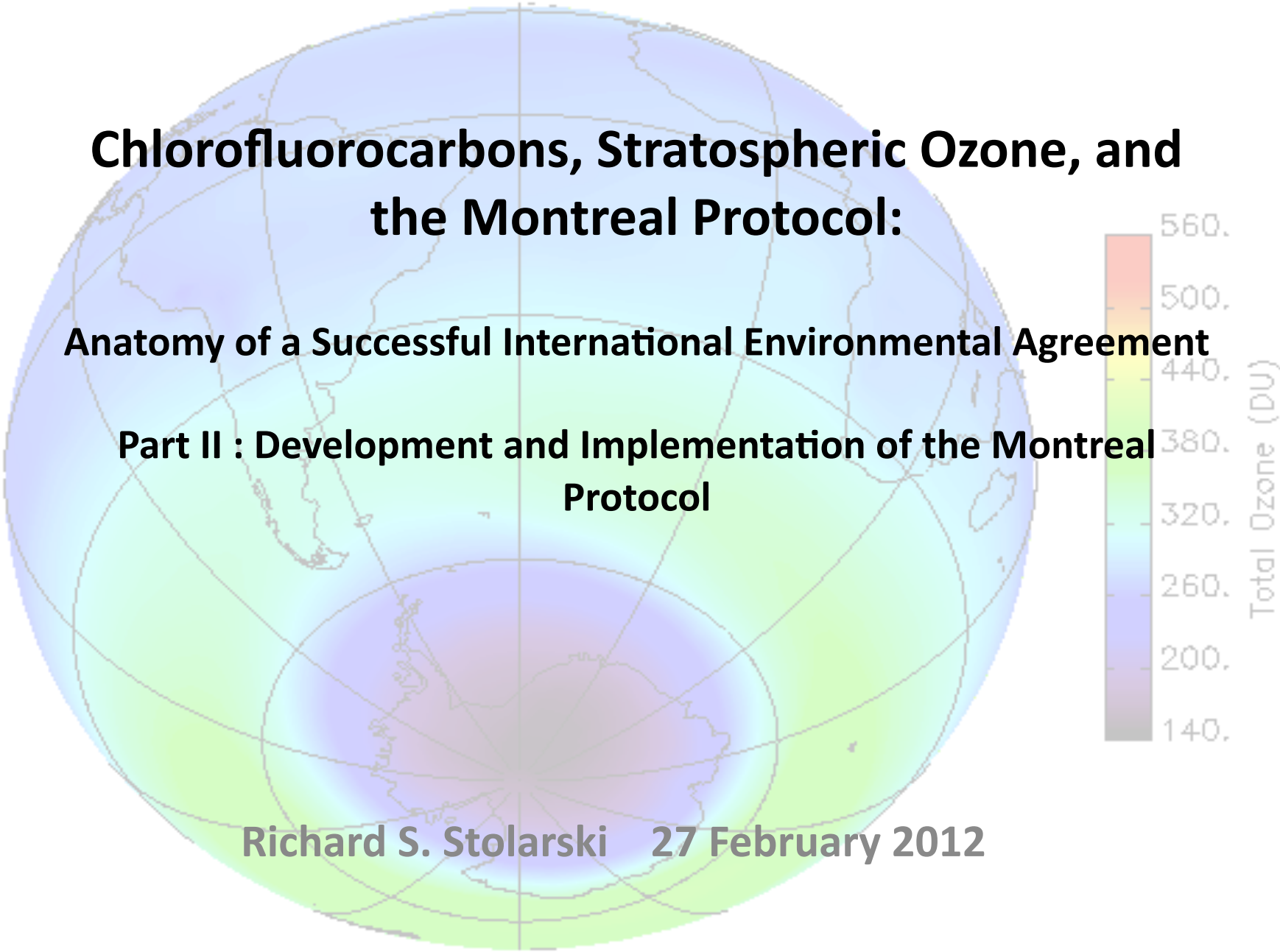
# Chlorofluorocarbons, Stratospheric Ozone, and the Montreal Protocol:

## Anatomy of a Successful International Environmental Agreement

## Part II : Development and Implementation of the Montreal Protocol




Richard S. Stolarski 27 February 2012

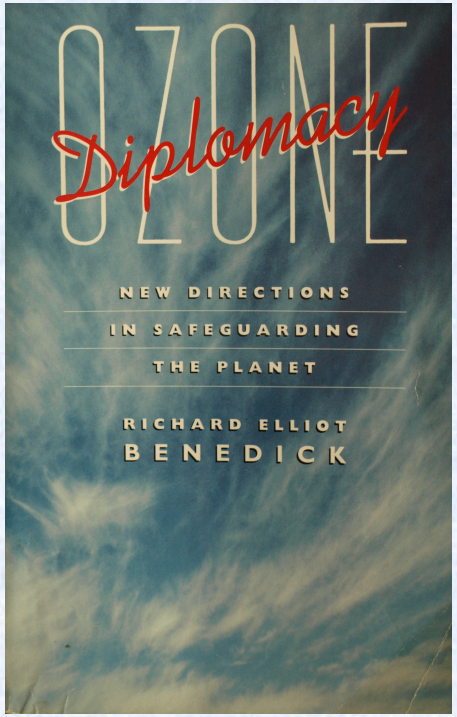
# The Vienna Convention and the Montreal Protocol: What are they?

- **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

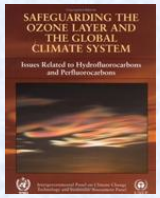
1980 1990 2000 2010

**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

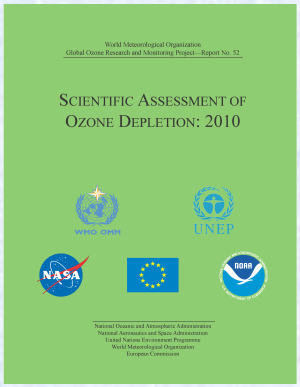
SAP Co-chairs

**Ayité-Lô Ajavon (Togo)**

**Paul Newman (USA)**

**John Pyle (UK)**

**A.R. Ravishankara (USA)**




Coordinator/Editor

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Special thanks to:

**Malcolm Ko (US), Ted Shepherd (Canada), and Susan Solomon (US)**

with reviews and Executive Summary

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

**Steve Montzka (USA), Stefan Reimann (Switz.)**

**Ch. 2: Stratospheric Ozone and Surface Ultraviolet Radiation**

**Anne Douglass (USA), Vitali Fioletov (Canada)**

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

**Slimane Bekki (Fr.), Greg Bodeker (NZ)**

**Ch. 4: Stratospheric Changes and Climate**

**Piers Forster (UK), Dave Thompson (USA)**

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

**John Daniel (USA), Guus Velders (Netherlands)**

**20 Questions and Answers**

**David Fahey (USA), Michaela Hegglin (Canada)**

# Ozone Depleting Substances (ODSs)

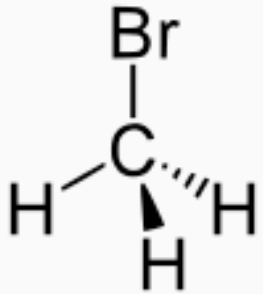
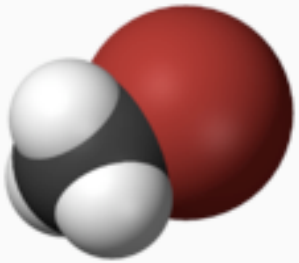
- CFC-11 $CCl_3F$
- CFC-12 $CCl_2F_2$
- CFC-113 $CCl_2FClF_2$
- Methyl chloroform $CH_3CCl_3$
- Carbon tetrachloride $CCl_4$
- HCFC-22 $CHClF_2$
- Halon 1211 $CBrClF_2$
- Halon 1301 $CBrF_3$

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

# Bromine Compounds

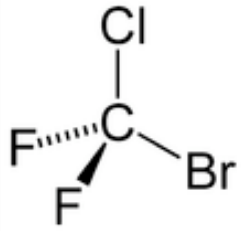
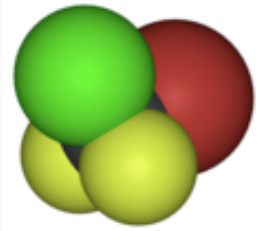
## Bromine is 50 to 60 times more efficient at destroying stratospheric ozone than chlorine

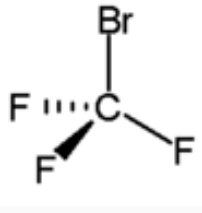
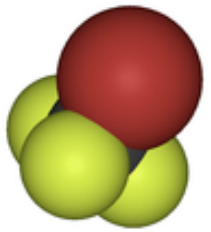
**Methyl Bromide is used extensively as a fumigant**

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

# Halons

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

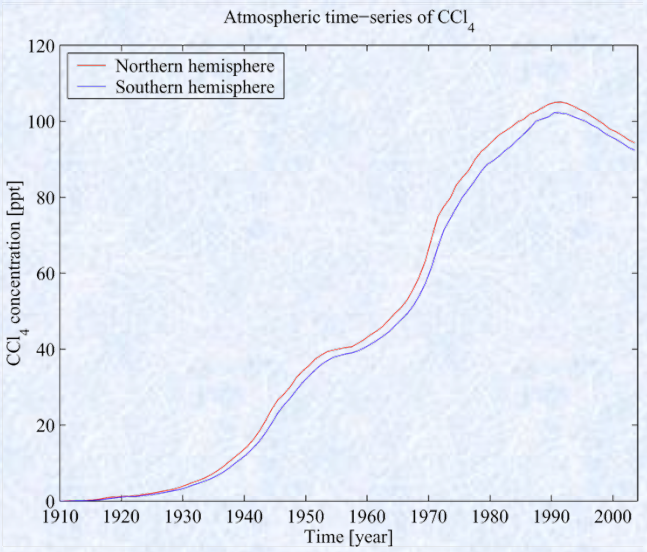
| Bromochlorodifluoromethane | |
|---|---|
|   |  |
| IUPAC name | Bromochlorodifluoromethane |
| Other names | Chlorodifluoromonobromomethane, Halon 1211, Halon 1211 BCF, BCF, Freon 12B1 |

| 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 |

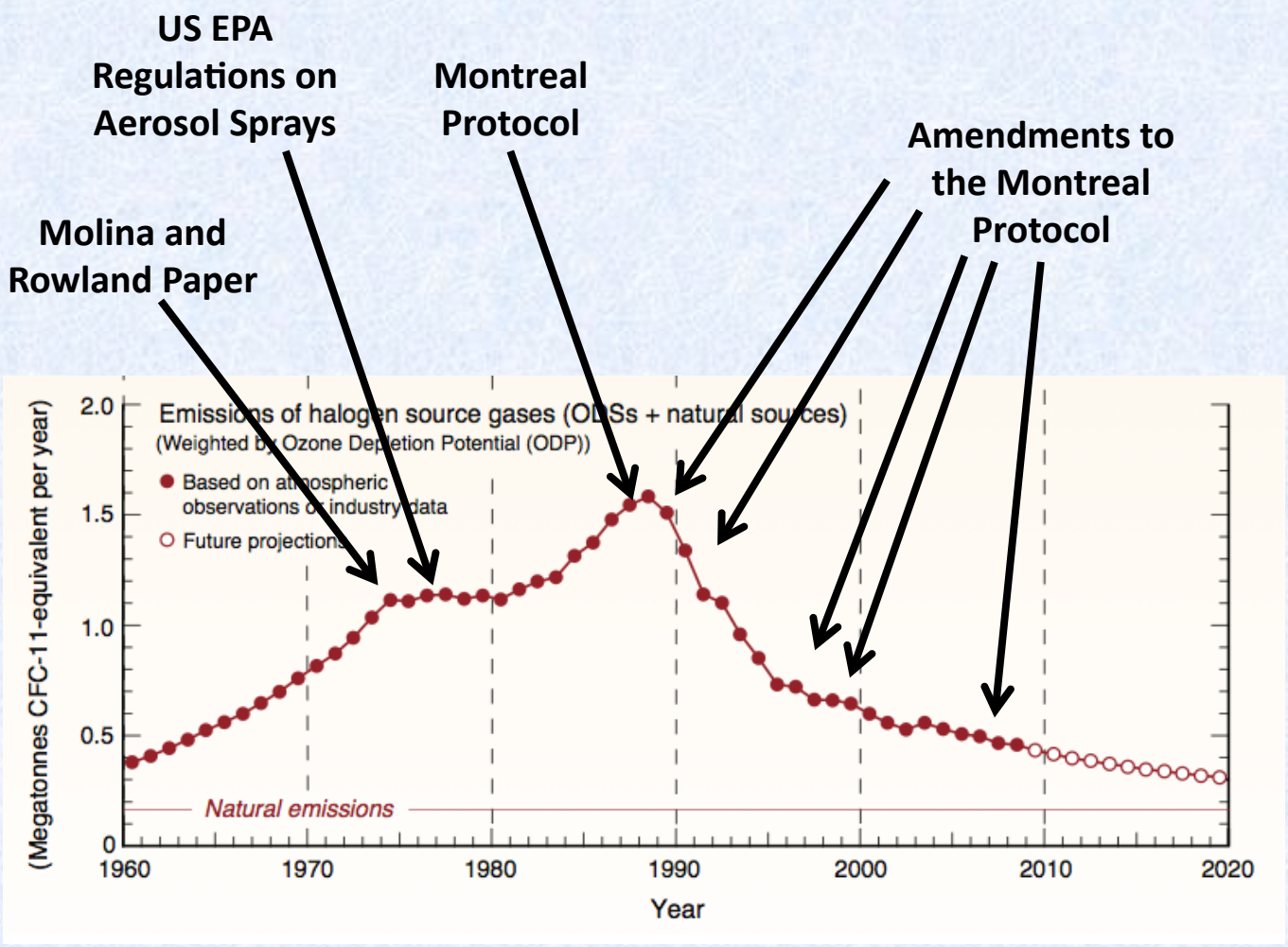
**Used in fire suppression at concentrations no higher than 7% v/v in air and can suppress many fires at 2.9% v/v**

# 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



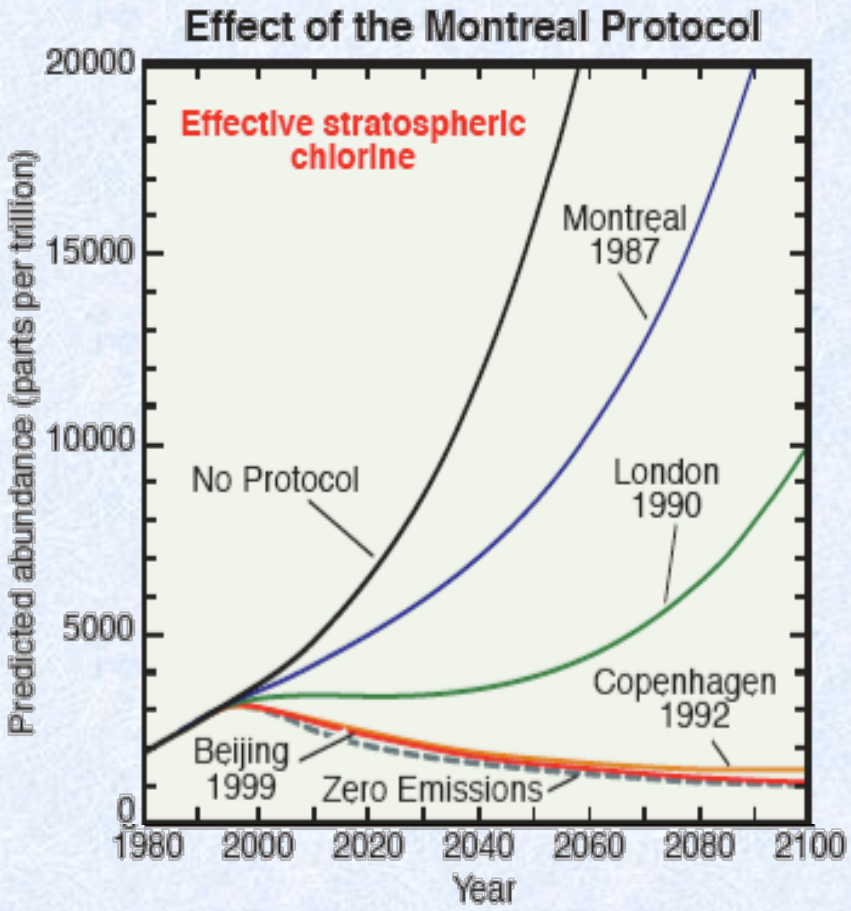
# The Montreal Protocol

**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

Hydrogen→ Shorter lifetime

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

Most commonly used in 1980s

**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**

↓

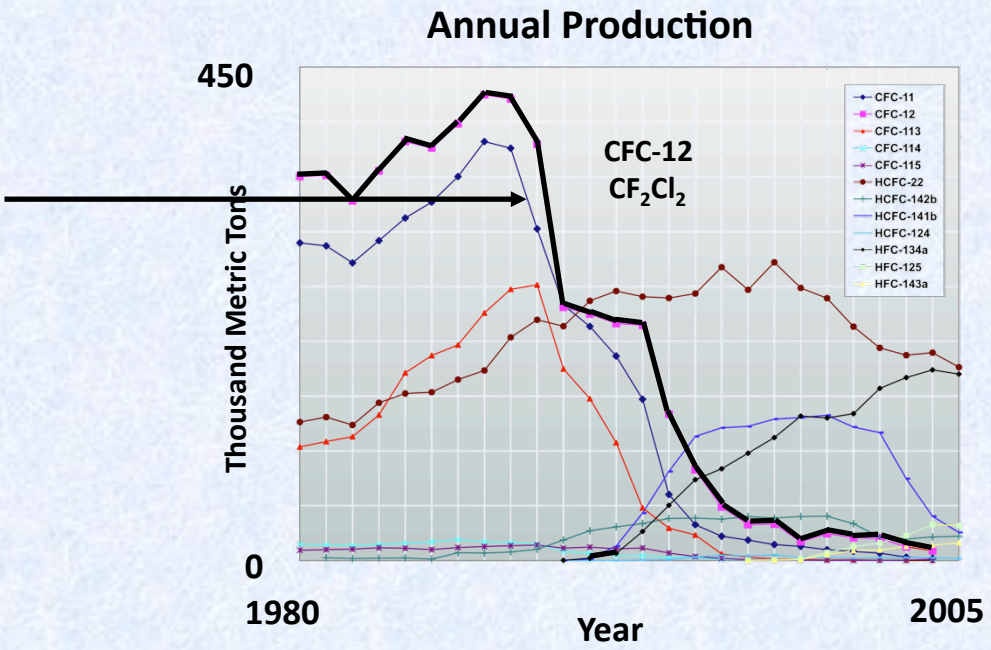
**HFCs – no chlorine, no ozone depletion**

↓

**? What next ?**

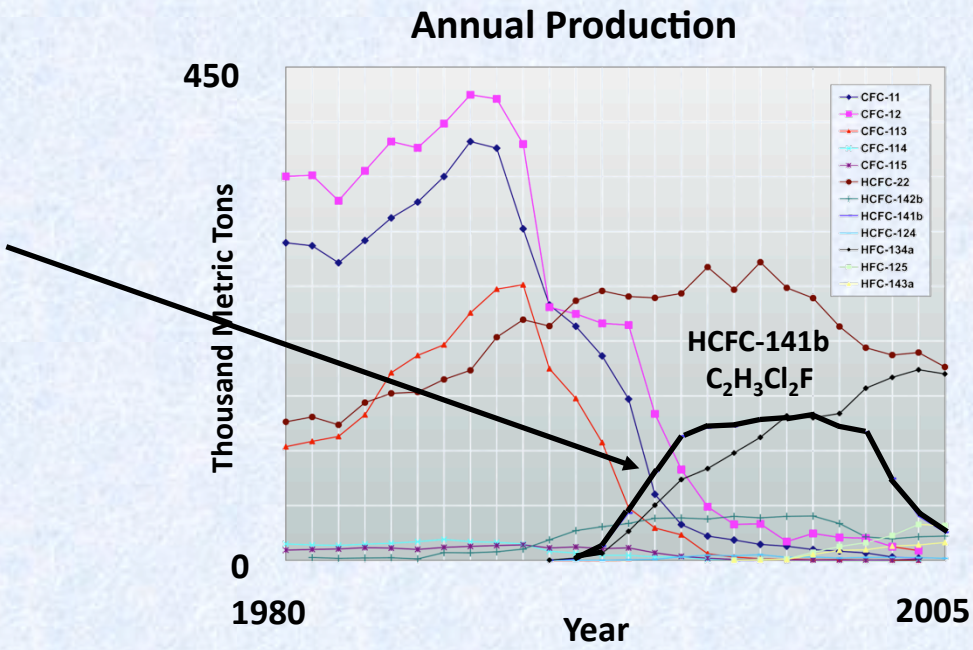
# Production of CFCs 11 and 12 Fell Off Rapidly with Montreal Protocol

- Production of fully-halogenated CFCs fell off rapidly



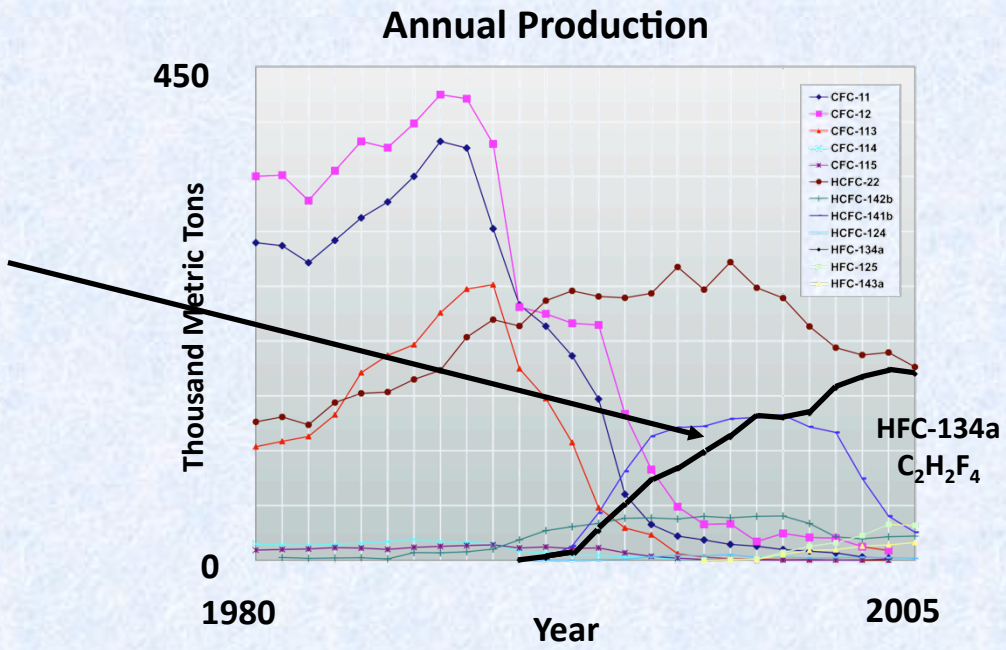
# Replacement HCFCs began to have increased production

- 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



# HCFCs are now beginning to be replaced by HFCs

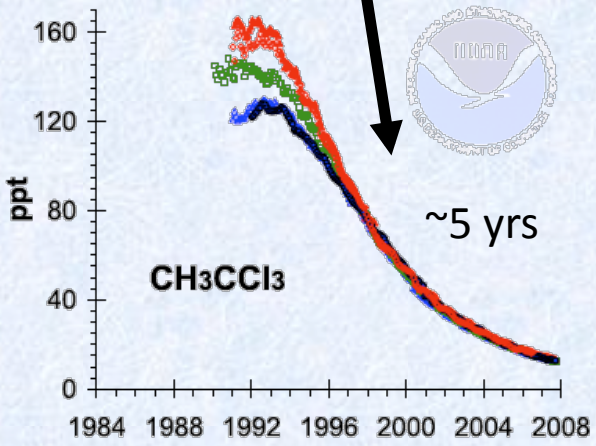
- HFCs, which contain no chlorine, have already begun to be phased in as replacements for HCFCs

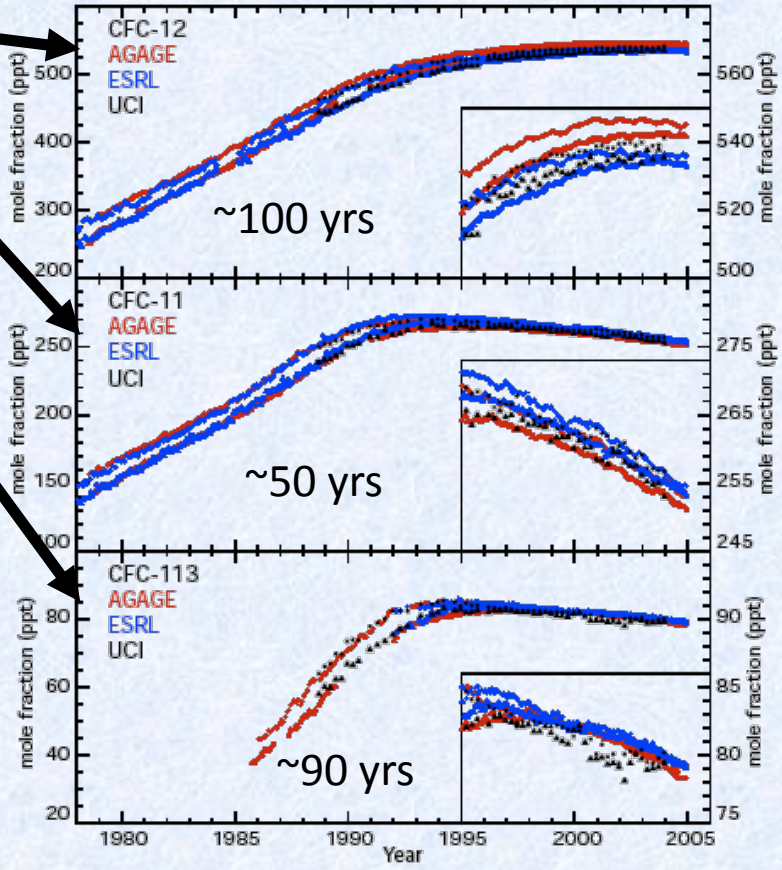



**HFCs are still greenhouse gases**

# 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**

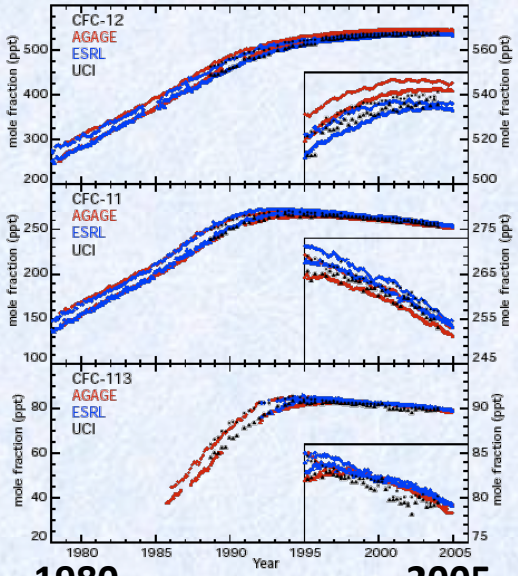
# The Protocol is having a real effect!

**1.** Controlled Substances are leveling off or decreasing

**2.** Stratospheric chlorine has begun to decrease

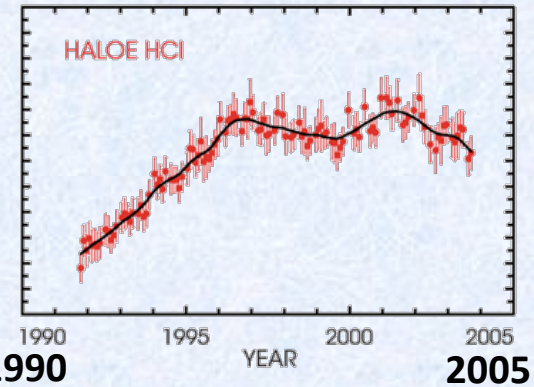
**3.** Ozone shows signs of responding to the leveling off of chlorine

**CFC-11,12,113**



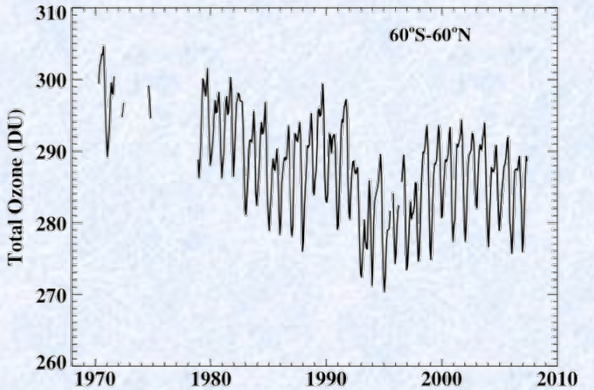

**1980** **2005**

**Stratospheric HCl**




**1990** **2005**

**Global Total Ozone**




**1970** **2010**

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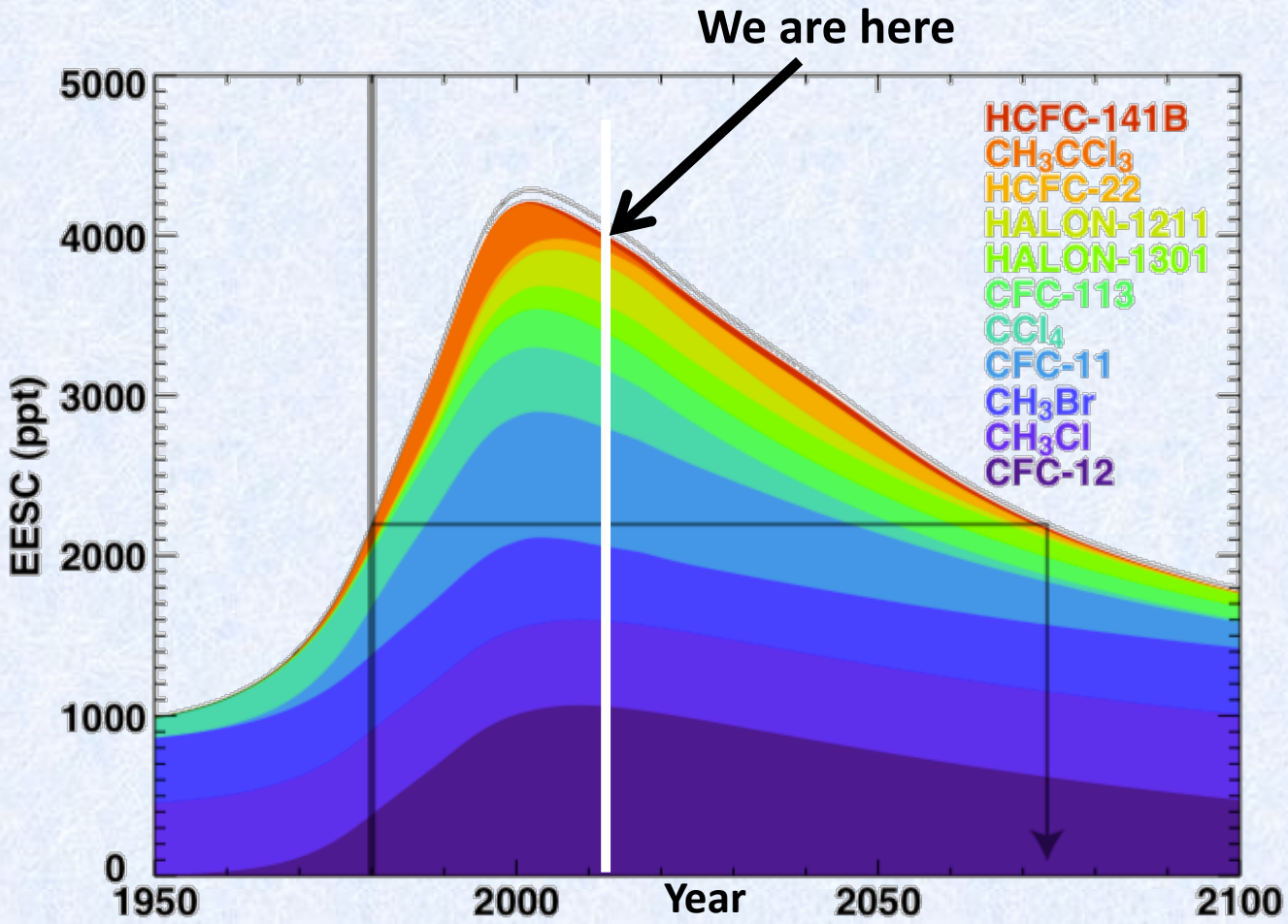
# We put these together into an "Equivalent Effective Stratospheric Chlorine" or EESC

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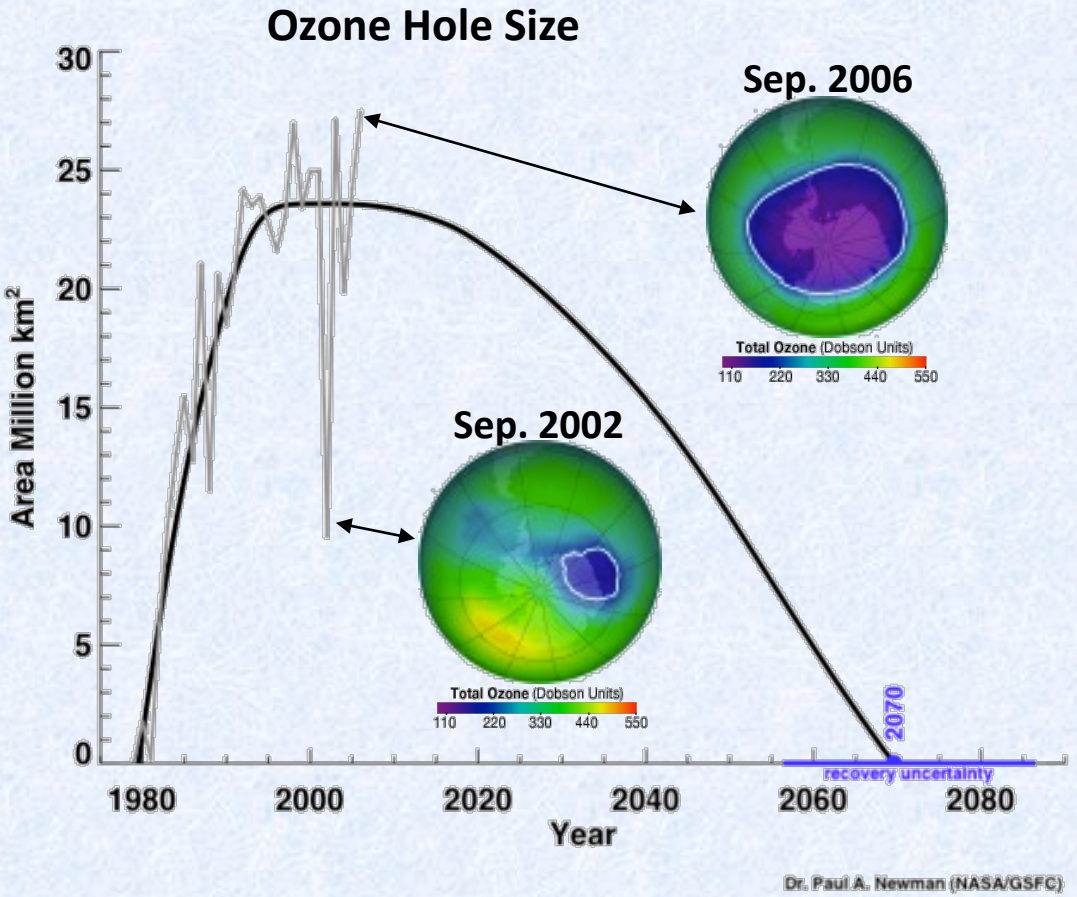
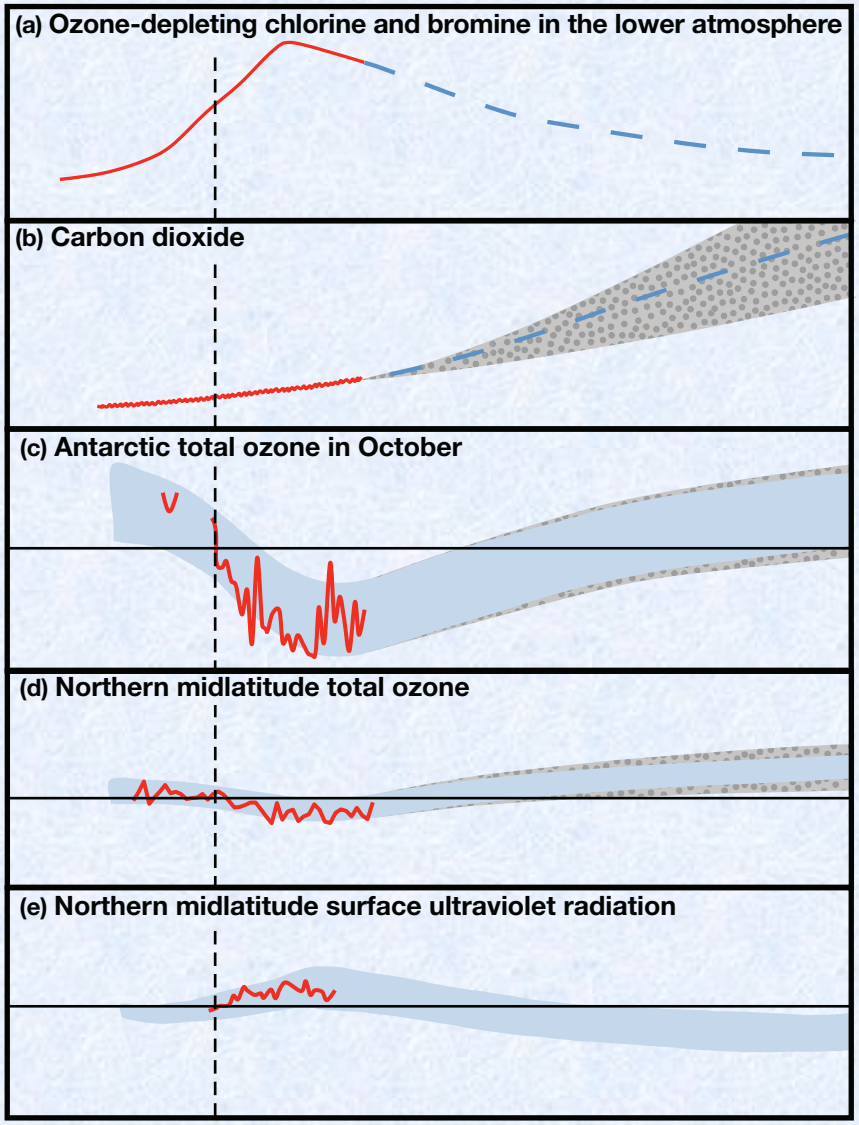
# Ozone Hole Recovery

- Caused by chlorine and bromine from human-produced gases
- Estimate that hole will begin to show size decreases by ~2023, and be similar to 1980 by 2070
- Recent occurrences of particularly small (2002) or large (2006) ozone holes are not indicative of a long-term trend.



# Key findings of the SAP




ODSs

ODSs are behaving as expected

Climate Change

Climate change and ozone layer are intricately coupled. Climate change will become more important. MP can potentially influence climate

Ozone hole

Ozone hole continues to persist, as expected. It is expected to recover later this century.

Global ozone

Global ozone depletion is smaller than the ozone hole. It has not gotten worse because of the MP. Expected to recover towards the middle of this century.

Global UV Change

Surface UV changes are small to date. In the future, it will be influenced by climate change more than ozone depletion.



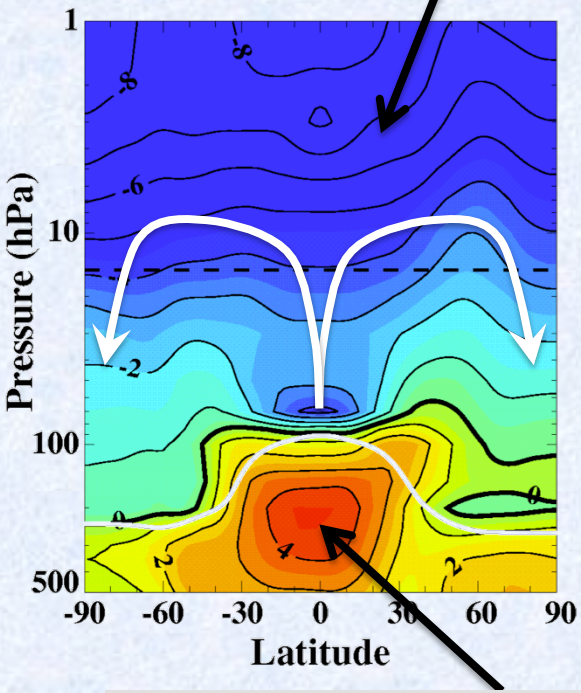
Figure ES-2, Scientific Assessment of Ozone Depletion: 2010

# GHGs change ozone levels
# Fixed ODS, increasing GHGs (2065-1980)

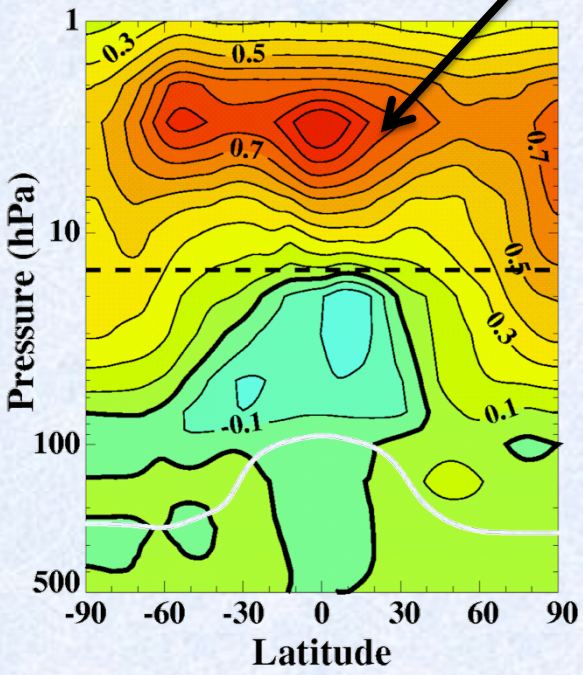
Stratosphere cools because of GHGs

$O_3$ increases in upper stratosphere

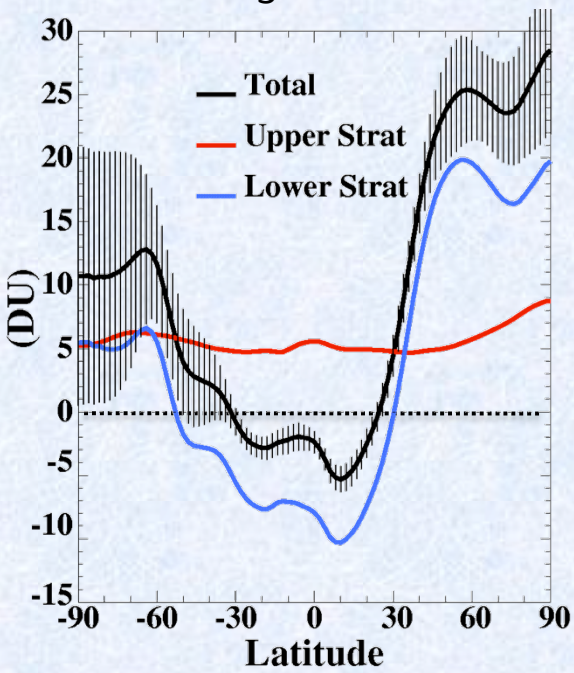
T (K)




$O_3$ (ppmv)




$O_3$ (DU)




Troposphere warms because of GHGs

Feng Li, NASA/GSFC



Li, Stolarski, and Newman, Atmos. Chem. Phys., 9, 2207-2213, 2009

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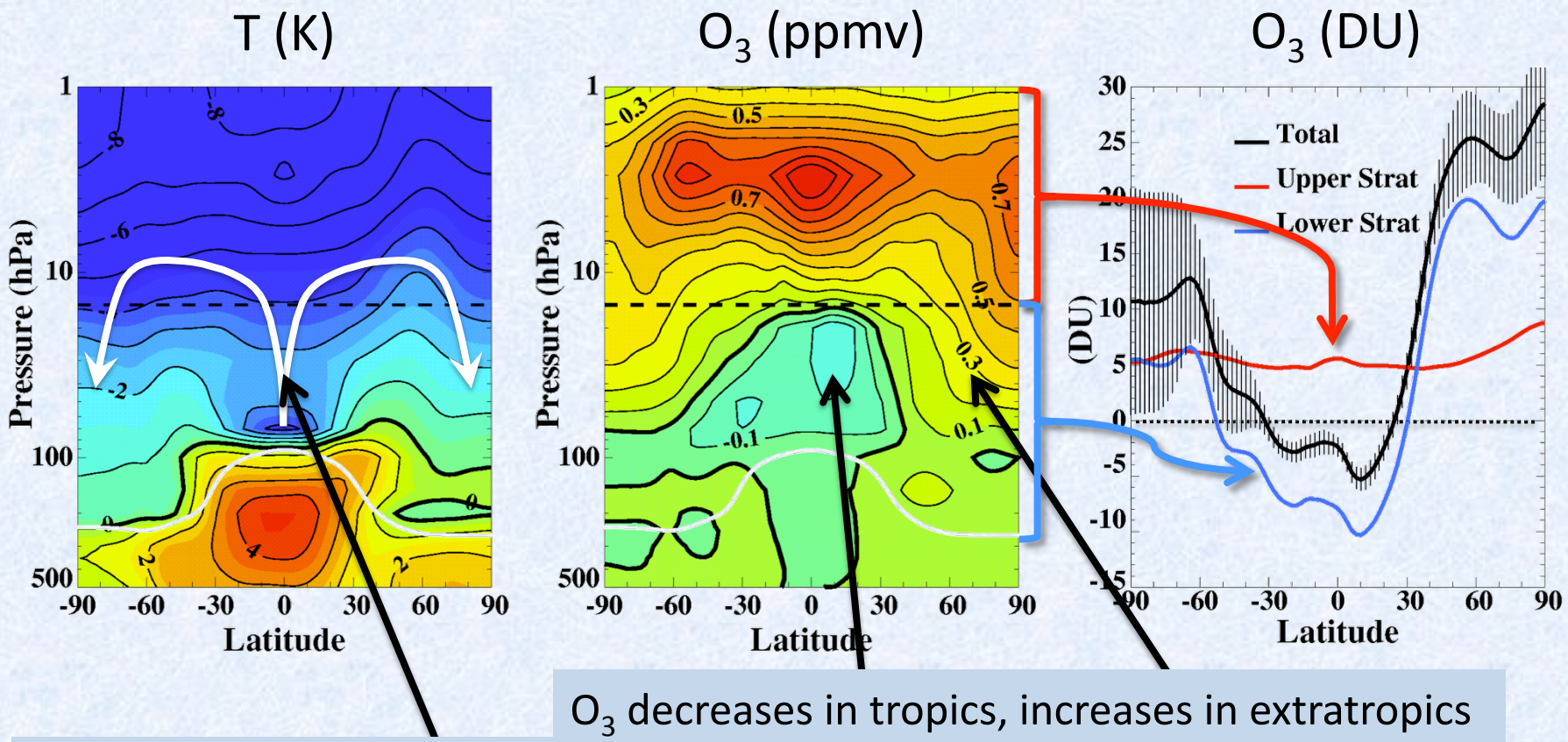


$O_3$ decreases in tropics, increases in extratropics

GHGs cause Brewer-Dobson circulation to accelerate

Feng Li, NASA/GSFC

Stolarski 2/27/2012 Waugh Class

Li, Stolarski, and Newman, Atmos. Chem. Phys., 9, 2207-2213, 2009

# GHGs change ozone levels
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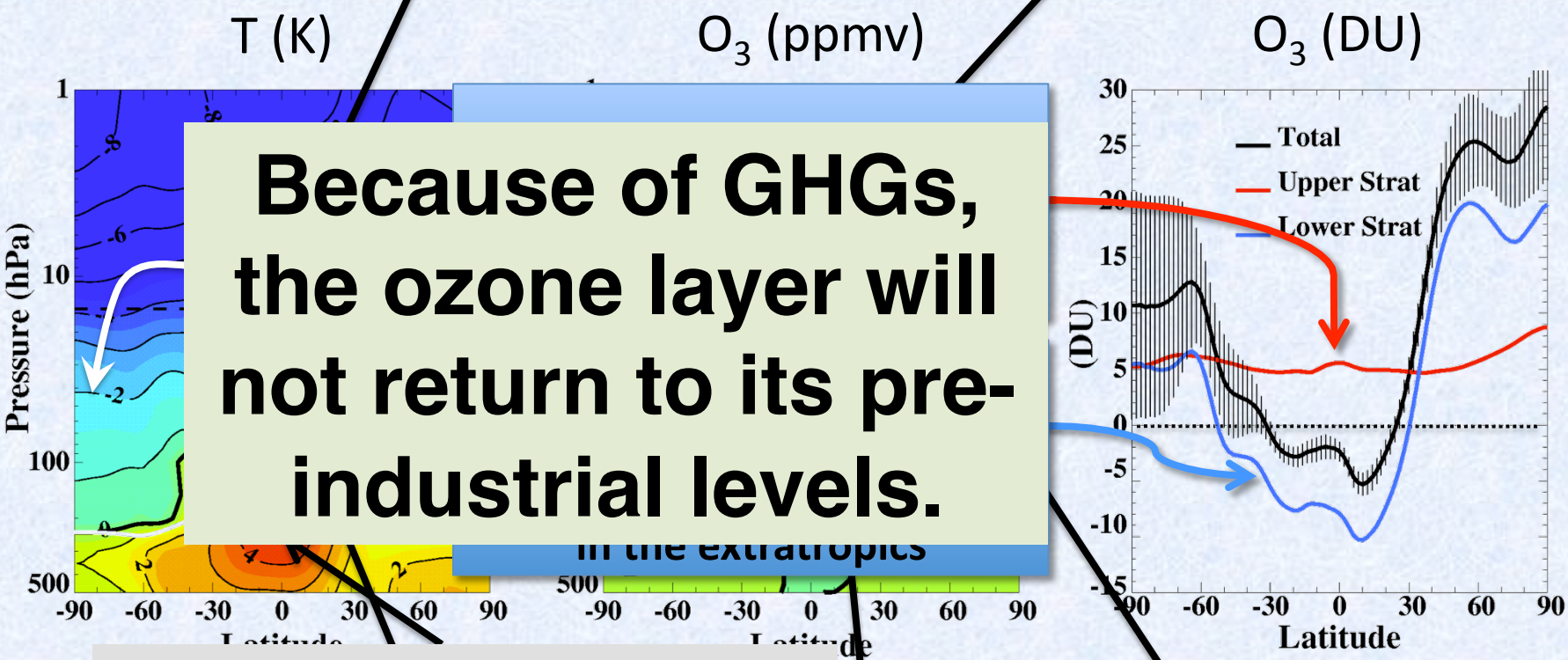
Stratosphere cools because of GHGs

$O_3$ increases in upper stratosphere




**Because of GHGs, the ozone layer will not return to its pre-industrial levels.**

Troposphere warms because of GHGs

$O_3$ decreases in tropics, increases in extratropics

GHGs cause Brewer-Dobson circulation to accelerate

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# 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?