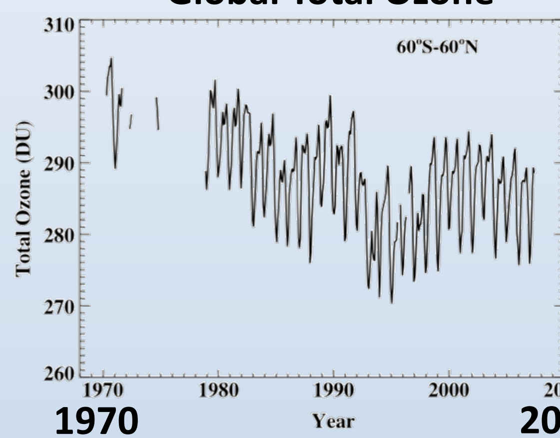
1980 **2005**

Stratospheric HCl



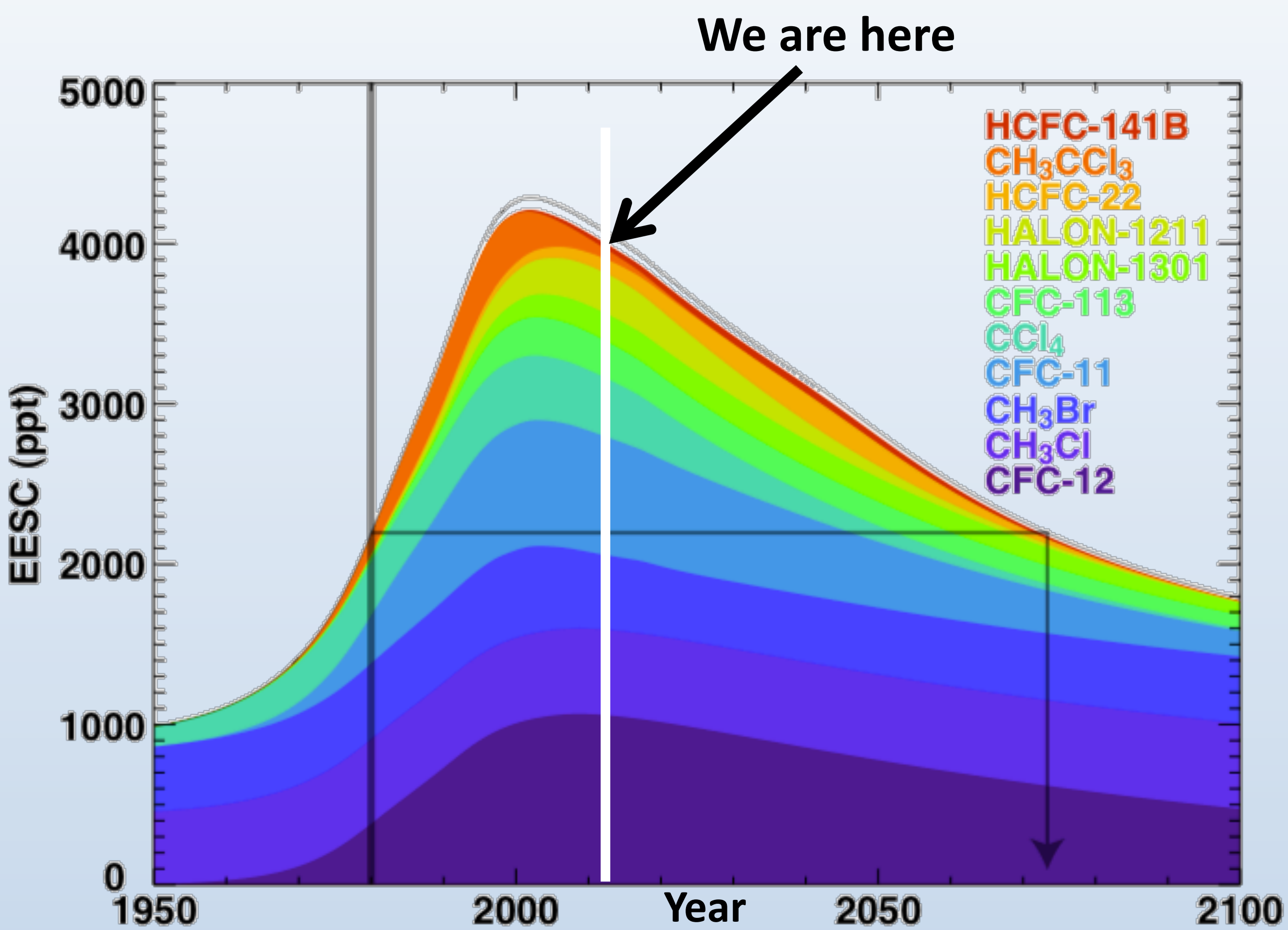
1990 **2005**

Global Total Ozone



1970 **2010**

We put these together into an "Equivalent Effective Stratospheric Chlorine" or EESC



Where is the Montreal Protocol Going?

- **Push to regulate HFCs**
  - **They have no ozone depletion potential**
  - **But they are a greenhouse gas**
  - **Production and atmospheric concentrations increasing because of Montreal Protocol**
- **Should Montreal Protocol regulate them?**
- **Or should they come under Kyoto Protocol?**
  - **Montreal regulates production**
  - **Kyoto regulates emission**
- **What about nitrous oxide?**
  - **Greenhouse gas**
  - **Ozone depleter**
  - **By-product of fertilizer application, among many other things**

Comparison Ozone vs Climate

- Vienna Convention (1985) ⟷ UNFCCC Framework Convention on Climate Change (Bonn, 1992)
- Montreal Protocol (1987) ⟷ Kyoto Protocol (1997)

Why has one worked so well while the other has not?

What do you think?

Some possible reasons for success of Montreal Protocol relative to Kyoto Protocol

- Smoking gun, i.e. ozone hole?
- Availability of replacements?
- CFCs less integral to our society?
- Press coverage?
- Nay-sayers/non-believers?
- IPCC vs Ozone Assessment?
- Regulating emission vs production?
- Nature of the problem (size and time scale of perturbation relative to natural variability)?
- Scare scenarios overplayed?

What else?