

Stratospheric Ozone: How We Came to Understand its Chemistry and Response to Perturbations

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A few background facts

- **Ozone in atmosphere “discovered” by measurement of cutoff of solar spectrum in UV (Cornú 1879, Hartley 1881)**
- **Ozone determined to be a layer at high altitude (in stratosphere) (Strutt [Rayleigh] 1917)**
- **Ozone column amount quantitatively measured by UV absorption (Fabry and Buisson 1919, Dobson 1924)**
- **First ozone theory by Chapman (1930)**

Historical Context

- The ozone issue was first posited in terms of Supersonic Transports (SSTs) impacting the atmosphere by Harold Johnston in 1971.
- The “fluorocarbon-ozone” theory was put forward by Molina and Rowland in 1974
- The negotiations for the Montreal Protocol were begun in 1985 and formulated into the protocol by 1987
- The ozone hole was discovered in 1985 and explained reasonably well in 1986
- Measurements showing anti-correlation of chlorine and ozone in the Antarctic vortex were made in 1987
- **How was so much discovered and explained in such a short time (16 years)?**

Some Chemistry History

Early work: study of ozone photochemistry in the laboratory

Fritz Weigert (1907) noted that addition of Chlorine (Cl_2) sped up rate of ozone recombination – **work was contemporary with early work on photosynthesis and on the photoelectric effect**

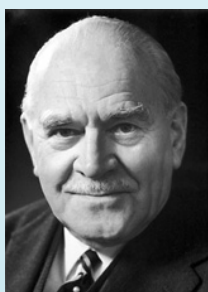
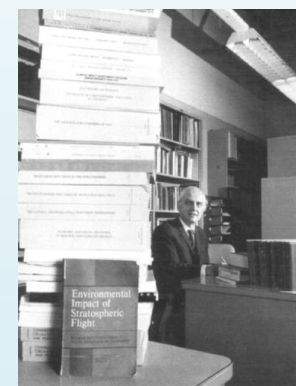


Sydney Chapman proposed the first ozone theory for the stratosphere in 1930

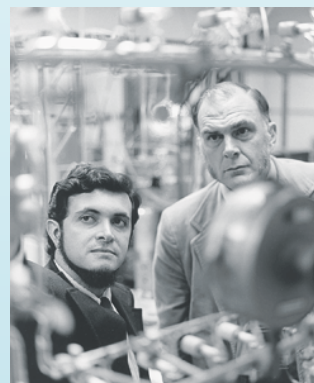


Paul Crutzen, in 1970, developed the early theory of the catalytic impact of nitrogen and hydrogen oxides on stratospheric ozone

Harold Johnston, in 1971, suggested that nitrogen oxides from proposed SSTs could deplete stratospheric ozone – CIAP program followed



Norrish and Porter – Nobel prize in chemistry 1967 for techniques to detect small concentrations of short-lived radicals



Molina and Rowland proposed that stratospheric ozone could be destroyed by chlorine released in the stratosphere from CFCs in 1974

H. J. Schumacher and the Ozone Chemical Mechanism

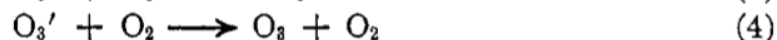
Schumacher, H. J. (1930), The mechanism of the photochemical decomposition of ozone, *Journal of the American Chemical Society*, 52(6), 2377–2391.



netics of the reaction. If we assume for the primary reaction the formation of an excited ozone molecule



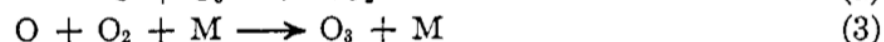
we have only a limited number of possible reactions that may follow, namely



These considerations show that the reaction



is quite probable. Neglecting the formation of chains, only the following reactions are possible



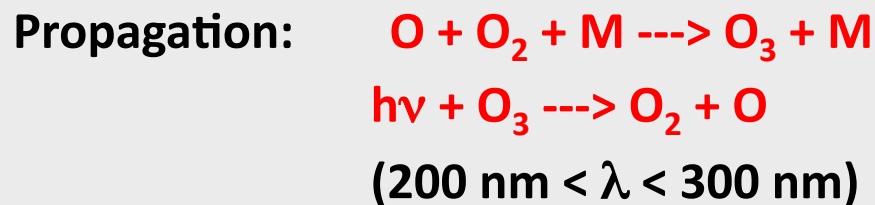
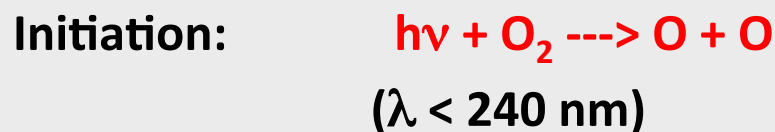
Before: excited ozone molecules

After: oxygen atoms from photodissociation

Ozone Photochemistry

Odd Oxygen (O atoms + O₃ molecules)

Chapman Theory 1930

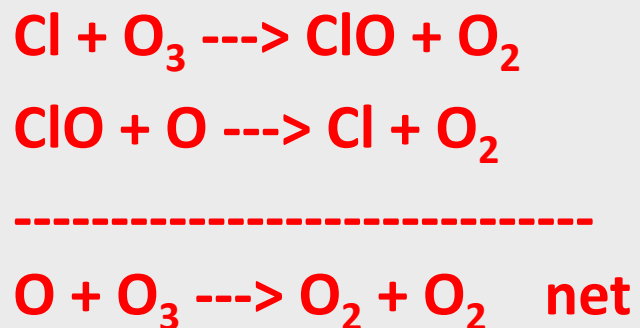


Ozone is continuously being made and destroyed in the atmosphere

Catalysis Accelerates Termination Reaction

Hydrogen oxides, Nitrogen oxides
Chlorine oxides, Bromine oxides

Example: Chlorine



Fritz Weigert first studied the impact of chlorine on ozone decomposition his laboratory in 1907



The Nobel Prize in Chemistry 1967

Manfred Eigen, Ronald G.W. Norrish, George Porter

The Nobel Prize in Chemistry 1967

Manfred Eigen

Ronald G.W. Norrish

George Porter



Manfred Eigen



Ronald George
Wreyford Norrish



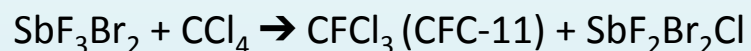
George Porter

The Nobel Prize in Chemistry 1967 was divided, one half awarded to Manfred Eigen, the other half jointly to Ronald George Wreyford Norrish and George Porter *"for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy"*.

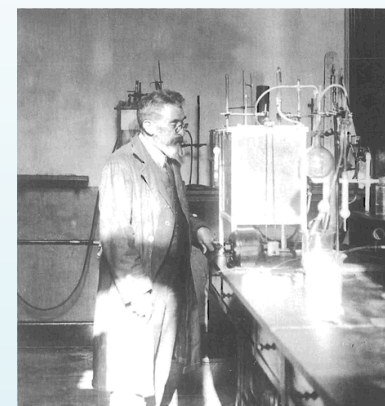
Early Synthesis of CFCs

Frederic Swarts

Belgian chemist: (1866 -1940). Swarts was one of only about a half dozen fluorine chemists in the world in the late part of the 19th century; he prepared the first chlorofluorocarbon, CFC-11 in the early 1890s.

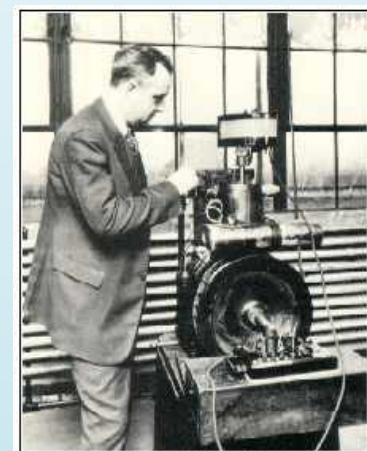


CCl_4 synthesized in
1839 by Regnault

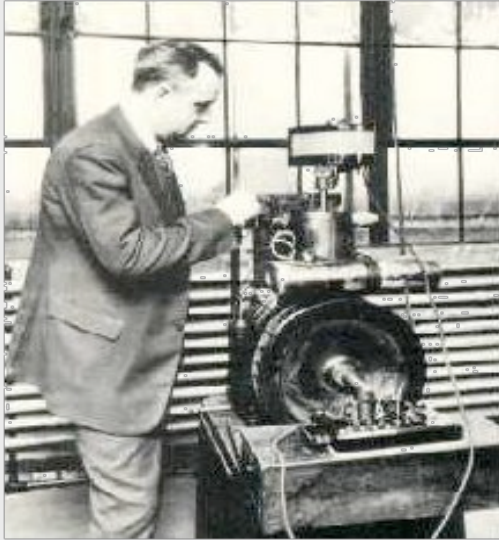


Thomas Midgley, Jr

1930: GM charged Midgley with developing a non-toxic and safe refrigerant for household appliances. He (along with Charles Kettering) synthesized dichlorodifluoromethane (CHCl_2F). CFCs replaced sulfur dioxide, methyl chloride or ammonia gases (toxic or explosive substances) previously used in heat pumps and refrigerators.



Thomas Midgley, Jr.



Thomas Midgley with the single cylinder laboratory engine used to test fuel additives.

- Came up with CFCs as a replacement for dangerous chemical in refrigerators, e.g. ammonia, sulfur dioxide
- Midgley also synthesized tetraethyl lead to reduce knocking in auto engines

The Curious Case of Thomas Midgley

Midgley became ill with polio and invented a mechanical bed to assist him: **but he died of his own invention when he became entangled in the pulleys and strangled himself !**

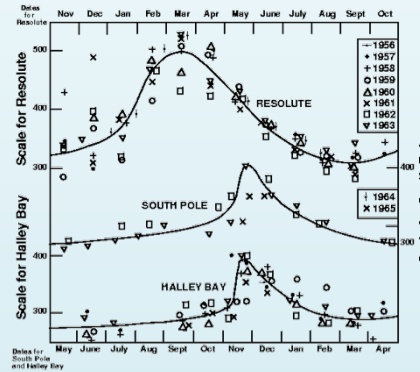
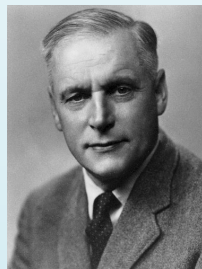
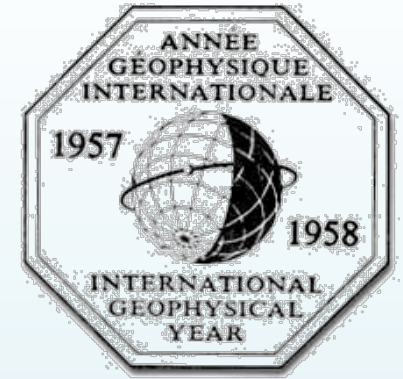


Stratospheric Meteorology, Dynamics, and Ozone



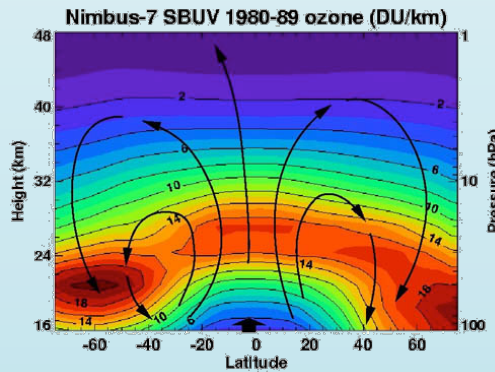
Léon Teisserenc de Bort discovers the stratosphere – a layer in which temperature no longer decreases with altitude

Unique nature of Antarctic vortex is revealed during the IGY 1957-8



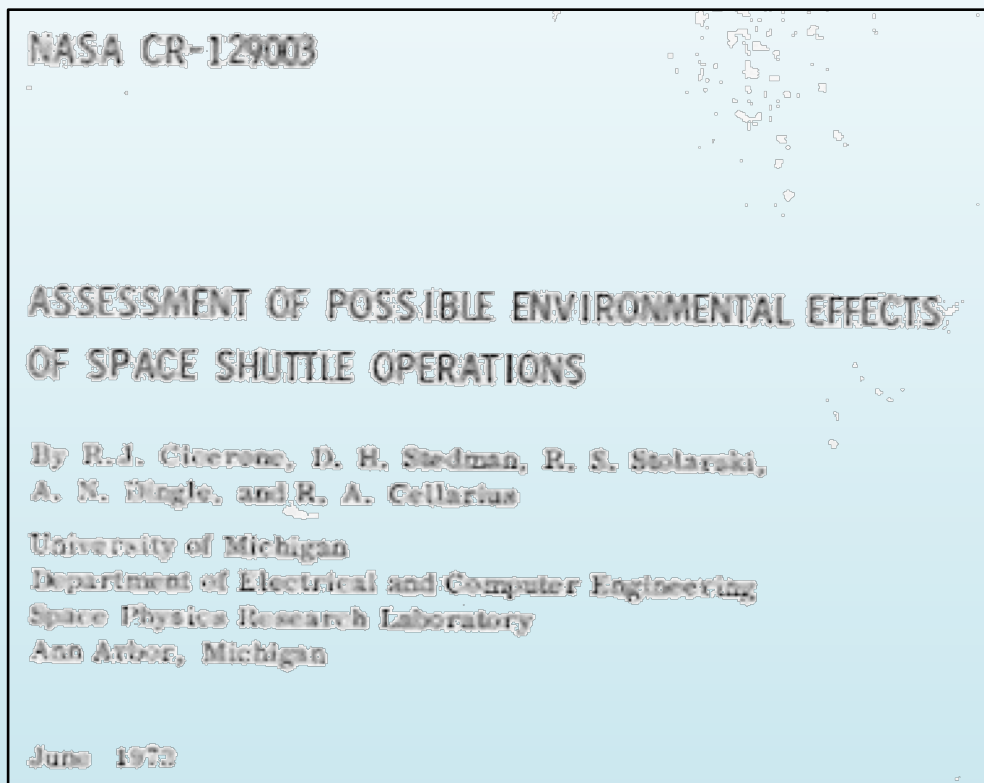
Dobson summarizes (1966) ozone measurements of IGY showing clear difference between Antarctic and Arctic

Brewer-Dobson Circulation (1951) helps explain water vapor and ozone distributions in the stratosphere

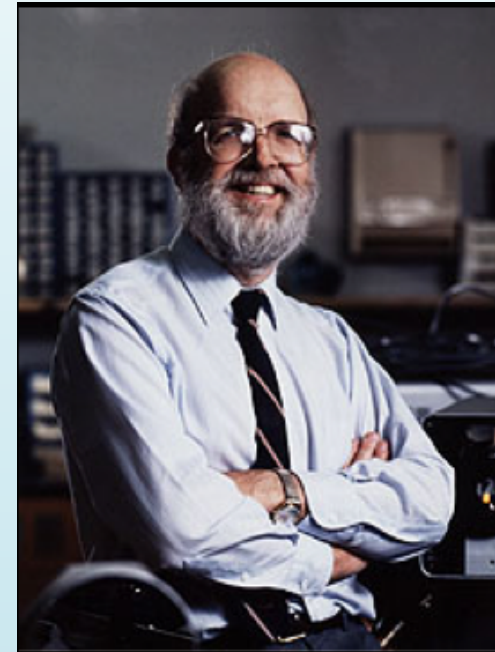


Polar Stratospheric Clouds are shown to be a ubiquitous feature of the winter Antarctic stratosphere

How did we get involved personally in chlorine chemistry in the atmosphere?



Stedman, circa 1972:
“Chlorine destroys ozone;
everybody knows that!”



How did we come to know about the importance of CFCs?

Article

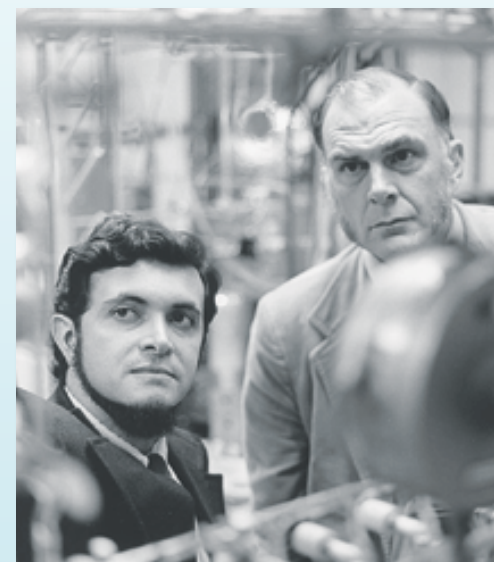
Nature **249**, 810-812 (28 June 1974) | doi:10.1038/249810a0

Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone

Mario J. Molina & F. S. Rowland

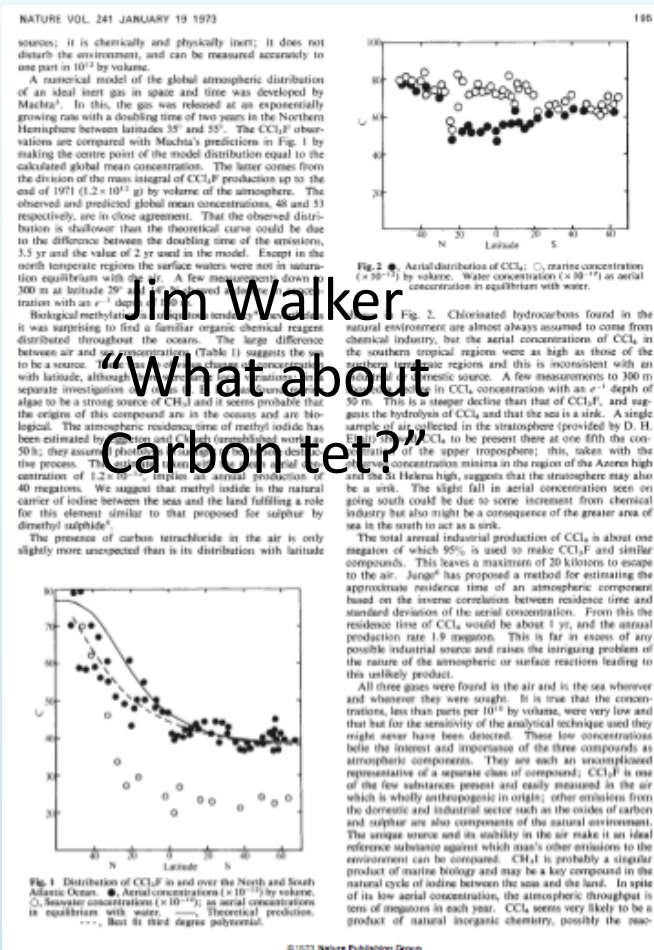
1. Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the Chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.



The information was out there for people like us to have put forward the fluorocarbon-ozone theory – but we didn't!

Lovelock et al. Nature, 1973



sources; it is chemically and physically inert; it does not disturb the environment, and can be measured accurately to one part in 10^{12} by volume.

A numerical model of the global atmospheric distribution of an ideal inert gas in space and time was developed by Machta⁷. In this, the gas was released at an exponentially growing rate with a doubling time of two years in the Northern Hemisphere between latitudes 35° and 35°. The CCl_2F_2 observations are compared with Machta's predictions in Fig. 1 by making the centre point of the model distribution equal to the calculated global mean concentration. The latter comes from the division of the mass integral of CCl_2F_2 production up to the end of 1971 (1.2×10^{12} g) by volume of the atmosphere. The observed and predicted global mean concentrations, 48 and 53 respectively, are in close agreement. That the observed distribution is shallower than the theoretical curve could be due to the difference between the doubling time of the emissions, 3.5 yr and the value of 2 yr used in the model. Except in the north temperate regions the surface waters were not in saturation equilibrium with the air. A few measurements down 300 m at latitude 29° also showed a marked disequilibrium with an e^{-1} depth.

Biological methylated hydrocarbons are abundant in the sea; it was surprising to find a familiar organic chemical reagent distributed throughout the oceans. The large difference between air and sea concentrations (Table 1) suggests the sea to be a source. The atmospheric concentration changes in step with latitude, although the sea concentration is constant. A separate investigation of the sea concentration of CCl_2 and CCl_2F_2 in the North Atlantic suggests that the sea is a source of CCl_2 and it seems probable that the origin of this compound are in the oceans and are biological. The atmospheric residence time of methyl iodide has been estimated by Johnson and Clegg (unpublished work, 1973); they assume a photochemical reaction as the sink in the stratosphere. The atmospheric residence time of CCl_2 is estimated to be 1.2 yr, which implies an aerial production of 40 megatons. We suggest that methyl iodide is the natural carrier of iodine between the sea and the land fulfilling a role for this element similar to that proposed for sulphur by dimethyl sulphide⁸.

The presence of carbon tetrachloride in the air is only slightly more unexpected than is its distribution with latitude

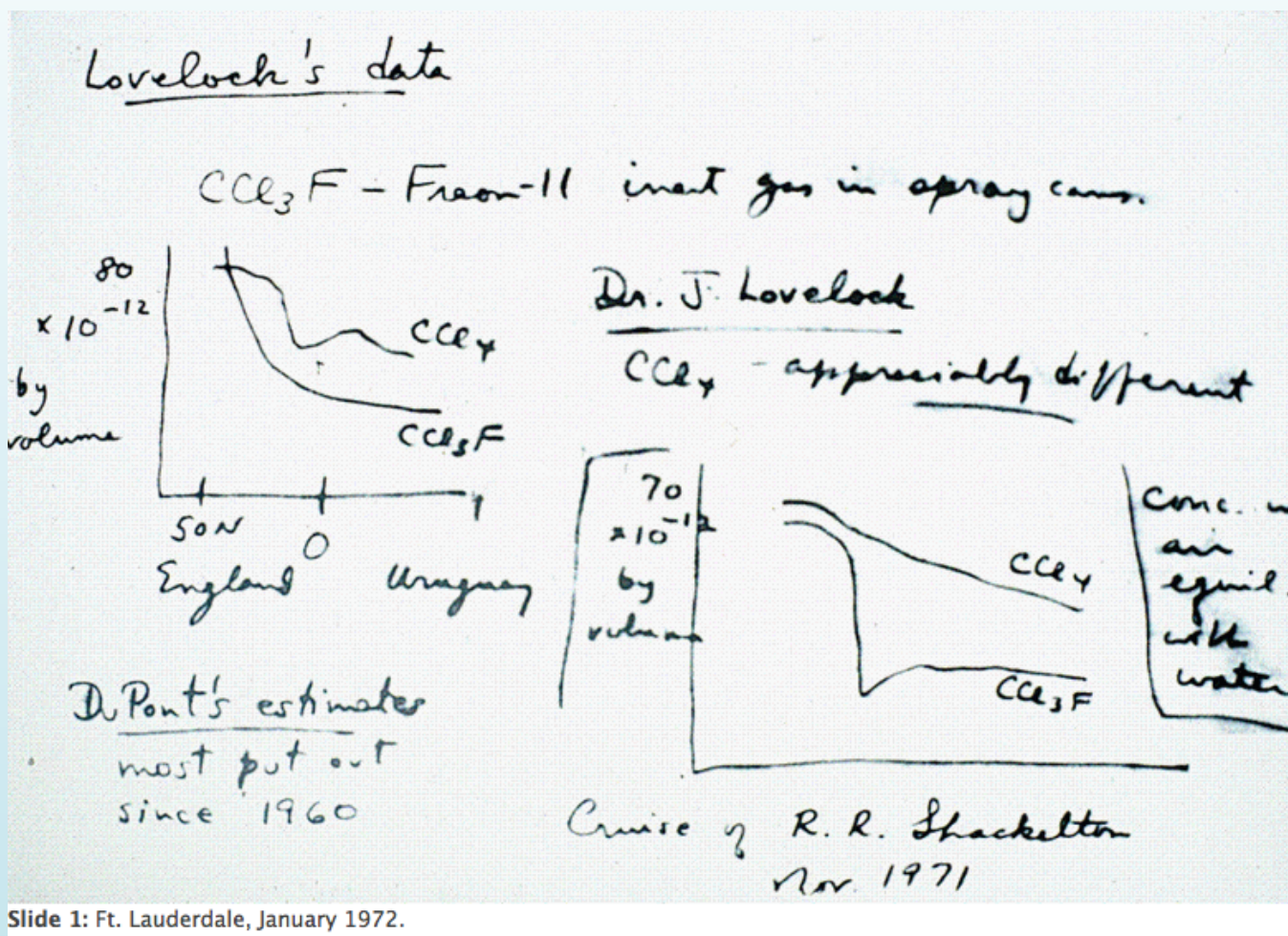
Fig. 2. Chlorinated hydrocarbons found in the natural environment are almost always assumed to come from chemical industry, but the aerial concentrations of CCl_2 in the southern tropical regions were as high as those of the northern temperate regions and this is inconsistent with an industrial source. A few measurements to 300 m depth in the North Atlantic show a marked disequilibrium in CCl_2 concentration with an e^{-1} depth of 50 m. This is a steeper decline than that of CCl_2F_2 , and suggests the hydrolysis of CCl_2 , and that the sea is a sink. A single sample of air collected in the stratosphere (provided by D. H. Bland) indicates CCl_2 to be present there at one fifth the concentration of the upper troposphere; this, taken with the low concentration minima in the region of the Azores high and the Haver high, suggests that the stratosphere may also be a sink. The slight fall in aerial concentration seen on going south could be due to some increment from chemical industry but also might be a consequence of the greater area of sea in the south to act as a sink.

The total annual industrial production of CCl_2 is about one megaton of which 95% is used to make CCl_2F_2 and similar compounds. This leaves a maximum of 20 kilotons to escape to the air. Jørgen⁹ has proposed a method for estimating the approximate residence time of an atmospheric component based on the inverse correlation between residence time and standard deviation of the aerial concentration. From this the residence time of CCl_2 would be about 1 yr, and the annual production rate 1.9 megatons. This is far in excess of any possible industrial source and raises the intriguing problem of the nature of the atmospheric or surface reactions leading to this unlikely product.

All three gases were found in the air and in the sea wherever and whenever they were sought. It is true that the concentrations, less than parts per 10^{12} by volume, were very low and that but for the sensitivity of the analytical technique used they might never have been detected. These low concentrations belie the interest and importance of the three compounds as atmospheric components. They are each an uncomplicated representative of a separate class of compound; CCl_2F_2 is one of the few substances present and easily retained in the air which is wholly anthropogenic in origin; other emissions from the domestic and industrial sector such as the oxides of carbon and sulphur are also components of the natural environment. The unique source and its solubility in the air make it an ideal reference substance against which man's other emissions to the environment can be compared. CH_4 is probably a regular product of marine biology and may be a key compound in the natural cycle of iodine between the sea and the land. In spite of its low aerial concentration, the atmospheric throughput in terms of megatons in each year, CCl_2 seems very likely to be a product of natural inorganic chemistry, possibly the reac-

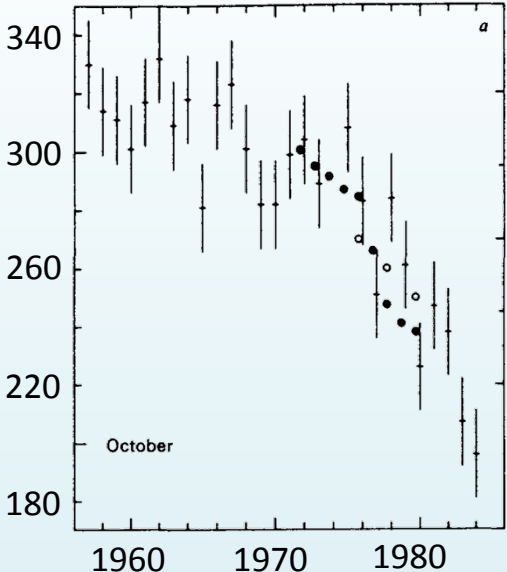
Chuck Kolb (to me), November 1973
 “Have you ever thought about Freons? They are inert in the troposphere, not soluble and don't absorb visible light. They will get up into the stratosphere where uv will produce chlorine.”

Rowland heard a talk by Lovelock – his notes below were the basis for studies by his new post-doc, Mario Molina



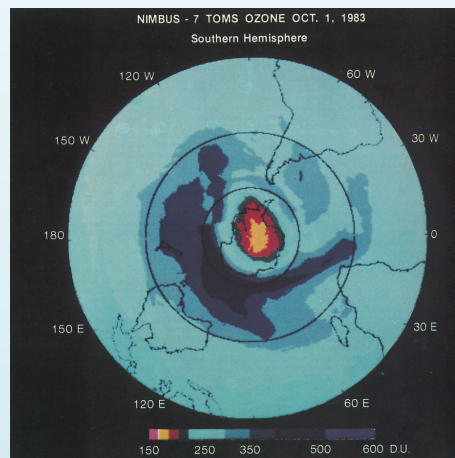
Slide 1: Ft. Lauderdale, January 1972.

Ozone Hole Discovery

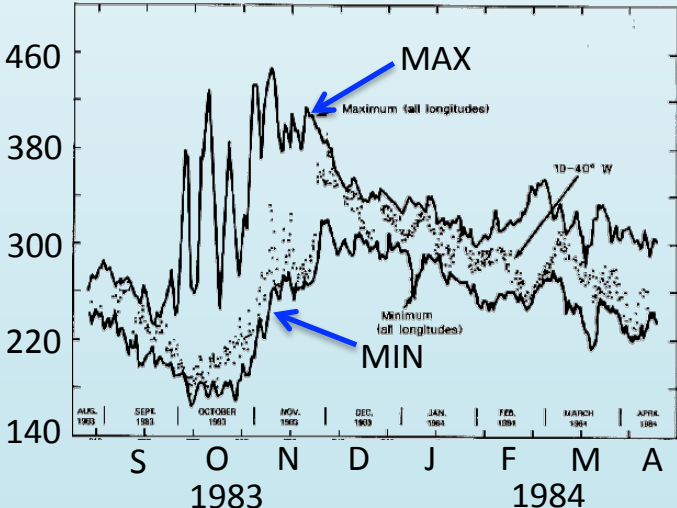


© British Antarctic Survey - www.photo.antarctica.ac.uk
Farman, Gardiner, & Shanklin (1985)

Discovered at the British Antarctic Survey station at Halley Bay from measurements begun during the IGY

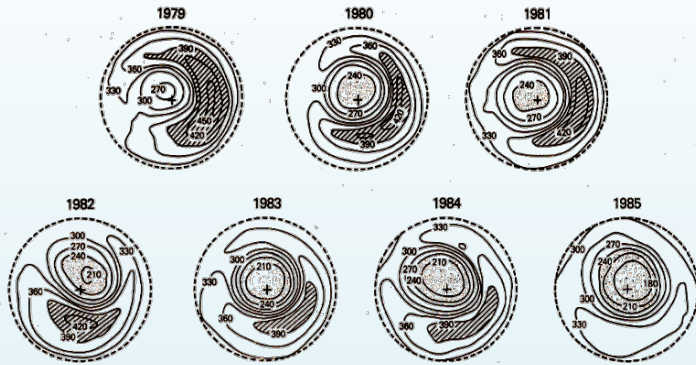


Original TOMS ozone hole map produced by Don Heath and PK Bhartia in 1985



Satellite measurements showed that Halley Bay was in best location for seeing ozone hole

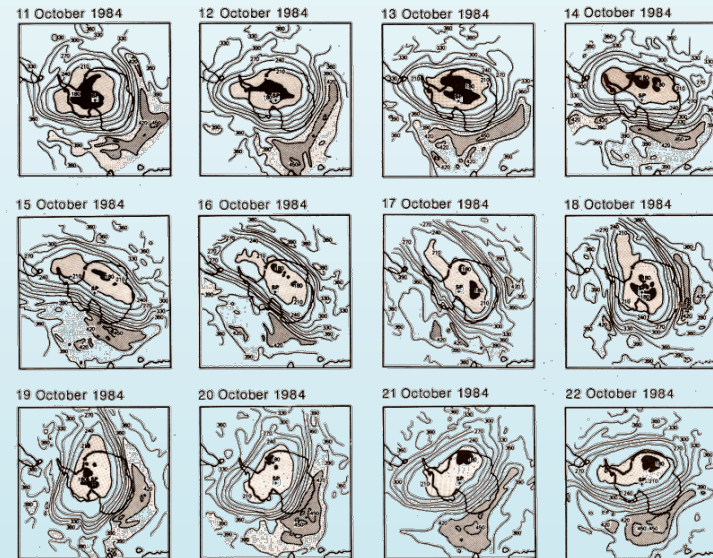
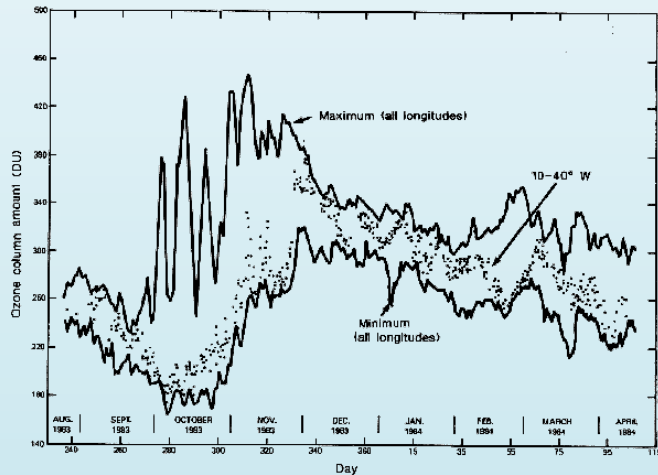
Figures from our 1986 Nature paper on the ozone hole



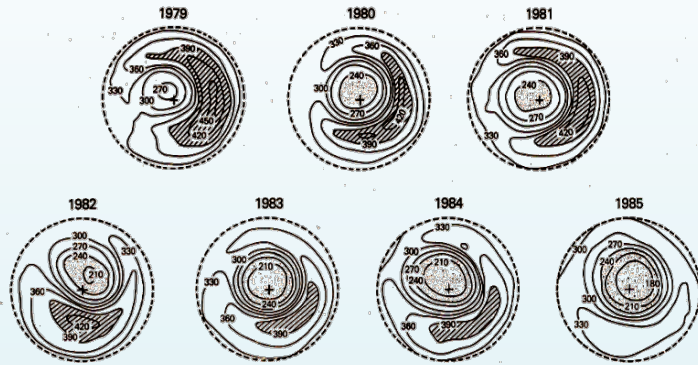
Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease

R. S. Stolarski, A. J. Krueger, M. R. Schoeberl,
R. D. McPeters, P. A. Newman & J. C. Alpert[®]

NASA/Goddard Space Flight Center, Laboratory for Atmospheres,
Greenbelt, Maryland 20771, USA



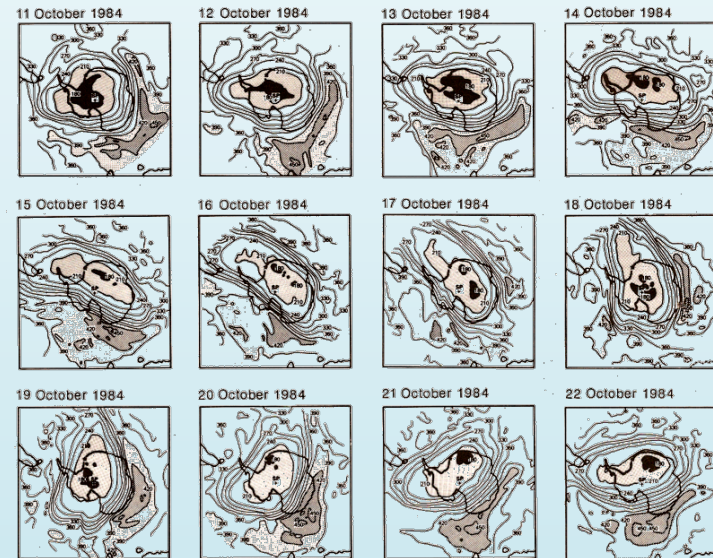
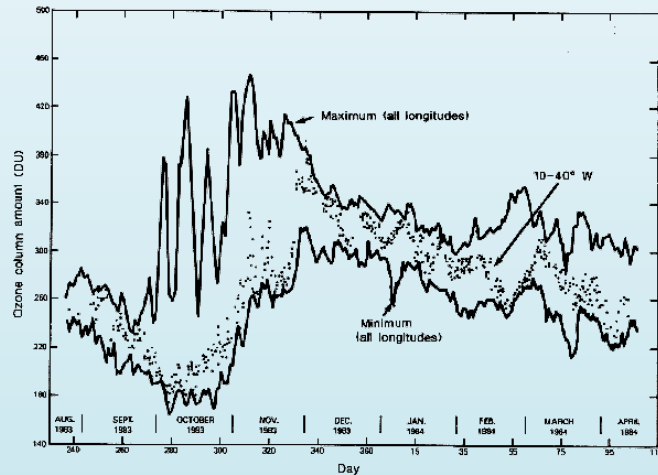
Figures from our 1986 Nature paper on the ozone hole



Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease

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Greenbelt, Maryland 20771, USA



What about the theory of the ozone hole?

Variety of Initial Theories of the Ozone Hole

- **Chlorine chemistry**
- **Dynamics – was ozone just moved around by wave motions but conserved over the entire polar region? No, there was a net decrease.**
- **Solar Cycle – NO_x chemistry variations induced by solar cycle- required N₂O change that was not observed.**
- **Other?**

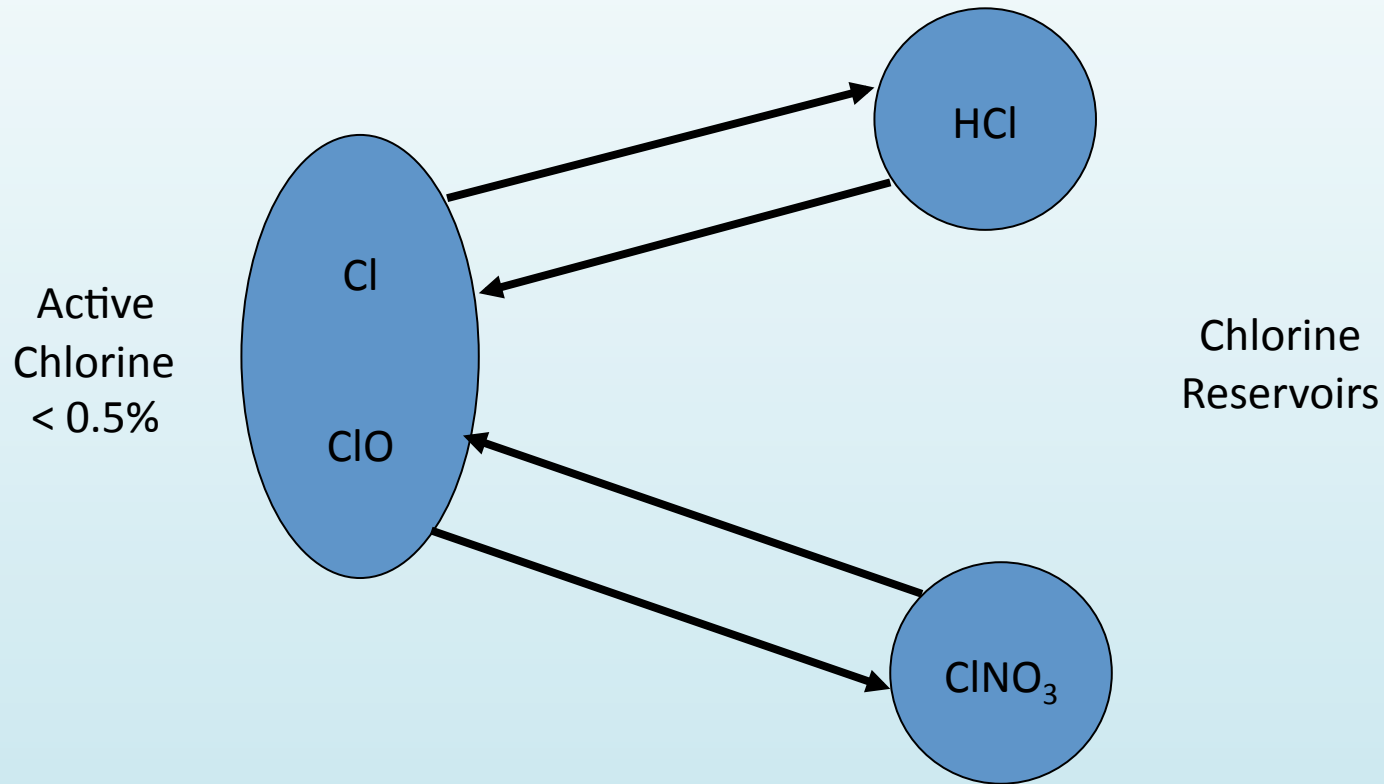
Feldafing Workshop, June 1984

The rationale for the scope of the present assessment report was based on information gained at a scientific workshop, entitled "Current Issues in Our Understanding of the Stratosphere and the Future of the Ozone Layer" which was held in Feldafing, Federal Republic of Germany in June 1984 with international participation, co-sponsored by NASA, FAA, WMO, and BMFT.

Sherry Rowland: "Missing Chemistry"

- Don't need to worry about fast channels
- What if one reservoir molecule reacted with another, e.g. ClONO_2 and HCl ?
- Molina (and Sato and Rowland independently) had been studying this reaction in the lab
- They found a small, but measureable rate coefficient
- Inserted into a model, the reaction implied that 30% of the global amount of ozone should have already disappeared
- Later reported that reaction was occurring on teflon walls of the experiment

Chlorine Photochemistry (normal)



Polar Stratospheric Clouds (PSCs)

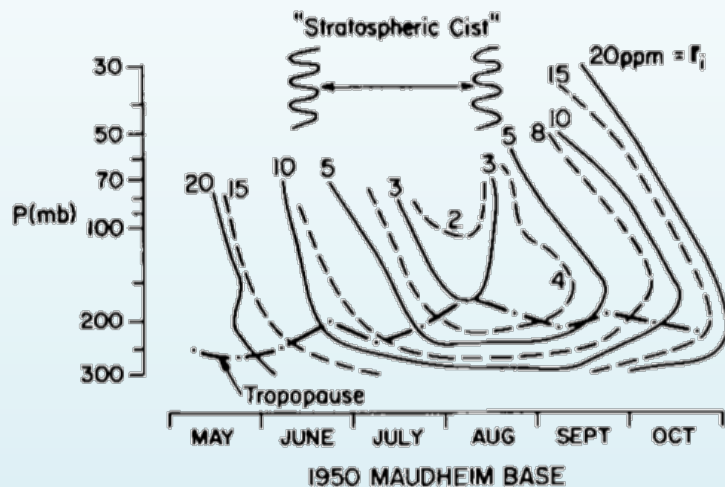


Fig. 1. Saturation mixing ratios of water vapor with respect to ice (in ppm, i.e. units of 10^{-6} g H_2O /g air) vs pressure for Maudheim base ($70^{\circ}03'S$, $10^{\circ}56'W$) during the 1950 Antarctic winter. The curves extend up to the bursting level of the balloons. The temperature data used were half-monthly means. The position of the half-monthly mean tropopause is indicated. The approximate dates over which "Stratospheric Cist" were reported are also indicated.

Tellus (1977), 29, 530–534

On the nature of persistent stratospheric clouds in the Antarctic

By JOHN L. STANFORD, *Physics Department, Iowa State University, Ames, Iowa 50011, U.S.A.*

(Manuscript received November 8, 1976; in final form January 26, 1977)

ABSTRACT

Thin, persistent very high clouds called "Stratospheric Cist" were reported at Maudheim base ($71^{\circ}03'S$, $10^{\circ}56'W$) during the 1950–51 austral winters. The nature of these clouds, whether they are H_2O or dust, is of importance in the proposed sink for stratospheric moisture in the Antarctic winter.

Results are presented from analyses of unpublished daily cloud reports and daily upper air measurements from the Maudheim expedition. The results reveal strong evidence that the "Stratospheric Cist" were stratospheric ice clouds. Given this identification, an upper limit of 6–7 ppm can be assigned to the water vapor mixing ratio in the lower stratosphere for the 1950–51 Antarctic winters.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 87, NO. C7, PAGES 5001–5008, JUNE 20, 1982

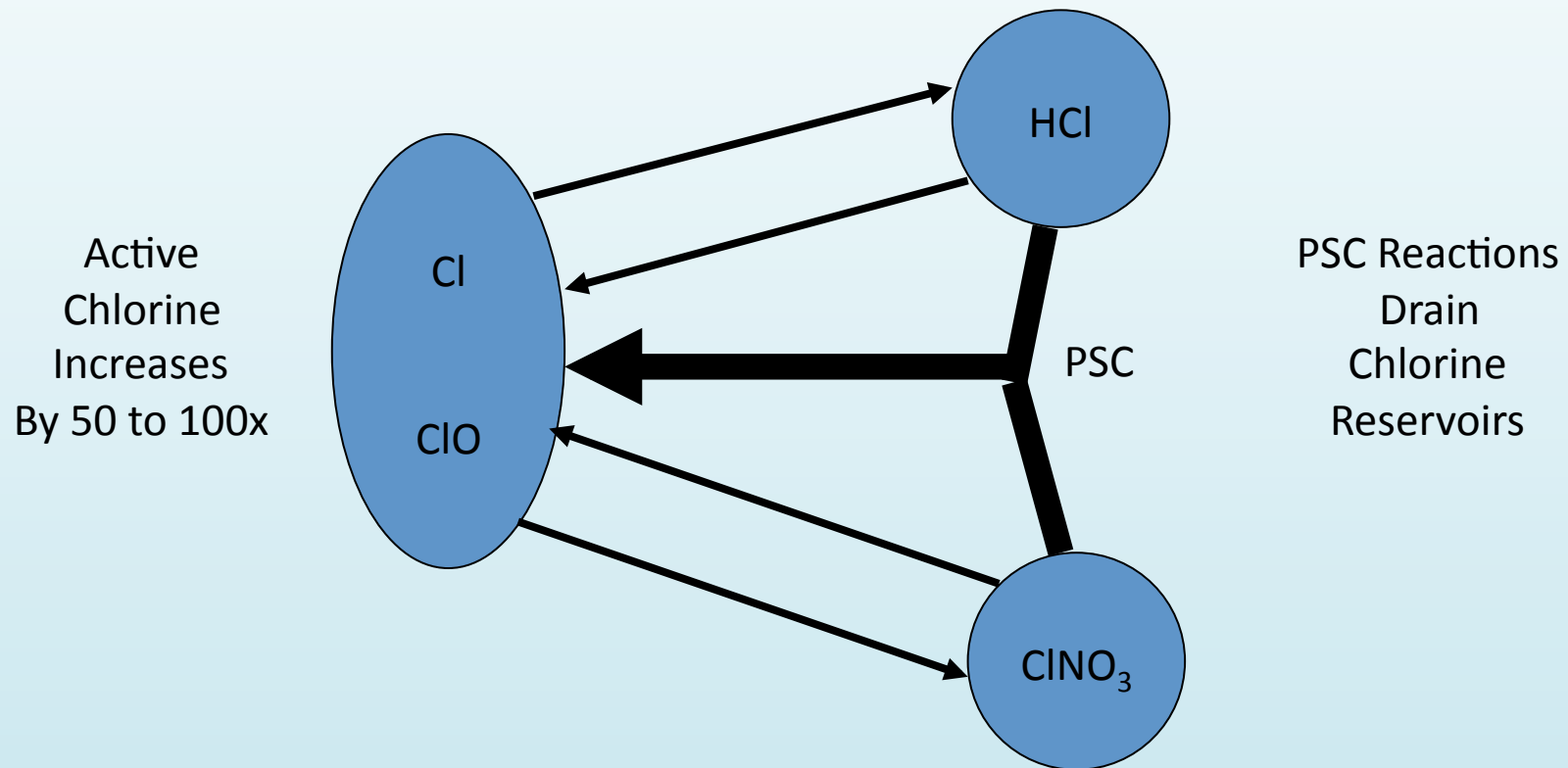
A Model of the Antarctic Sink for Stratospheric Water Vapor

ANNE R. DOUGLASS¹ AND JOHN L. STANFORD

Department of Physics, Iowa State University, Ames, Iowa 50011

Model calculations have been performed to quantitatively estimate the amount of stratospheric H_2O removed by freeze out during the winter in the Antarctic region. The model uses realistic temperature and wind fields based on Hartmann's Nimbus 5 temperature grids. For the 1973 Antarctic winter stratosphere, initial water vapor mixing ratios of 2.7 and 3.0 ppm lead to removal of 1.6 and 2.7×10^{10} kg H_2O from the lower stratosphere. This annual sink magnitude is small, representing about 2% of the total stratospheric H_2O burden and about 10% of the apparent sink identified by Ellsaesser (1974). However, a sink of this magnitude is close to the lower rate estimates of water produced in the stratosphere by methane oxidation. The sink is not large enough to balance additional, proposed water vapor sources.

Chlorine Photochemistry (polar)



This still did not make ozone go away fast enough to explain the ozone hole

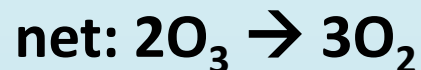
J. Phys. Chem. 1987, 91, 433–436

Production of Cl_2O_2 from the Self-Reaction of the ClO Radical

L. T. Molina and M. J. Molina*

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109
(Received: April 22, 1986; In Final Form: September 15, 1986)

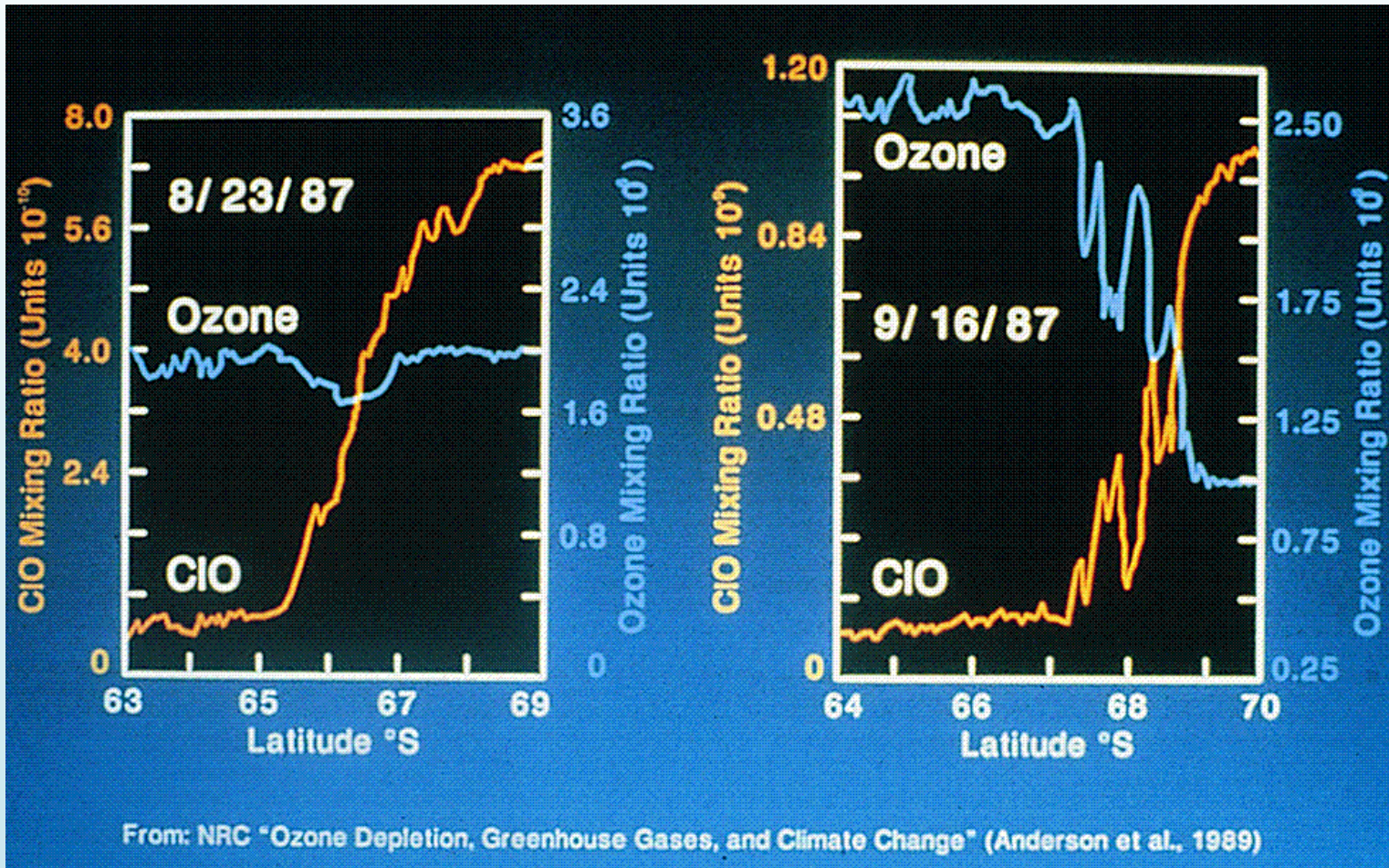
- $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ (x2)
- $\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$



without involvement of atomic oxygen

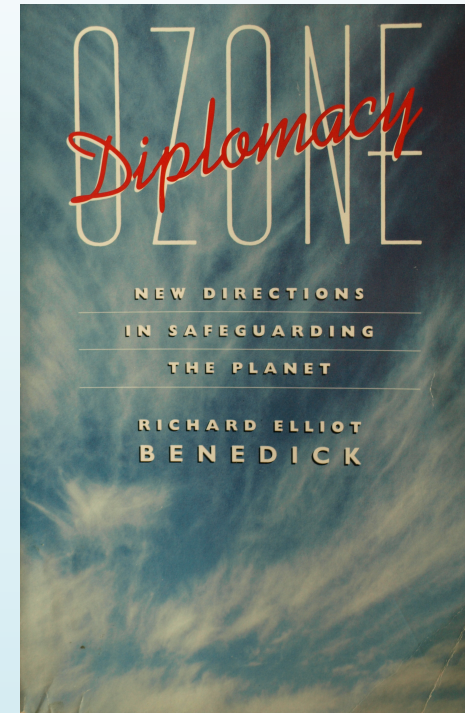
“Smoking Gun Slide”

Quickly demonstrated that the chlorine theory of the ozone hole was the correct theory



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

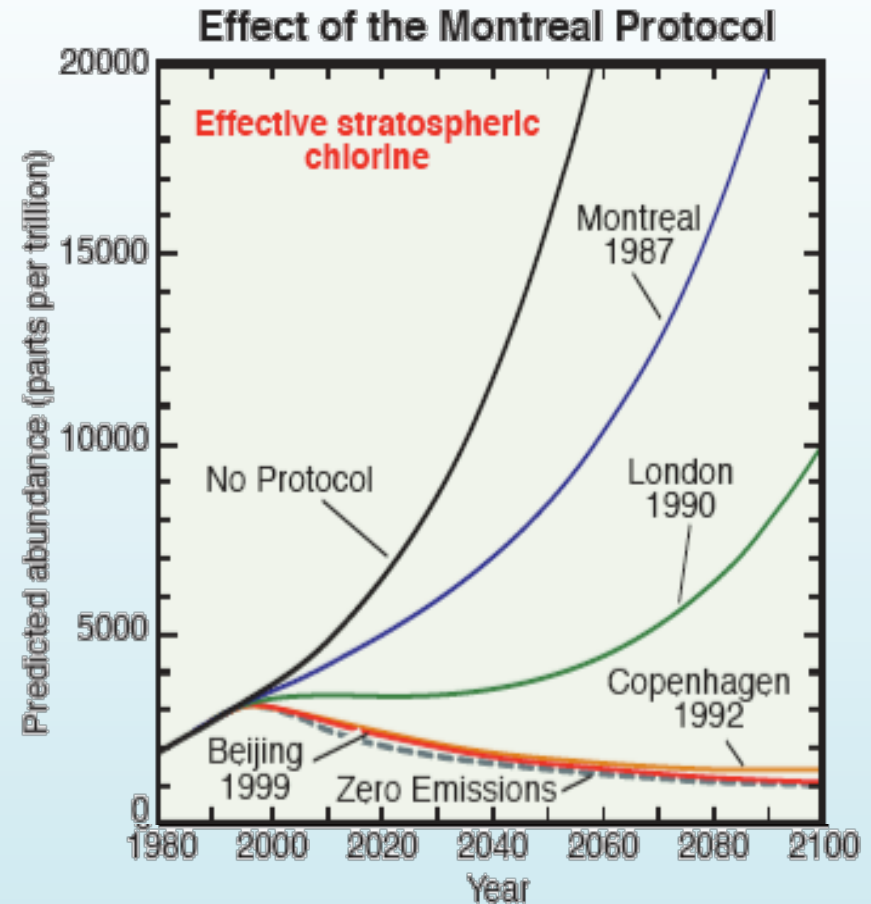
The Montreal Protocol

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

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)**

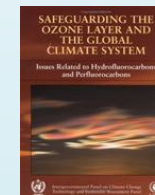


**WMO Atmospheric
Ozone - 1985**

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**



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

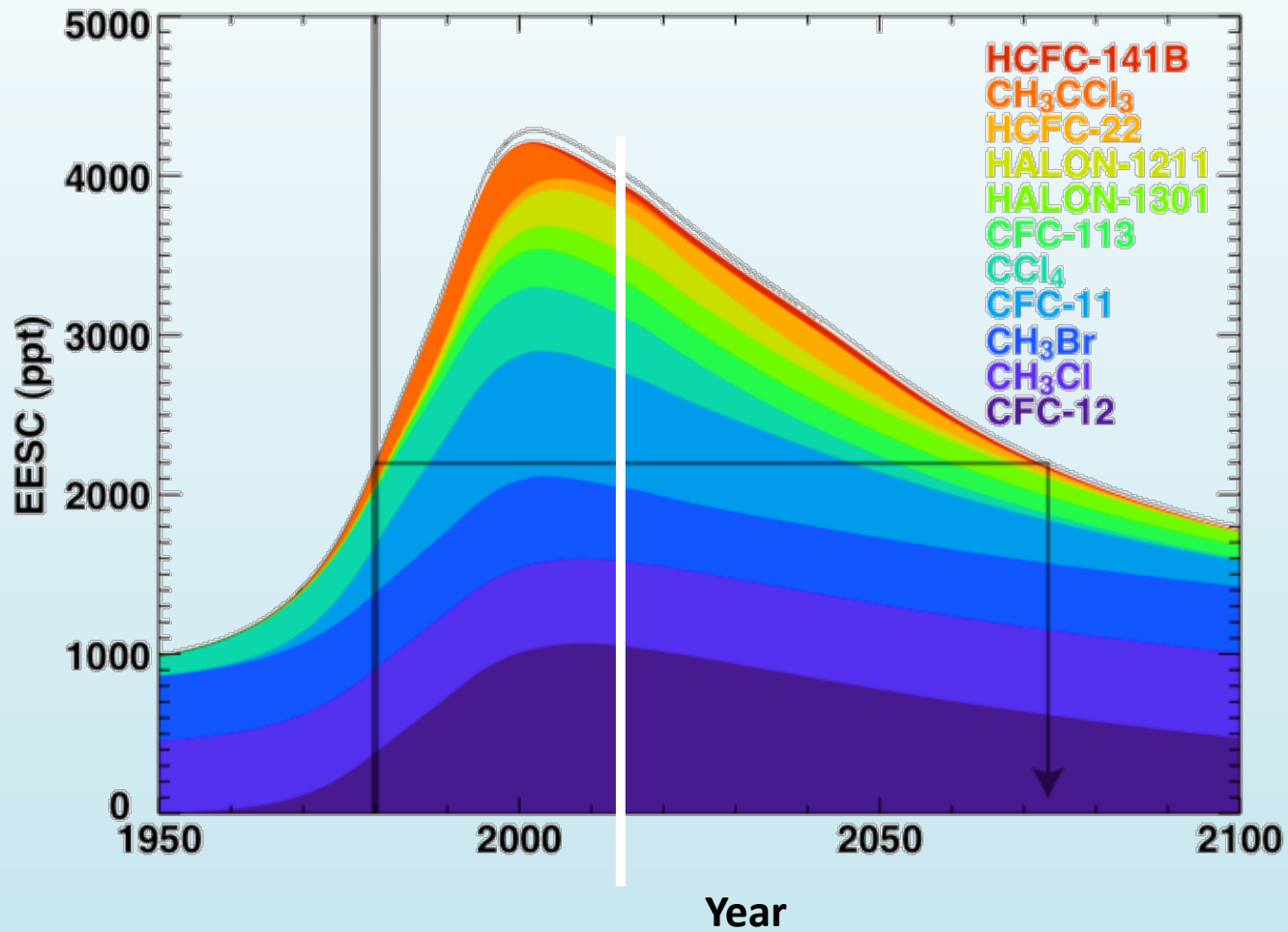
An aside on giving talks on hot issues such as the fluorocarbon-ozone issue was at one time

- **You are an expert on science: separate your science from any opinions on what should be done by society.**
- **There are no dumb questions: Even if you have heard a question a thousand times, respect the questioner.**
- **Be prepared: you know the standard questions so you should have a prepared approach to these.**
- **If you don't know the answer, say so.**

Comments on the Future of Stratospheric Ozone

- Chlorine is being removed from the atmosphere as the Montreal Protocol limits CFC and HCFC production
- Ozone should recover, but not to the same levels because of the changes in greenhouse gases that also impact ozone
- Future amounts of ozone will be controlled by nitrous oxide (N_2O) and carbon dioxide (CO_2)

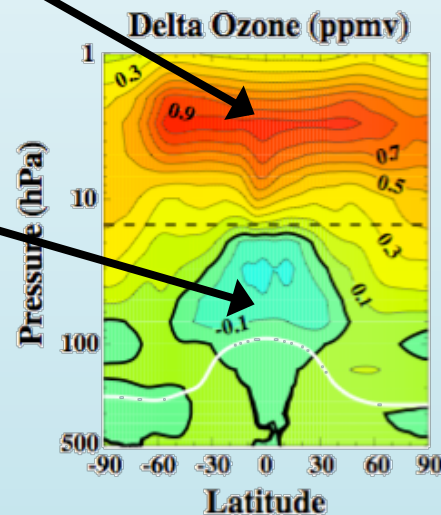
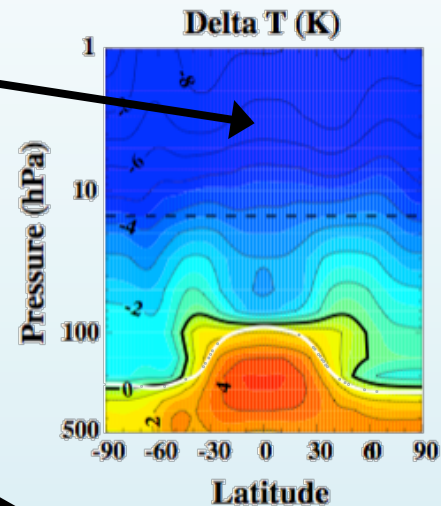
We put these together into an “Equivalent Effective Stratospheric Chlorine” or EESC



The Post-CFC Ozone Layer

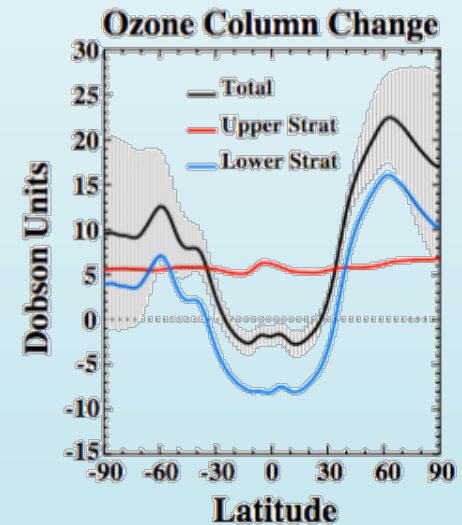
What will the stratospheric ozone layer look like after CFCs have been removed?

- Greenhouse gases cool the stratosphere
- Cooling slows ozone loss in upper stratosphere leading to ozone increase
- Lower stratospheric circulation speeds up leading to tropical ozone decrease and mid-latitude ozone increase



Results from the GEOS CCM
2065-1980

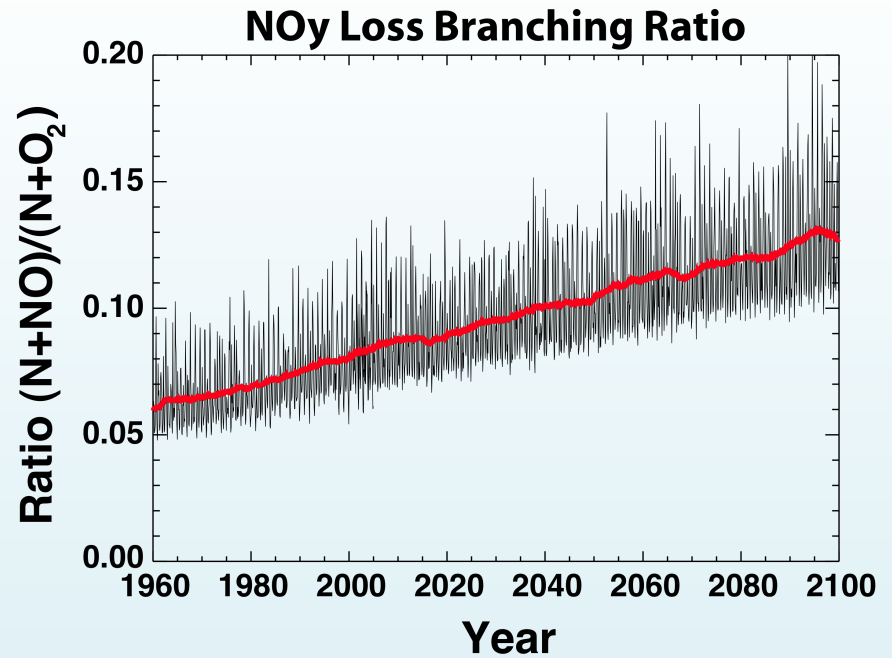
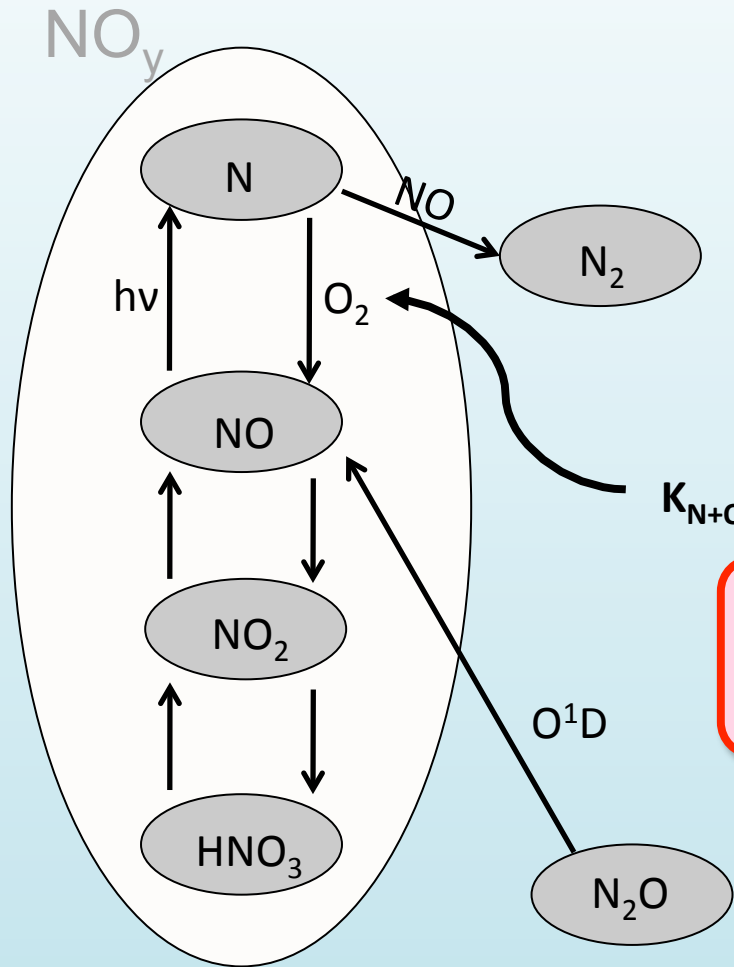
Net result is a column ozone increase at mid to high latitudes and almost no change near the equator



What about N₂O?

- **N₂O is the source of NO_y that can catalytically destroy ozone**
- **Several papers have claimed that increasing N₂O is an existential threat to the ozone layer**
- **The situation is a bit more complex**

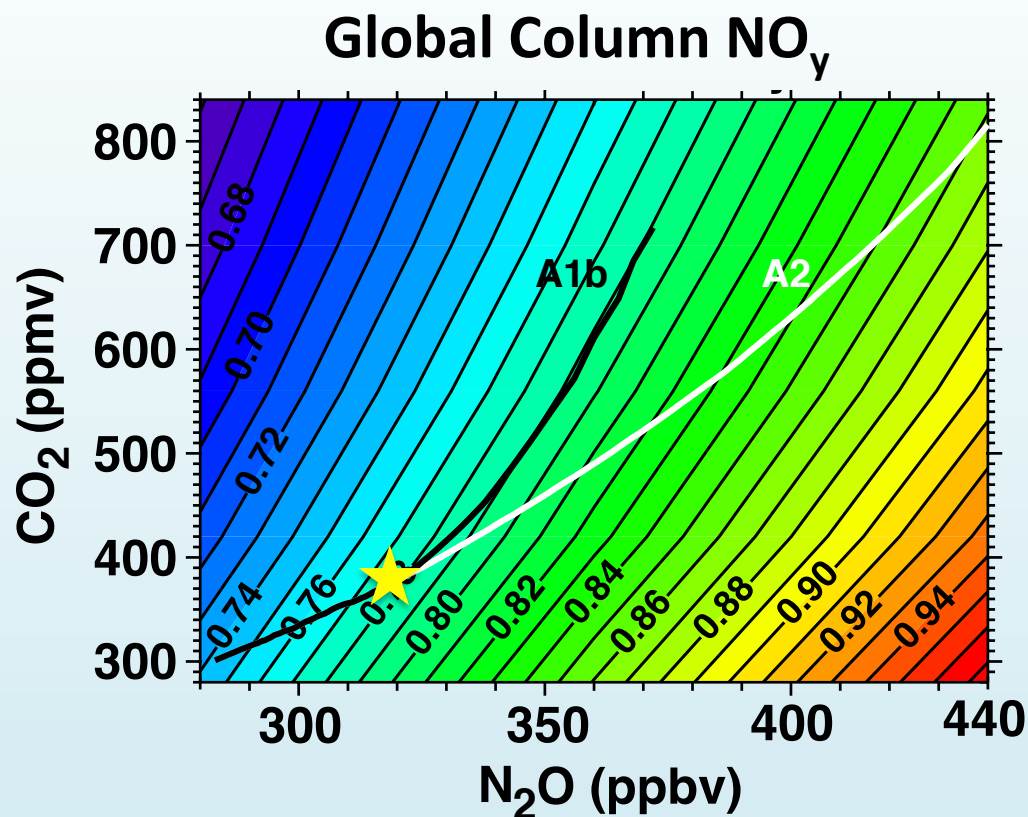
N atoms, formed by photolysis of NO, can either reform NO or can react with NO to remove NO_y



$$K_{N+O_2} = 1.5 \times 10^{-11} \text{ EXP}(-3600/T)$$

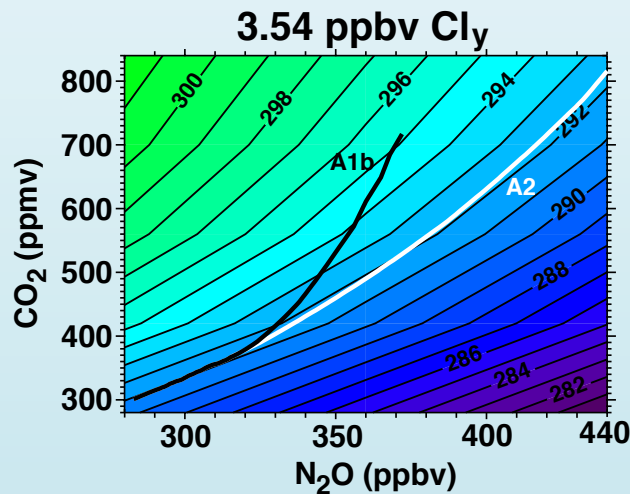
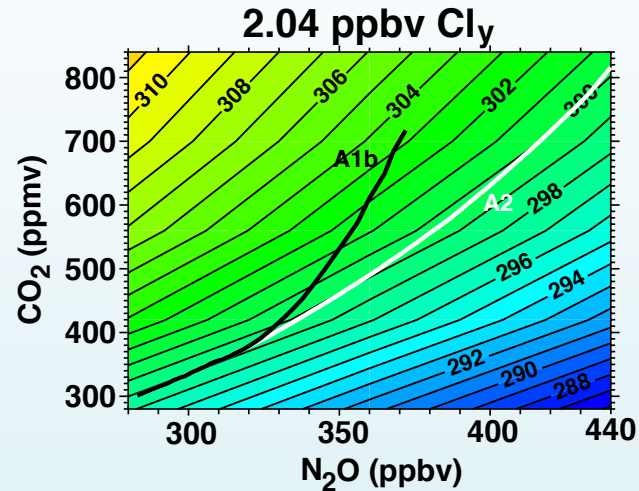
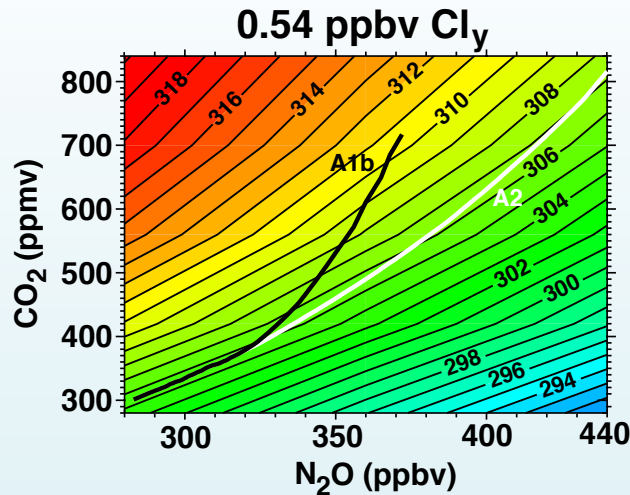
The branching ratio is strongly temperature dependent: low temperatures → more NO_y loss

The evolution of stratospheric NO_y



- Depends on the relative change of N_2O and CO_2 in the future
- A1b scenario leads to constant future NO_y
- A2 scenario leads to increasing NO_y

Ozone Scenarios



- Chlorine dominates ozone change
- Amount of global “super-recovery” depends on relative scenario for N₂O and CO₂ change

Final thoughts

- **Details are important, but if you don't try to step back and see the big picture you can waste a lot of time on the wrong details**
- **Opportunities abound: will you recognize them? Will you follow up on them? Or will you just let them pass by?**
- **Ideas are cheap – Selection of good ones and follow through on them is what counts.**