Mid-Latitude Stratospheric Chemistry

AOSC/CHEM 433 & AOSC/CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919

Today:

- **Background on CFCs**
- **Ozone Depletion Potenial**
- **Importance of how a chemical cycle is completed wrt odd-oxygen loss**
- **Role of halogens and aerosol loading on mid-latitude ozone**
- **Connection to recent research**

Lecture 15

3 November 2020

Announcements

- Problem Set #3 has been posted:

  https://www2.atmos.umd.edu/~rjs/class/fall2020/problem_sets/ACC_2020_problem_set_03.pdf

  and is due a week from today. Please get started early.

- Due to "popular demand", this problem set will be completed outside of ELMS: prefer you mail me and Laura McBride either one PDF file (entire P Set) or two PDF files (one per question) when the problem set is complete, with an email subject such as:

  AOSC 433: Problem Set 3 *or* CHEM 633: Problem Set 3 , etc

- No AT for Lecture 17 a week from today. However, please try to complete the short reading.

Wavelength Bin (nm)	Actinic Flux (10^{14} photons cm^{-2} sec^{-1}) for SZA = 30 degs	Absorption Cross Sections (cm^2/molecule)			
	15 km	CF_2BrCl	CH_3Br	$CHBr_3$	CH_2Br_2
202-205	0.00	1.16E-18	7.84E-19	4.38E-18	2.17E-18
205-210	0.00	1.17E-18	7.13E-19	4.52E-18	2.25E-18
210-215	0.00	1.07E-18	5.87E-19	5.01E-18	2.49E-18
215-220	0.00	8.69E-19	4.34E-19	5.67E-18	2.68E-18
220-225	0.00	6.68E-19	3.04E-19	5.71E-18	2.60E-18
225-230	0.00	4.72E-19	1.91E-19	4.94E-18	2.22E-18
230-235	0.00	3.29E-19	1.15E-19	3.92E-18	1.67E-18
235-240	0.00	2.13E-19	6.11E-20	3.02E-18	1.14E-18
240-245	0.00	1.35E-19	3.12E-20	2.49E-18	7.03E-19
245-250	0.00	7.91E-20	1.43E-20	1.98E-18	4.00E-19
250-255	0.00	4.61E-20	6.51E-21	1.52E-18	2.11E-19
255-260	0.00	2.44E-20	2.64E-21	1.03E-18	1.04E-19
260-265	0.00	1.31E-20	1.10E-21	6.69E-19	4.82E-19
265-270	0.00	6.40E-20	4.12E-22	4.00E-19	2.19E-20
270-275	0.00	3.24E-20	1.64E-22	2.40E-19	9.69E-20
275-280	0.00	1.47E-21	6.21E-23	1.33E-19	4.23E-21
280-285	0.00	6.99E-22	2.46E-23	7.52E-20	1.85E-21
285-290	0.00	3.08E-22	7.00E-24	3.99E-20	8.20E-22
290-292	0.00	1.76E-22	0.00E+00	2.54E-20	4.99E-22
292-294	0.00	1.27E-22	0.00E+00	1.94E-20	2.82E-22
294-296	0.01	9.12E-23	0.00E+00	1.49E-20	2.10E-22
296-298	0.03	6.54E-23	0.00E+00	1.12E-20	1.80E-22
298-300	0.08	4.68E-23	0.00E+00	8.38E-21	9.20E-23
300-302	0.17	3.35E-23	0.00E+00	6.26E-21	9.20E-23
302-304	0.39	2.43E-23	0.00E+00	4.66E-21	9.20E-23
304-306	0.67	1.84E-23	0.00E+00	3.47E-21	9.20E-23
306-308	0.99	1.37E-23	0.00E+00	2.60E-21	9.20E-23
308-310	1.27	9.67E-24	0.00E+00	1.93E-21	9.20E-23
310-312	1.87	6.86E-24	0.00E+00	1.46E-21	9.20E-23
312-314	2.26	4.86E-24	0.00E+00	1.11E-21	9.20E-23
314-316	2.52	3.46E-24	0.00E+00	8.32E-22	4.55E-23
316-318	3.05	2.51E-24	0.00E+00	6.21E-22	4.55E-23
318-320	3.09	1.86E-24	0.00E+00	4.59E-22	1.00E-24
320-325	9.47	0.00E+00	0.00E+00	2.80E-22	1.00E-24
325-330	13.45	0.00E+00	0.00E+00	1.32E-22	0.00E+00
330-335	14.04	0.00E+00	0.00E+00	6.69E-23	0.00E+00
335-340	13.25	0.00E+00	0.00E+00	3.29E-23	0.00E+00
340-345	14.01	0.00E+00	0.00E+00	1.72E-23	0.00E+00
345-350	13.79	0.00E+00	0.00E+00	8.56E-24	0.00E+00
350-355	15.47	0.00E+00	0.00E+00	5.28E-24	0.00E+00
355-360	13.58	0.00E+00	0.00E+00	2.58E-24	0.00E+00

Please review Lecture 10 for proper use of these numbers to find a photolysis frequency (i.e. J value) for these four compounds.
Please pay attention to units!
https://www2.atmos.umd.edu/~rjs/class/fall2020/problem_sets/TableA_pset03.xls &
https://www2.atmos.umd.edu/~rjs/class/fall2020/problem_sets/TableB_pset03.xls

1.8.1 Table 1C: NO_x Reactions

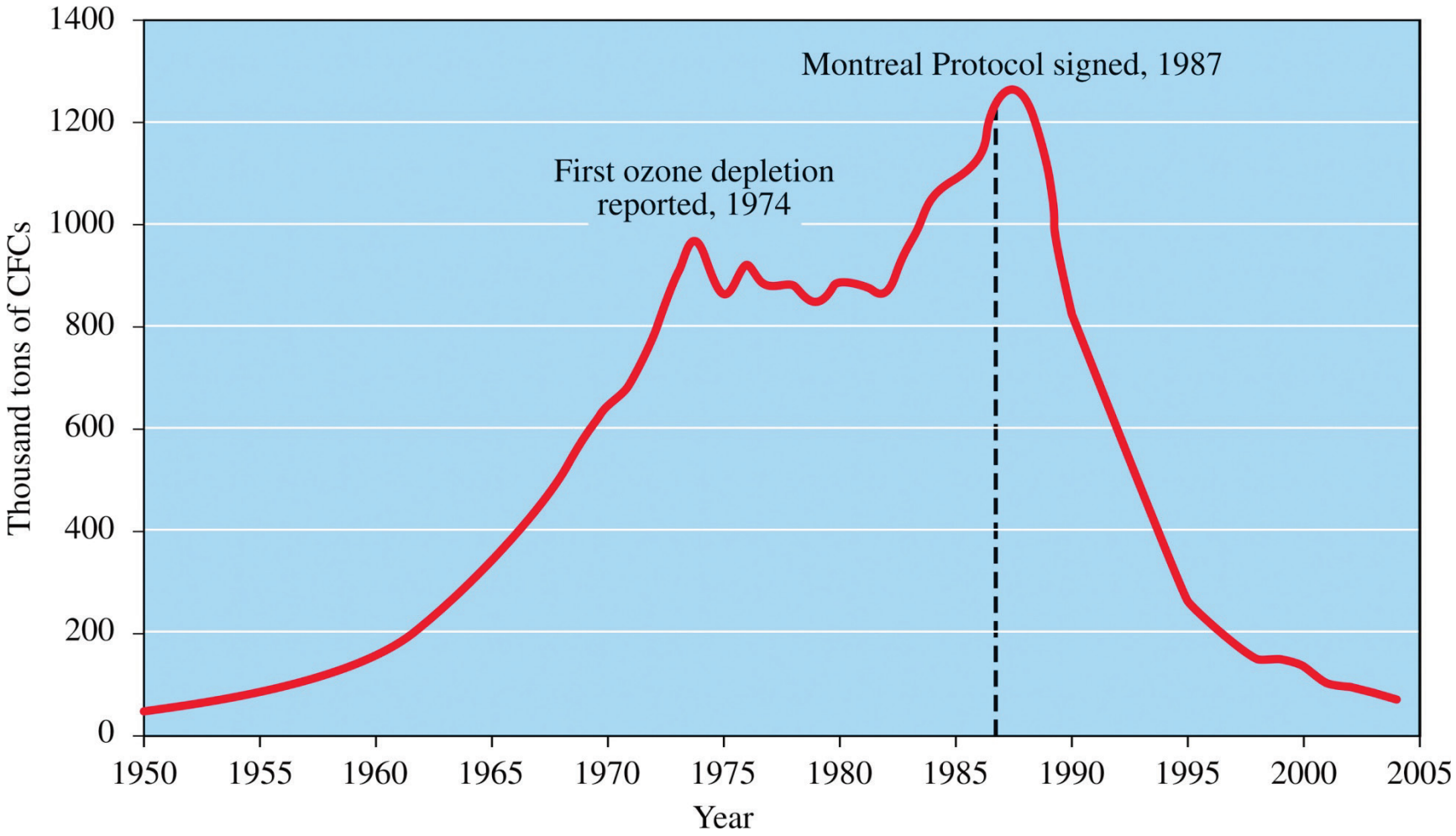
Reaction	Temperature Range of Exp. Data (K) [a]	A-Factor	E/R	k(298 K)[b]	f(298 K)[c]	g	Note
$O + NO \xrightarrow{M} NO_2$		(See Table 2-1)					
$O + NO_2 \rightarrow NO + O_2$	199–2300	5.1×10^{-12}	-210	1.04×10^{-11}	1.1	20	C 1
$O + NO_2 \xrightarrow{M} NO_3$		(See Table 2-1)					
$O + NO_3 \rightarrow O_2 + NO_2$	298–329	1.0×10^{-11}	0	1.0×10^{-11}	1.5	150	C 2
$O + N_2O_5 \rightarrow$ products	223–300			$<3.0\times10^{-16}$			C 3
$O + HNO_3 \rightarrow OH + NO_3$	298			$<3.0\times10^{-17}$			C 4
$O + HO_2NO_2 \rightarrow$ products	228–297	7.8×10^{-11}	3400	8.6×10^{-16}	3.0	750	C 5
$H + NO_2 \rightarrow OH + NO$	195–2000	4.0×10^{-10}	340	1.3×10^{-10}	1.3	300	C 6
$OH + NO \xrightarrow{M} HONO$		(See Table 2-1)					
$OH + NO_2 \xrightarrow{M} HNO_3$		(See Table 2-1)					
$OH + NO_3 \rightarrow$ products	298			2.2×10^{-11}	1.5		C 7
$OH + HONO \rightarrow H_2O + NO_2$	278–1400	1.8×10^{-11}	390	4.5×10^{-12}	1.5	+200 –500	C 8
$OH + HNO_3 \rightarrow H_2O + NO_3$	218–1100	(See Note)			1.2		C 9
$OH + HO_2NO_2 \rightarrow$ products	218–335	1.3×10^{-12}	–380	4.6×10^{-12}	1.3	+270 –500	C10
$OH + NH_3 \rightarrow H_2O + NH_2$	228–2360	1.7×10^{-12}	710	1.6×10^{-13}	1.2	200	C11
$HO_2 + NO \rightarrow NO_2 + OH$	183–1270	3.3×10^{-12}	–270	8.0×10^{-12}	1.15	20	C12

Please review Lecture 11 for proper use of these numbers to find a rate constant: i.e., $k(T) = A\times\exp(-E/RT)$

Please pay attention to units!

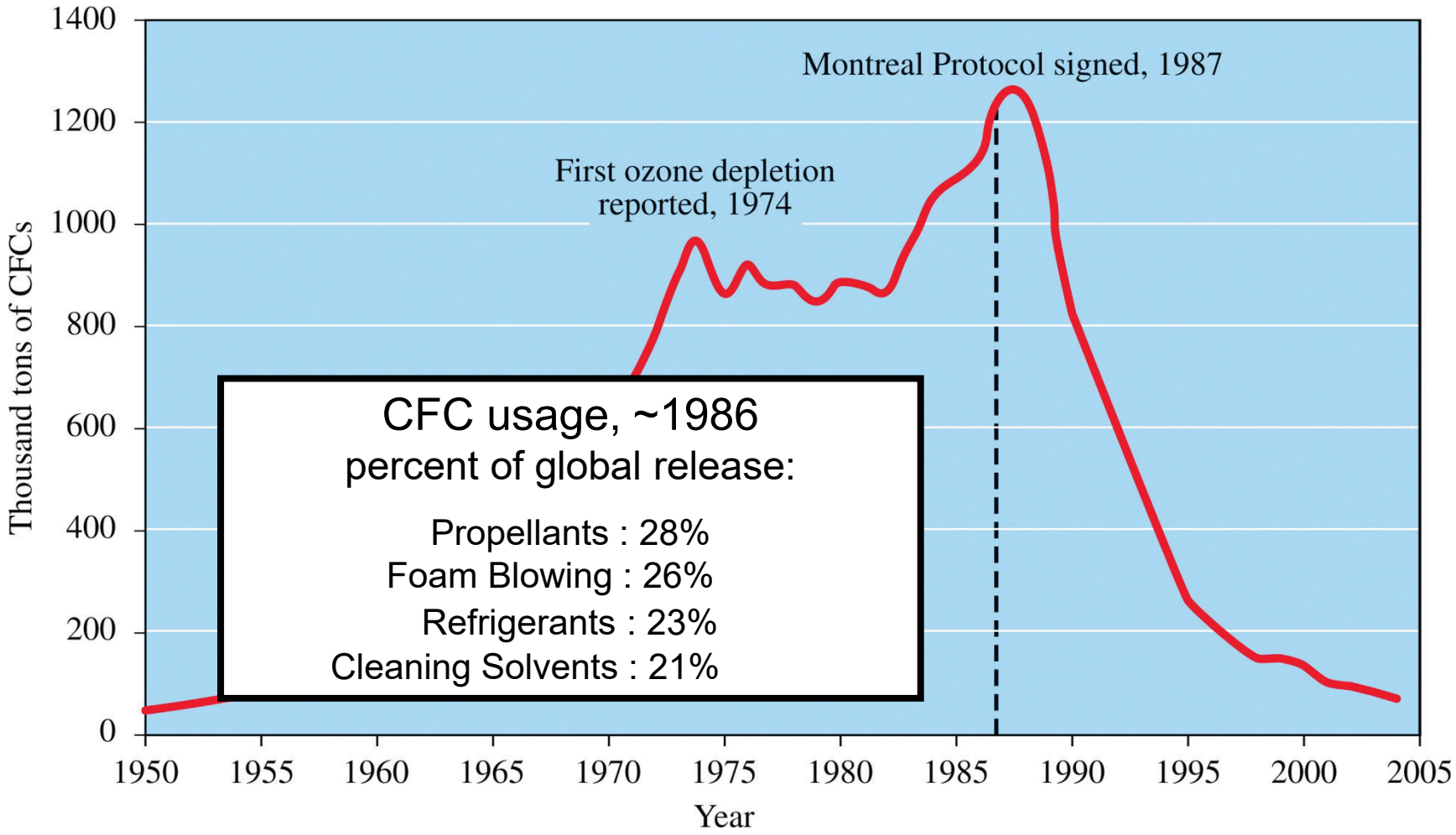
https://www2.atmos.umd.edu/~rjs/class/fall2020/problem_sets/JPL2015_Bimolecular_Rates_pset03.pdf

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons



Global Production of CFCs, Fig. 2.19, Chemistry in Context

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons



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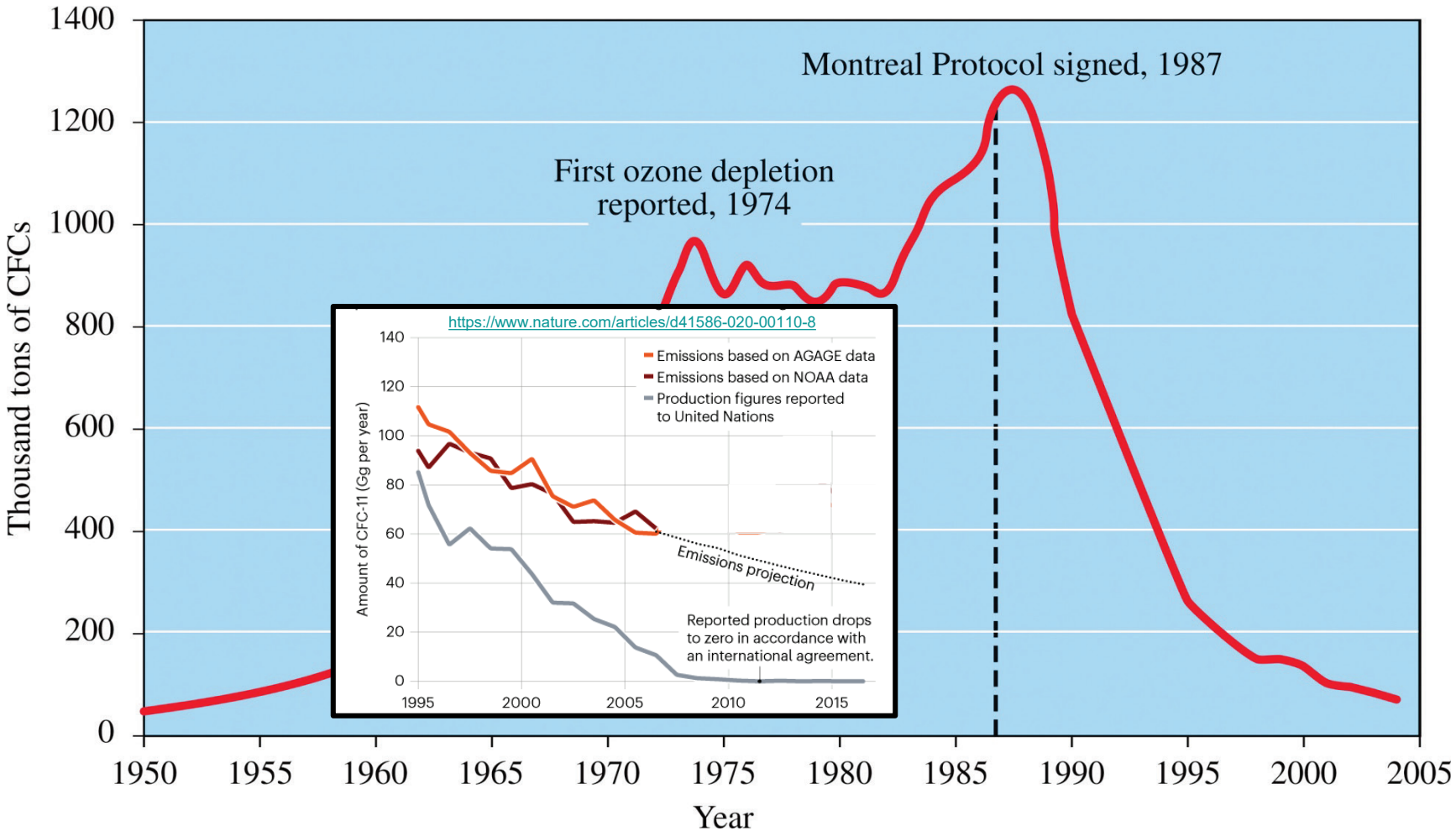
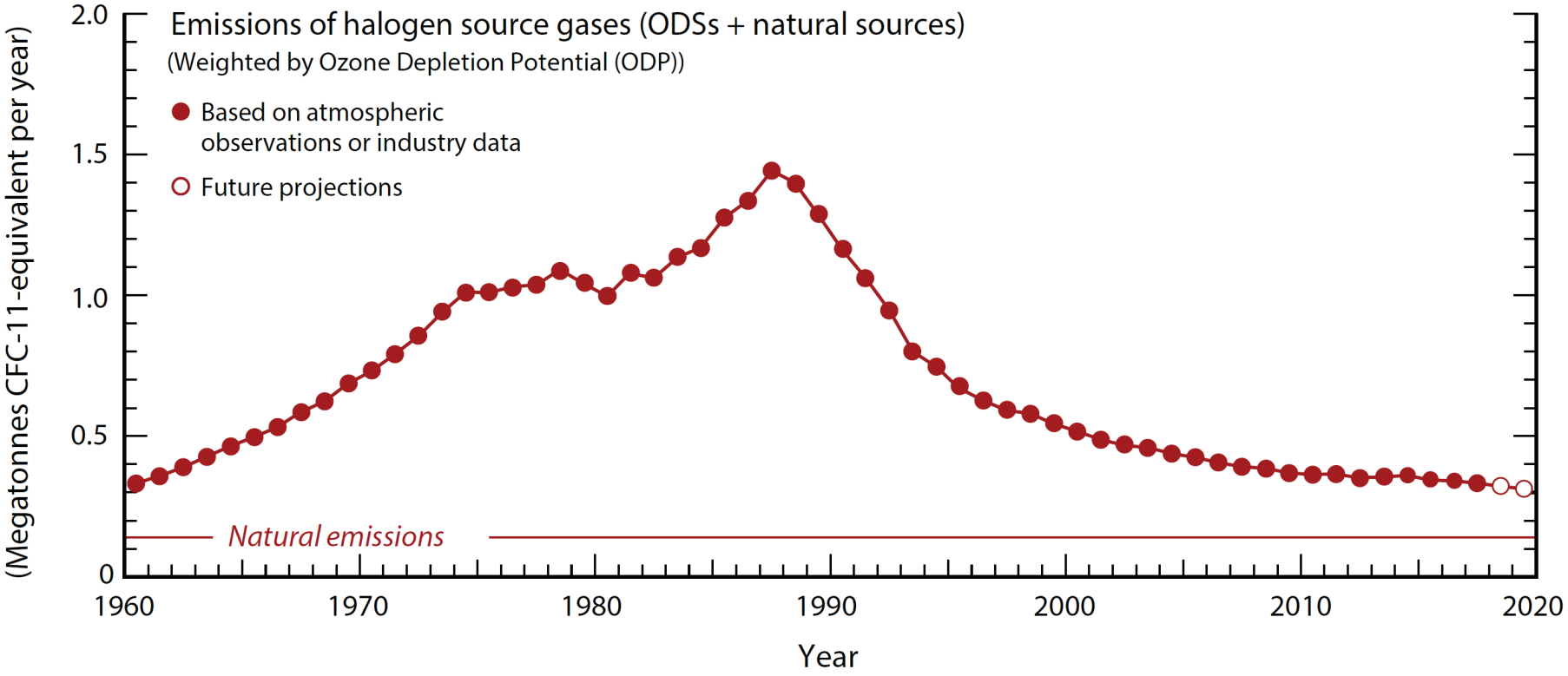


Global Production of CFCs, Fig. 2.19, Chemistry in Context

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons

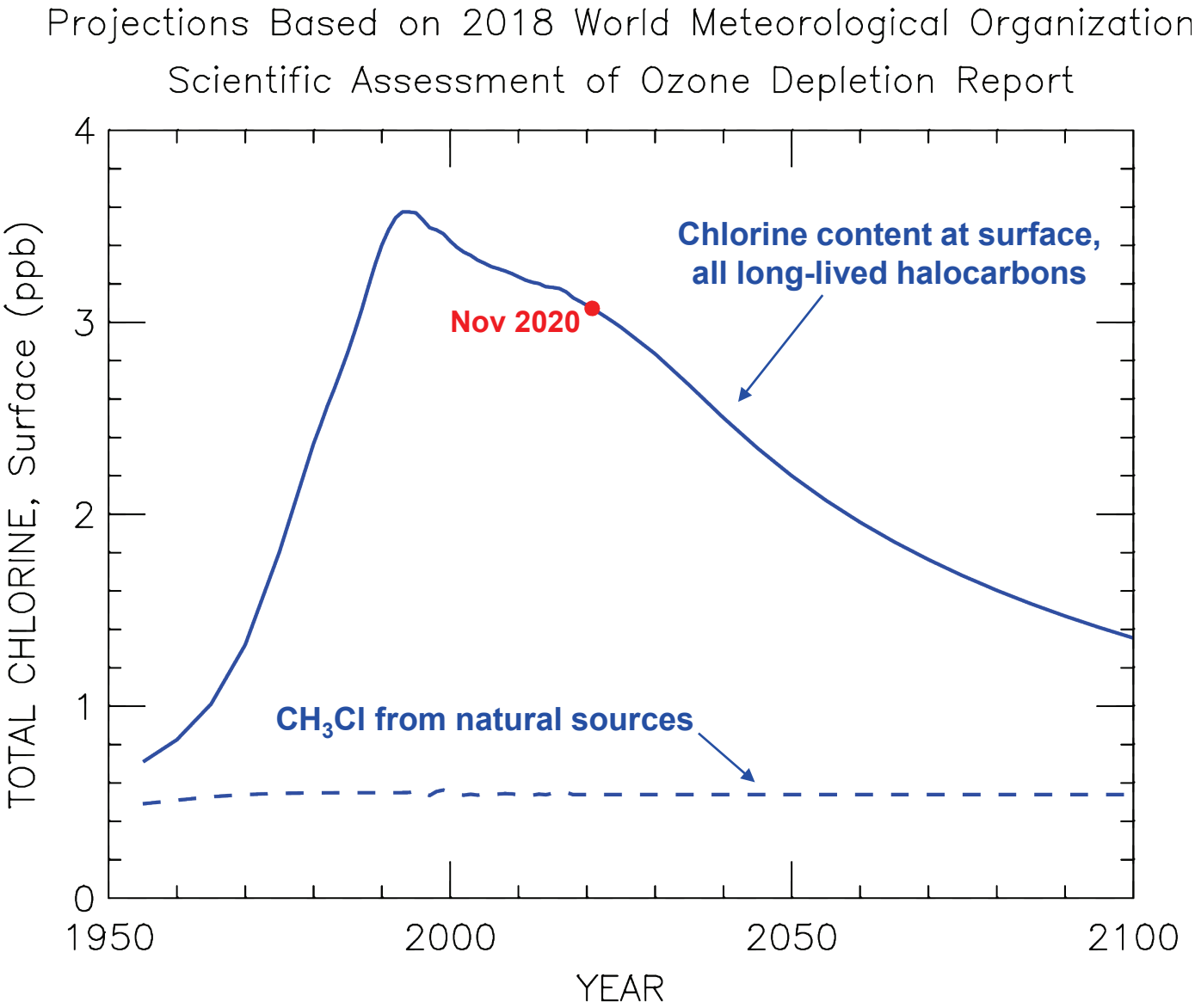
Global Emmisions of all CFCs, **Fig Q0-1, *WMO/UNEP Twenty QAs Ozone***



Why was the introduction of Freon-12 as a refrigerant gas in the 1930s hailed as a great triumph?

By what mechanism does Freon-12 fall apart and in what region of the atmosphere does this occur?

Montreal Protocol Has Banned Industrial Production of CFCs & Other ODS



2018 WMO Scientific Assessment of Ozone Depletion Report:
https://www.esrl.noaa.gov/csd/assessments/ozone/2018

Chlorine Source Gases

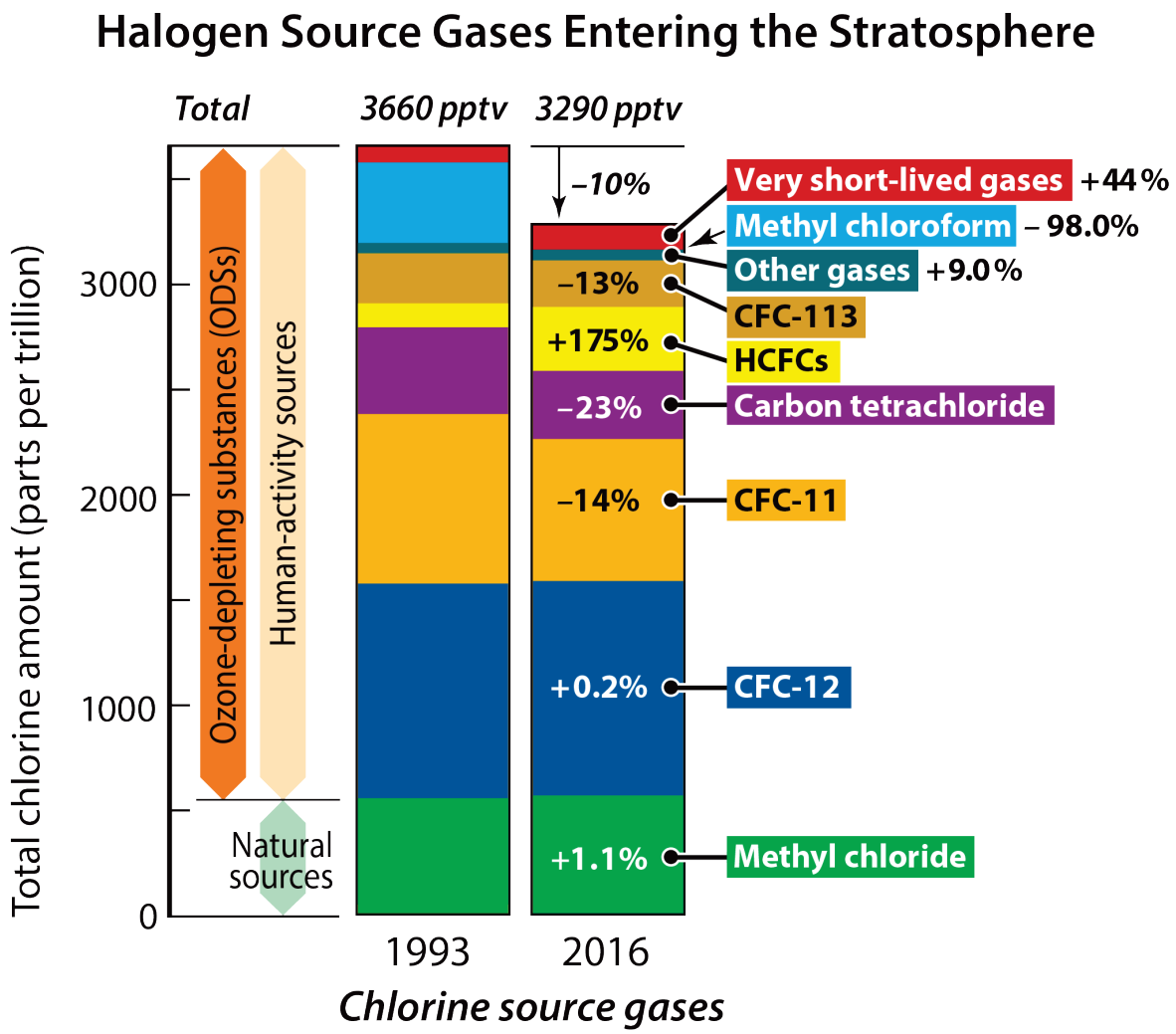


Fig Q6-1, *WMO/UNEP Twenty QAs Ozone*

Ozone Depletion Potential and Halocarbons

Table Q6-1. Atmospheric lifetimes, global emissions, Ozone Deletion Potentials, and Global Warming Potentials of some halogen source gases and HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Ozone Depletion Potential (ODP)[b]
Halogen Source Gases		
Chlorine Gases		
CFC-11 (CCl_3F)	52	1
Carbon tetrachloride (CCl_4)	32	0.87
CFC-113 (CCl_2FCClF_2)	93	0.81
CFC-12 (CCl_2F_2)	102	0.73
Methyl chloroform (CH_3CCl_3)	5.0	0.14
HCFC-141b (CH_3CCl_2F)	9.4	0.102
HCFC-142b (CH_3CClF_2)	18	0.057
HCFC-22 (CHF_2Cl)	12	0.034
Methyl chloride (CH_3Cl)	0.9	0.015
Bromine Gases		
Halon-1301 ($CBrF_3$)	65	15.2
Halon-1211 ($CBrClF_2$)	16	6.9
Methyl bromide (CH_3Br)	0.8	0.57
Hydrofluorocarbons (HFCs)		
HFC-23 (CHF_3)	228	0
HFC-143a (CH_3CF_3)	51	0
HFC-125 (CHF_2CF_3)	30	0
HFC-134a (CH_2FCF_3)	14	0
HFC-32 (CH_2F_2)	5.4	0
HFC-152a (CH_3CHF_2)	1.6	0
HFO-1234yf ($CF_3CF{=}CH_2$)	0.03	0

$$\text{ODP (species "}i\text{")} = \frac{\text{global loss of } O_3 \text{ due to unit mass emission of "}i\text{"}}{\text{global loss of } O_3 \text{ due to unit mass emission of CFC-11}}$$

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continuous

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continuous

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$$\approx \frac{(\alpha\, n_{Br} + n_{Cl})}{3} \frac{\tau_i}{\tau_{\text{CFC-11}}} \frac{MW_{\text{CFC-11}}}{MW_i}$$

continuous

where :

τ is the global atmospheric lifetime

MW is the molecular weight

n is the number of chlorine or bromine atoms

α is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

Ozone Depletion Potential and Halocarbons

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continuous

$$\text{ODP (species "}i\text{")} = \frac{\text{global loss of } O_3 \text{ due to unit mass emission of "}i\text{"}}{\text{global loss of } O_3 \text{ due to unit mass emission of CFC-11}}$$

$$\approx \frac{(\alpha\, n_{Br} + n_{Cl})}{3} \frac{\tau_i}{\tau_{CFC\text{-}11}} \frac{MW_{CFC\text{-}11}}{MW_i}$$

continuous

where :

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$\alpha = 60$

Ozone Depletion Potential and Halocarbons

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continuous

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$$\approx \frac{(\alpha\, n_{Br} + n_{Cl})}{3} \frac{\tau_i}{\tau_{\text{CFC-11}}} \frac{MW_{\text{CFC-11}}}{MW_i}$$

continuous

where :

τ is the global atmospheric lifetime

MW is the molecular weight

n is the number of chlorine or bromine atoms

α is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

$\alpha = 60$

Halons (anthropogenic halocarbons containing bromine) much worse for ozone than CFCs or (anthropogenic halocarbons containing only chlorine)

Ozone Depletion Potential and Halocarbons

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continuous

$$\text{ODP (species "}i\text{")} = \frac{\text{global loss of } O_3 \text{ due to unit mass emission of "}i\text{"}}{\text{global loss of } O_3 \text{ due to unit mass emission of CFC-11}}$$

$$\approx \frac{(\alpha\, n_{Br} + n_{Cl})}{3} \frac{\tau_i}{\tau_{\text{CFC-11}}} \frac{MW_{\text{CFC-11}}}{MW_i}$$

continuous

where :

τ is the global atmospheric lifetime

MW is the molecular weight

n is the number of chlorine or bromine atoms

α is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

HFCs (anthropogenic halocarbons containing only hydrogen, fluorine, & carbon) pose no threat to the ozone layer

Ozone Depletion

According to Section 2.8 of Chemistry in Context, how much depletion of stratospheric ozone at mid-latitudes (60°S to 60°N) has occurred?

According to the Question 12 of the WMO/UNEP QAs, how much depletion of the Global Total Ozone layer has occurred?

Also, state whether your are either "good" or "concerned" with the different estimates for depletion of the ozone layer given in Question 12 of the WMO/UNEP QAs, compared to Section 28 of Chemistry in Context (i.e, your answer to the prior question).

Ozone Depletion

According to Section 2.8 of Chemistry in Context, how much depletion of stratospheric ozone at mid-latitudes (60°S to 60°N) has occurred?

About 8%

According to the Question 12 of the WMO/UNEP QAs, how much depletion of the Global Total Ozone layer has occurred?

Also, state whether your are either "good" or "concerned" with the different estimates for depletion of the ozone layer given in Question 12 of the WMO/UNEP QAs, compared to Section 28 of Chemistry in Context (i.e, your answer to the prior question).

Ozone Depletion

According to Section 2.8 of Chemistry in Context, how much depletion of stratospheric ozone at mid-latitudes (60°S to 60°N) has occurred?

About 8%

According to the Question 12 of the WMO/UNEP QAs, how much depletion of the Global Total Ozone layer has occurred?

Depletion of ozone layer maximized at about 5% in early 1990s and has been at about 2 to 3% since about 2010.

Also, state whether your are either "good" or "concerned" with the different estimates for depletion of the ozone layer given in Question 12 of the WMO/UNEP QAs, compared to Section 28 of Chemistry in Context (i.e, your answer to the prior question).

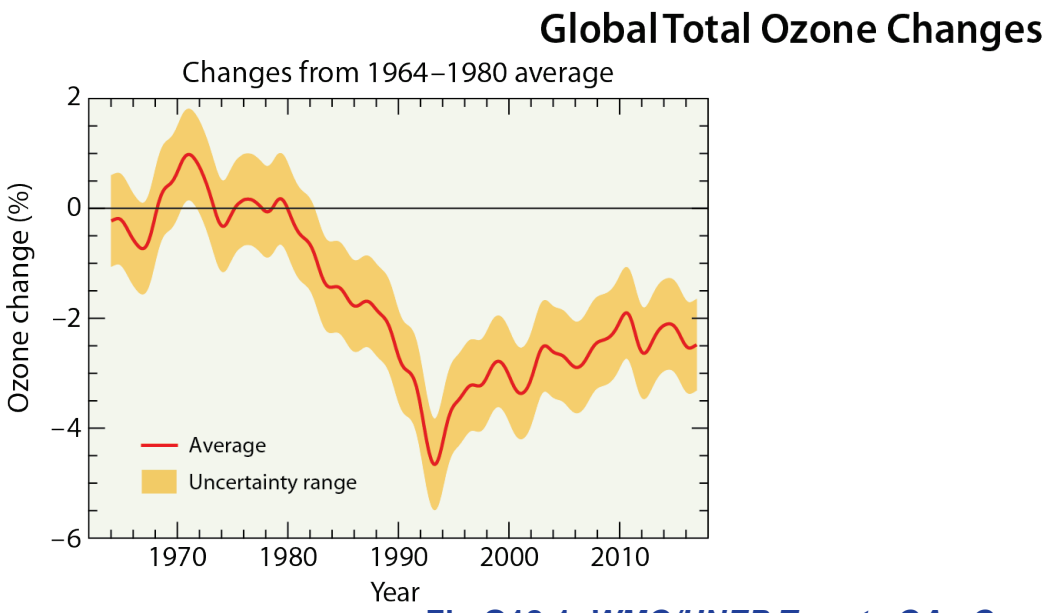


Fig Q12-1, *WMO/UNEP Twenty QAs Ozone*

Ozone Depletion

According to Section 2.8 of Chemistry in Context, how much depletion of stratospheric ozone at mid-latitudes (60°S to 60°N) has occurred?

About 8%

According to the Question 12 of the WMO/UNEP QAs, how much depletion of the Global Total Ozone layer has occurred?

Depletion of ozone layer maximized at about 5% in early 1990s and has been at about 2 to 3% since about 2010.

Also, state whether your are either "good" or "concerned" with the different estimates for depletion of the ozone layer given in Question 12 of the WMO/UNEP QAs, compared to Section 28 of Chemistry in Context (i.e, your answer to the prior question).

Not concerned because a particular figure in Q12 shows that for some latitudes, the depletion in ozone in 2012 to 2016 relative to 1964-1980 was even larger than the value given in *Chemistry in Context*.

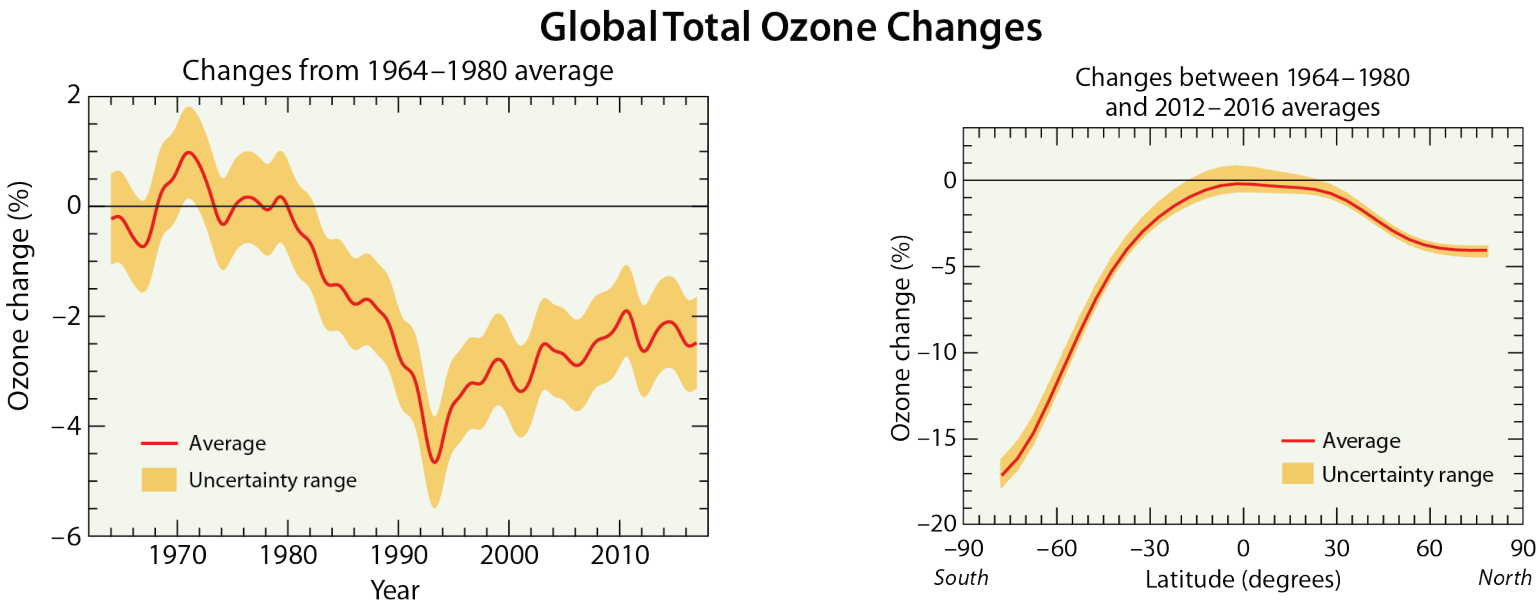
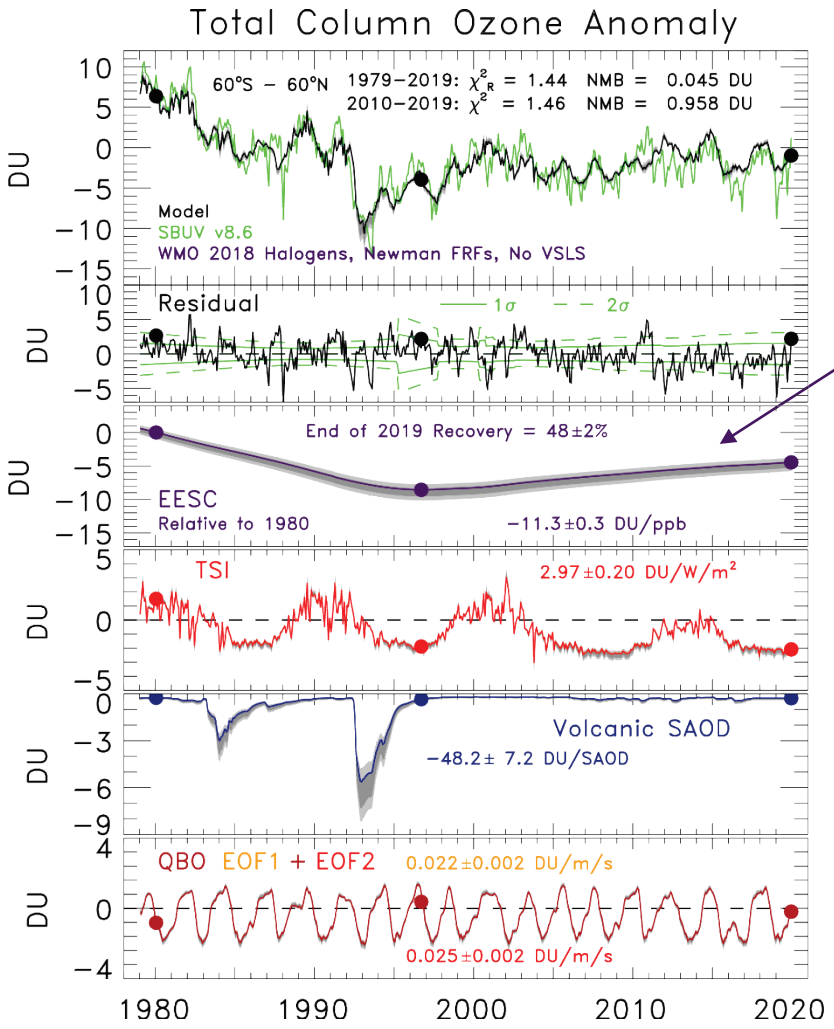


Fig Q12-1, *WMO/UNEP Twenty QAs Ozone*

Mid-Latitude Ozone Depletion

Total column ozone anomaly is deseasonalized, cosine latitude weighted average of total column ozone collected between 60°S and 60°N, relative to the mean total column abundance over the entire time period.



"Expected" recovery of near global ozone layer for end of 2019 relative to maximum depletion since 1980, driven by atmospheric halogens

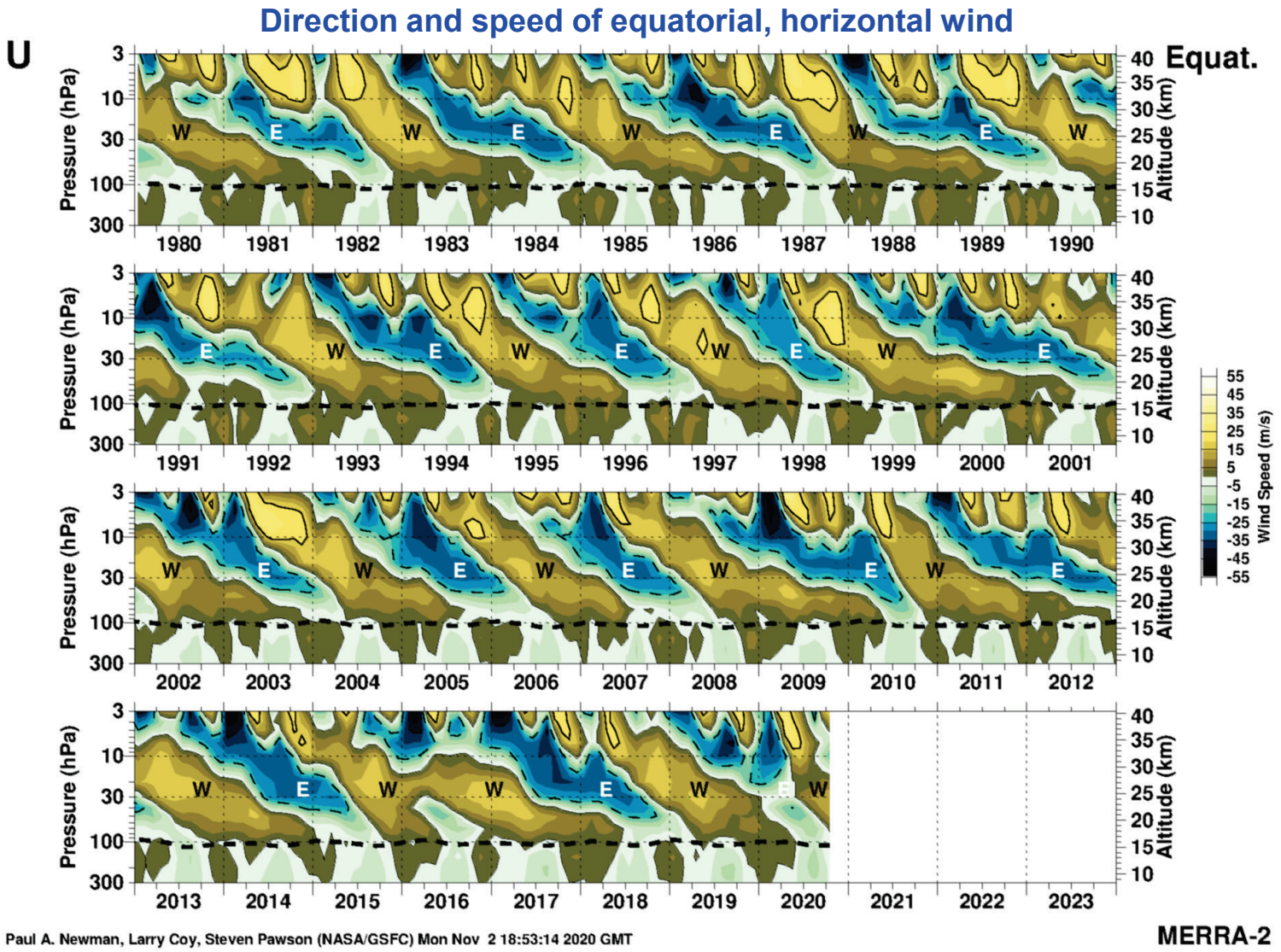
Circles (•) placed at 1980, column minimum due to EESC, & end of 2019

Multiple linear regression of total ozone column anomaly as a function of equivalent effective stratospheric chlorine (**EESC**), total solar irradiance (**TSI**), stratospheric aerosol optical depth (**SAOD**), and the quasi-biennial oscillation (**QBO**) has long been used to quantitatively assess factors that drive variations in the thickness of the ozone layer.

Note: EESC = Inorganic Stratospheric Chlorine + 60× Inorganic Stratospheric Bromine

Salawitch *et al.*, In Prep, 2020

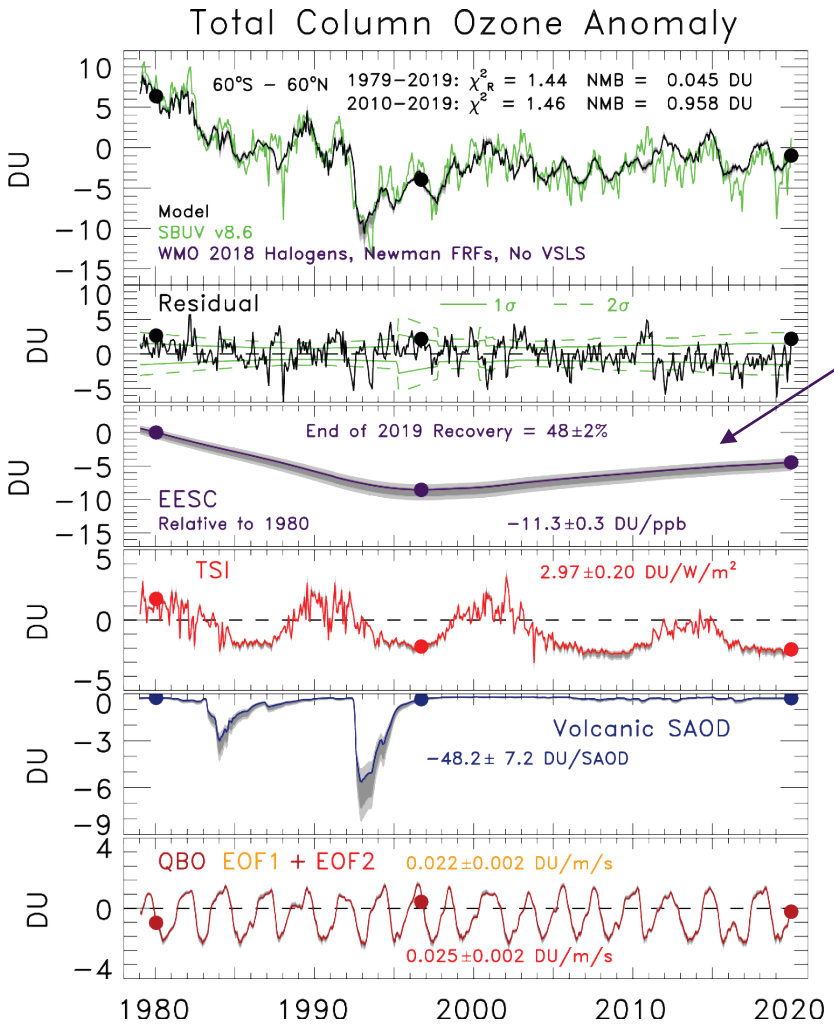
Quasi-Biennial Oscillation of Stratospheric Winds



https://acd-ext.gsfc.nasa.gov/Data_services/met/qbo/qbo.html

Mid-Latitude Ozone Depletion

Total column ozone anomaly is deseasonalized, cosine latitude weighted average of total column ozone collected between 60°S and 60°N, relative to the mean total column abundance over the entire time period.



"Expected" recovery of near global ozone layer for end of 2019 relative to maximum depletion since 1980, driven by atmospheric halogens

Note:

a) this model predicts significant recovery of the global ozone layer should be underway

despite:

b) regular "ups" and "downs" of ozone caused by the 11-year solar cycle

c) major ozone depletion after volcanic eruptions large enough to greatly enhance stratospheric aerosol optical depth (SAOD)

d) regulars "ups" and "downs" of ozone caused by the so-called quasi-biennial oscillation of the direction of the horizontal wind in the lower stratosphere

Salawitch *et al.*, In Prep, 2020

Chapman Chemistry

$$[O_3] = \left(\frac{J_1 \, k_2}{J_3 \, k_4} \right)^{1/2} f_{O2} \, [M]^{3/2}$$

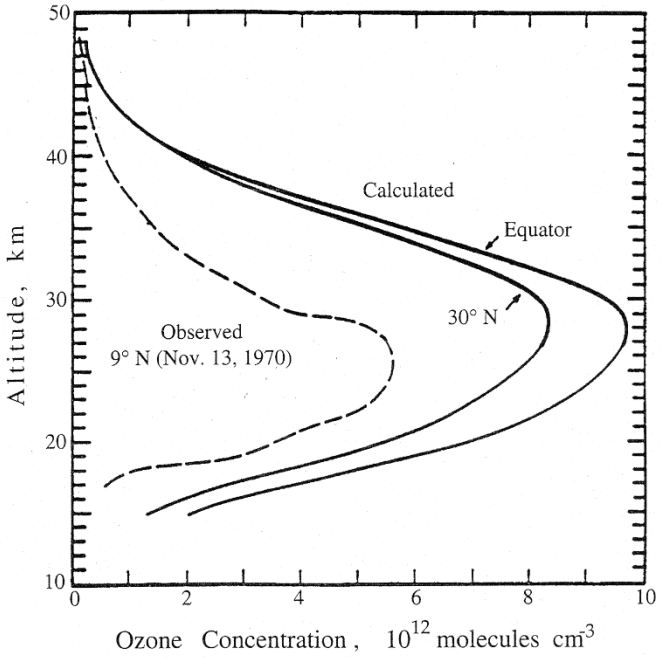


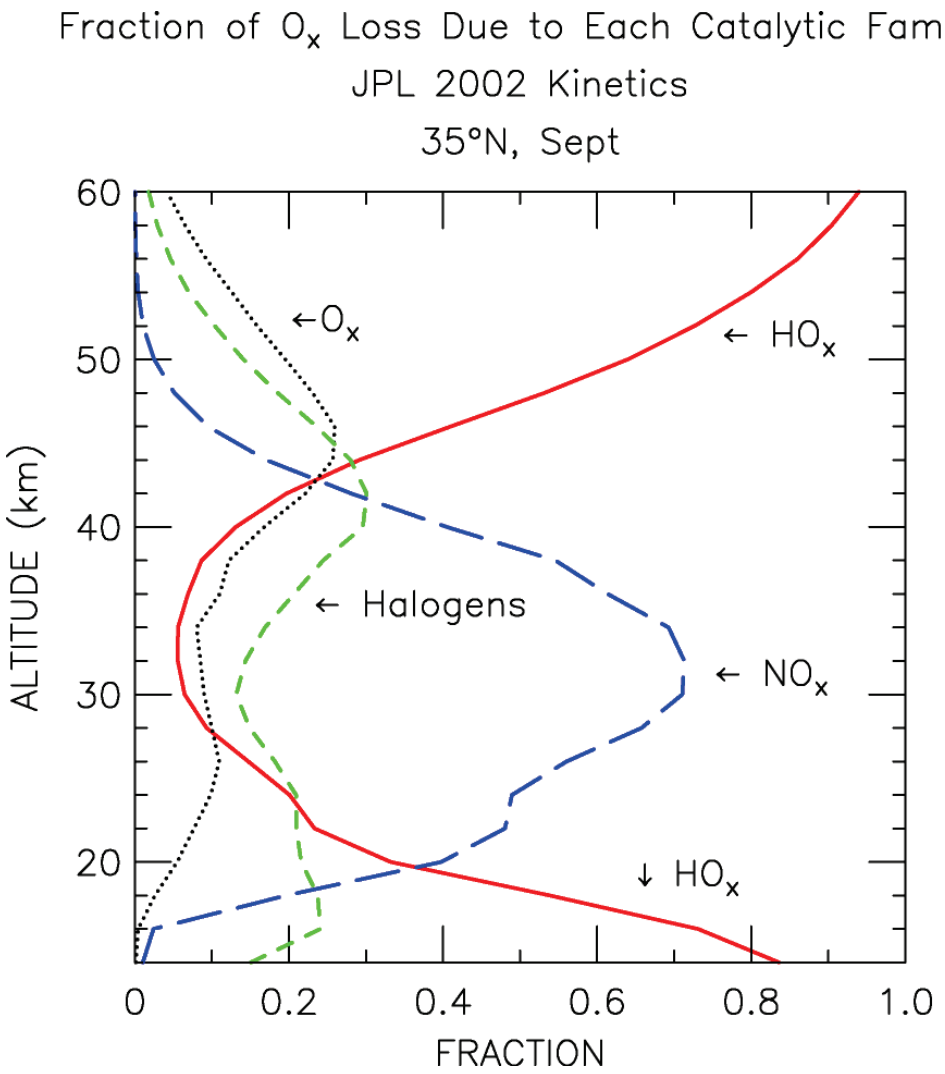
FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

$[O_3]$ falls off with increasing altitude (high in stratosphere), at a rate determined by $[M]^{3/2}$, because:

$[O_3]$ falls off with decreasing altitude (low in stratosphere) due to a rapid drop in J_1, reflecting:

Observed $[O_3]$ < Chapman $[O_3]$: why ?!?

Stratospheric Photochemistry: Odd Oxygen Loss By Families



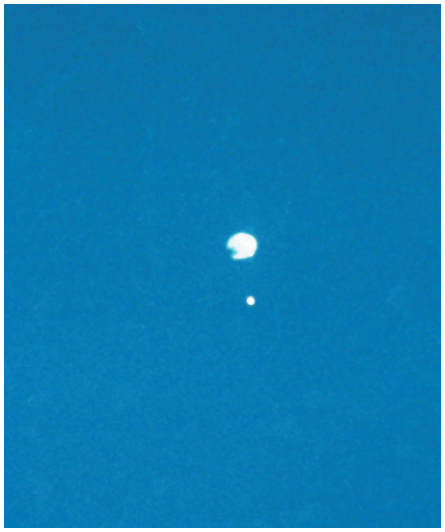
Lecture 9, Slide 10

Calculated fraction of odd oxygen loss due to various families of radicals

After Osterman *et al.*, *GRL*, 24, 1107, 1997;
Sen *et al.*, *JGR*, 103, 3571. 1998;
Sen *et al.*, *JGR*, 104, 26653, 1999.

Fairbanks, Alaska : Summer 1998

Fairbanks, Alaska : Summer 1998



Roll the Tape

https://www.youtube.com/watch?v=i47s97wBujY

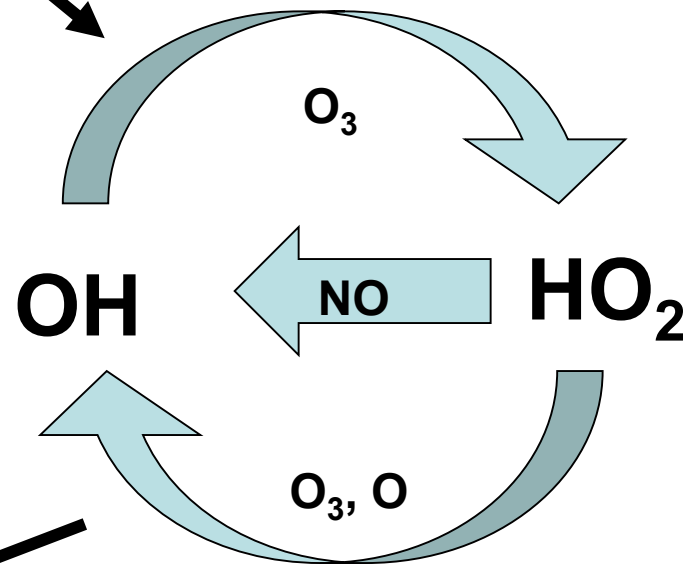
https://www.youtube.com/watch?v=M_0RcVD_9QQ

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

Production : $O^1D + H_2O \rightarrow OH + OH$

$O^1D + CH_4 \rightarrow OH + CH_3$



Loss: $OH + HO_2 \rightarrow H_2O + O_2$

$OH + HNO_3 \rightarrow H_2O + NO_3$

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO_2 formation:

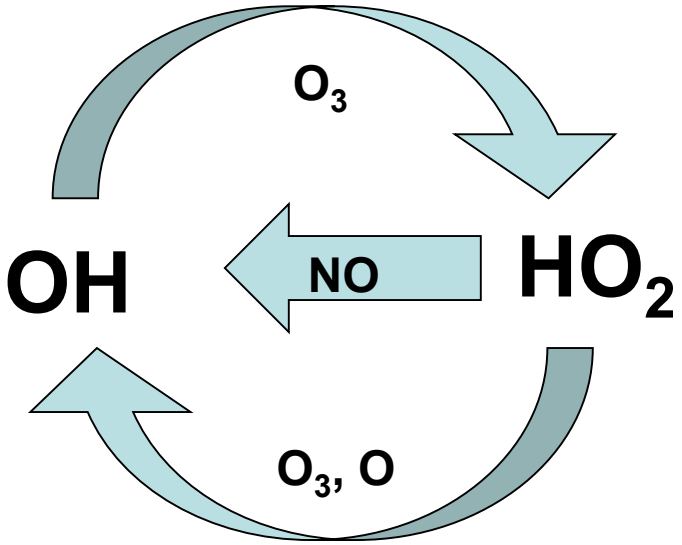
$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (1)$$

HO_2 loss:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (2)$$

or $$HO_2 + O \rightarrow OH + O_2 \qquad (3)$$

or $$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \qquad (4)$$



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or $$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \qquad (4)$$

HO_2 loss step (2):

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$

Net:

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO_2 formation:

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (1)$$

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HO_2 loss step (2):

$$\cancel{OH} + O_3 \rightarrow \cancel{HO_2} + O_2$$
$$\cancel{HO_2} + NO \rightarrow \cancel{OH} + NO_2$$

Net: $$O_3 + NO \rightarrow O_2 + NO_2$$

HO_x : OH and HO_2

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HO_2 loss step (2):

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$$\cancel{HO_2} + NO \rightarrow \cancel{OH} + NO_2$$

Net: $$O_3 + NO \rightarrow O_2 + NO_2$$

This is followed quickly by:

$$NO_2 + h\nu \rightarrow NO + O$$

Yielding final "net":

$$O_3 \rightarrow O + O_2$$

Null cycle

with respect to production & loss of odd oxygen

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO_2 formation:

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (1)$$

HO_2 loss:

$$HO_2 + NO \rightarrow OH + NO_2 \quad (2)$$

or $$HO_2 + O \rightarrow OH + O_2 \quad (3)$$

or $$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \quad (4)$$

HO_2 loss step (3):

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O \rightarrow OH + O_2$$
$$\text{Net: } O_3 + O \rightarrow O_2 + O_2$$

HO_2 loss step (4):

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O_3 \rightarrow OH + O_2 + O_2$$
$$\text{Net: } O_3 + O_3 \rightarrow O_2 + O_2 + O_2$$

Catalytic Ozone (Odd Oxygen) Loss Cycles

Odd Oxygen Loss - HO_x

$$\frac{d\,(\text{Odd Oxygen})}{dt} = -2\,k_4\,[HO_2][O_3] - 2\,k_3\,[HO_2][O] \qquad \text{Eq (7)}$$

The reactions:

$$HO_2 + O \rightarrow OH + O_2 \qquad (3)$$
$$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \qquad (4)$$

are rate limiting steps for O_3 loss by two catalytic cycles:

Cycle (1) Net :

$$O_3 + O \rightarrow 2\,O_2$$

Cycle (2) Net :

$$O_3 + O_3 \rightarrow 3\,O_2$$

As a convenient short hand, **we consider HO_2 to be odd oxygen**

Then:

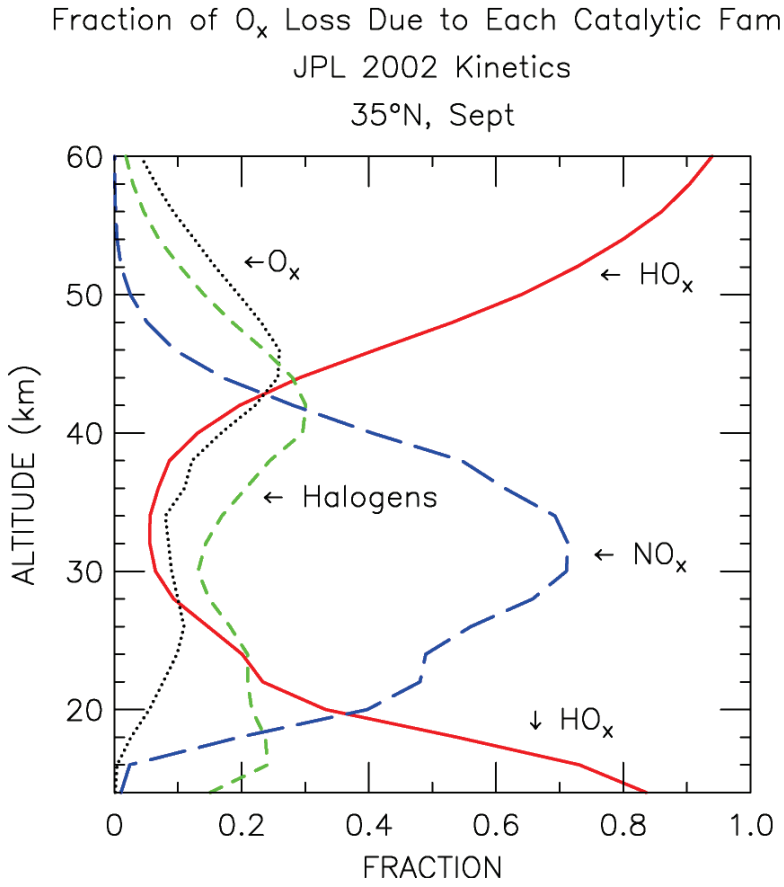
clear now that reactions (3) and (4) each consume two odd oxygens at rates determined by $2\,k_3\,[HO_2]\,[O]$ and $2\,k_4\,[HO_2][O_3]$

Odd Oxygen Loss - HO_x

At what altitudes will loss of ozone by these rate limiting steps be dominant ?

$$HO_2 + O \rightarrow OH + O_2 \qquad (3)$$
$$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \qquad (4)$$

One dominates at low altitude, the other at high altitude ⇒ which is which ?!?



Odd Oxygen Loss - HO_x

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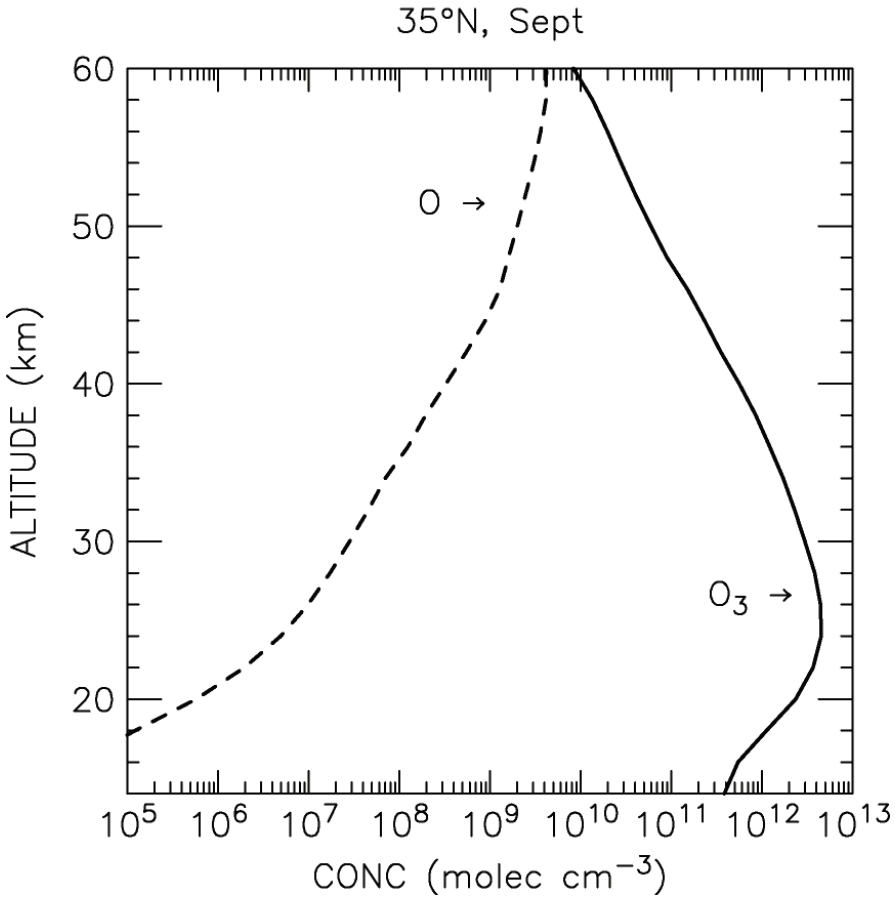
One dominates at low altitude, the other at high altitude ⇒ which is which ?!?

Hint:



Odd Oxygen Loss - HO_x

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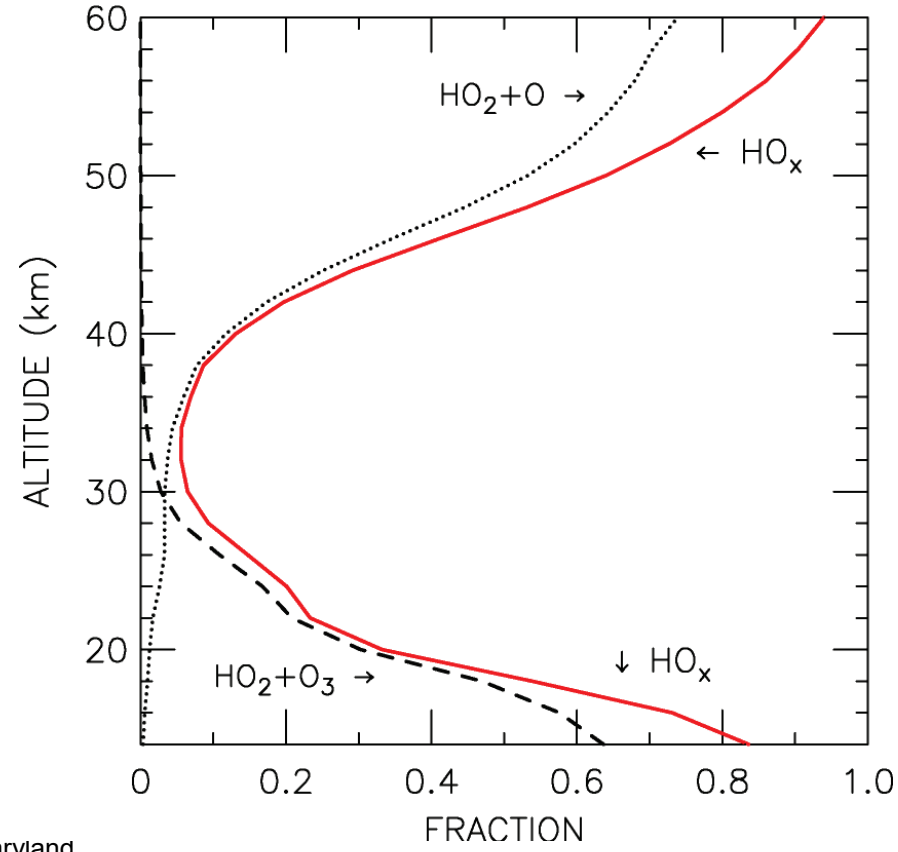
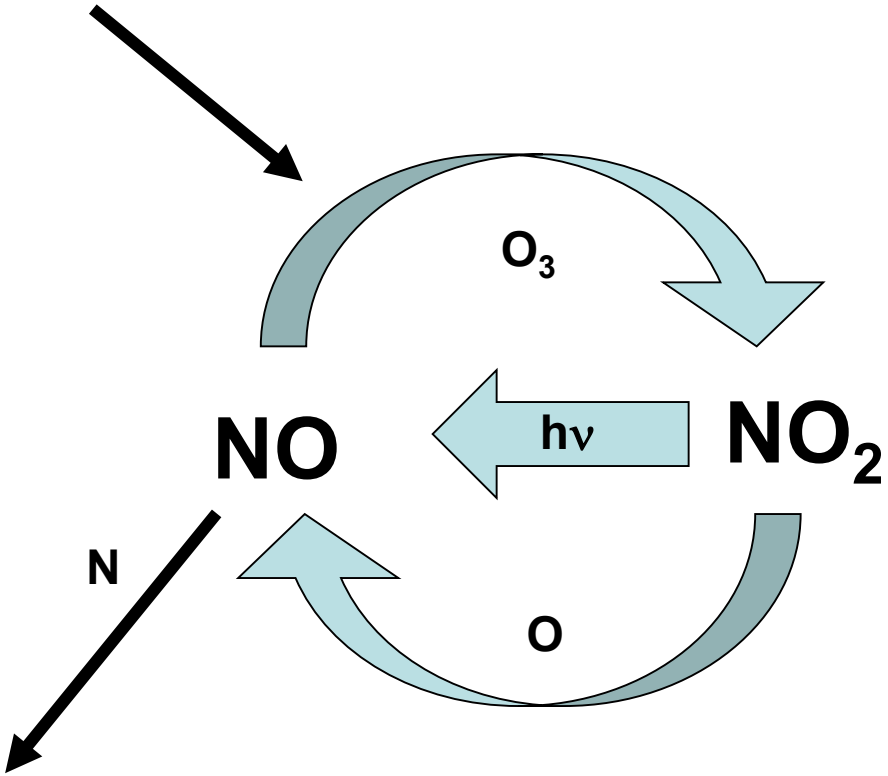


NO_x : NO and NO_2

NO and NO_2 are central to stratospheric and tropospheric photochemistry

Stratospheric **Production : $O^1D + N_2O \rightarrow NO + NO$**



Final sinks : $N + NO \rightarrow N_2 + O$ (uppermost stratosphere)
HNO_3 solubility & rainout (lowermost stratosphere)

NO_x : NO and NO_2

NO and NO_2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

NO_2 formation:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

NO_2 loss:

$$NO_2 + h\nu \rightarrow NO + O \qquad (2)$$

or $$NO_2 + O \rightarrow NO + O_2 \qquad (3)$$

NO_2 loss step (2):

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + h\nu &\rightarrow NO + O \\ \hline \text{Net:}\quad O_3 + h\nu &\rightarrow O + O_2 \end{aligned}$$

NO_2 loss step (3):

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + O &\rightarrow NO + O_2 \\ \hline \text{Net:}\quad O_3 + O &\rightarrow 2\,O_2 \end{aligned}$$

Can show:

$$\frac{dO_3}{dt} + \frac{dO}{dt} = \frac{d\,(\text{Odd Oxygen})}{dt} = -2\,k_3\,[NO_2][O]$$

As a convenient short hand, **we consider NO_2 to be odd oxygen**

N_2O and NO_y

Loss of N_2O occurs mainly in the stratosphere due to:

photolysis – main sink

reaction with electronically excited $O(^1D)$ – minor sink

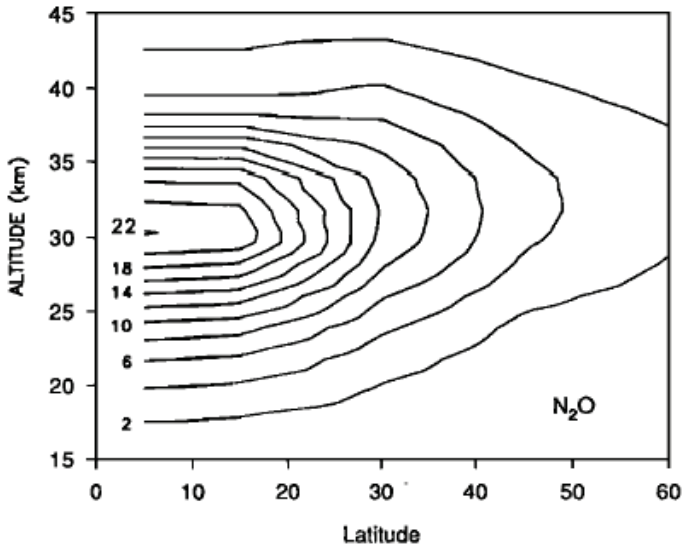


Fig. 11. Diurnally averaged loss rate for N_2O (10^2 molecules cm^{-3} s^{-1}) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of N_2O by reaction with $O(^1D)$ as well as photolysis.

Minschwaner, Salawitch, and McElroy, *JGR*, 1993

The minor sink for N_2O loss has a path that results in "reactive nitrogen": **Lecture 6, Slide 68**

$N_2O + O(^1D) \rightarrow NO + NO$

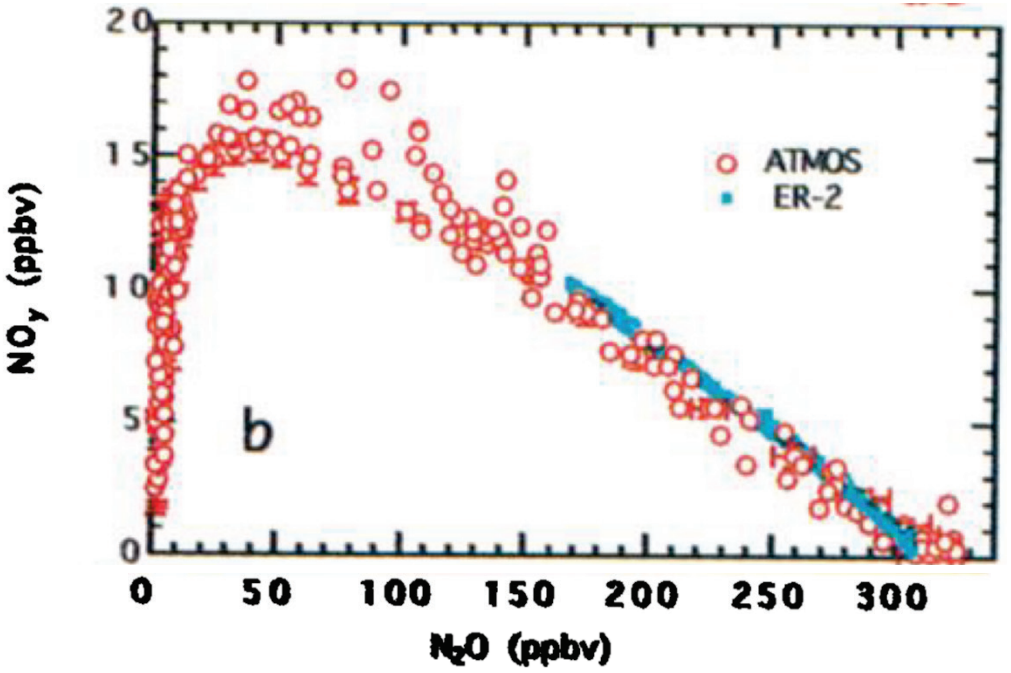
Reactive nitrogen (NO_y) is crucial to stratospheric chemistry

Oxides of nitrogen catalyze loss of stratospheric O_3 & participate in a series of chemical reactions that affect partitioning of hydrogen and chlorine radicals, etc.

N_2O and NO_y

Loss of N_2O occurs mainly in the stratosphere due to:

- **photolysis – main sink**
- **reaction with electronically excited $O(^1D)$ – minor sink**



ATMOS: NASA Atmospheric Trace Molecule Spectroscopy Experiment that flew on the Nov 1994 STS-66 Space Shuttle mission

ER-2: NASA Earth Reconnaissance 2 research aircraft that can sample air at 20 km (~66,000 feet), civilian version of the U2 spy plane

Chang *et al.*, *GRL*, 1996

The minor sink for N_2O loss has a path that results in "reactive nitrogen":

$$N_2O + O(^1D) \rightarrow NO + NO$$

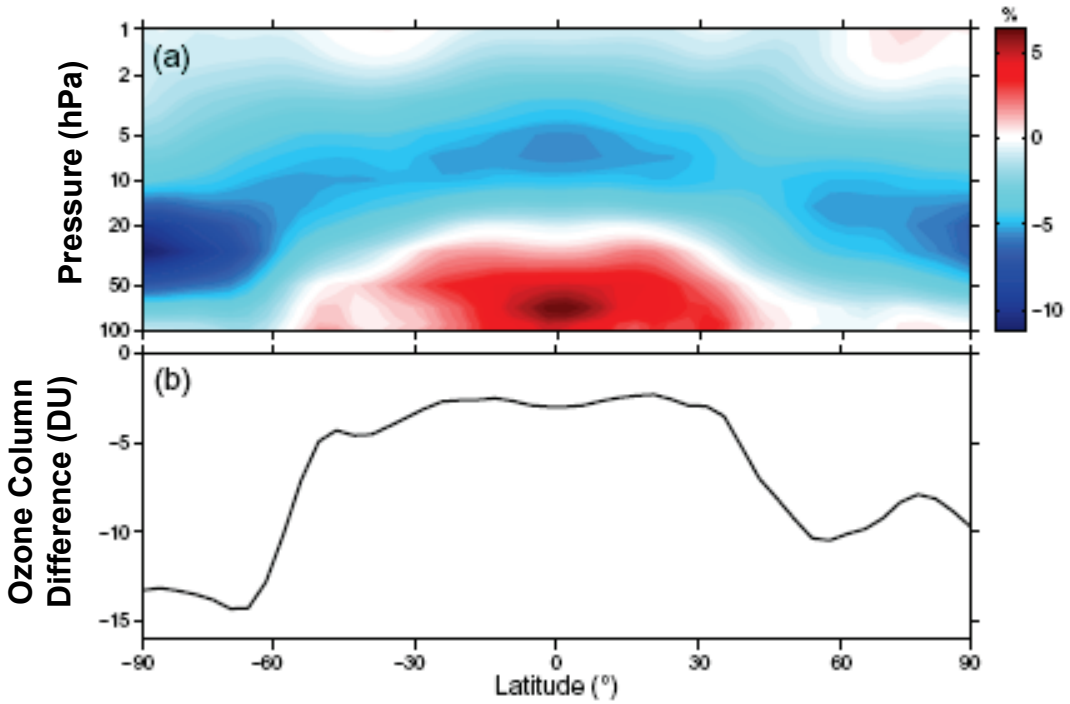
Reactive nitrogen (NO_y) is crucial to stratospheric chemistry

Oxides of nitrogen catalyze loss of stratospheric O_3 & participate in a series of chemical reactions that affect partitioning of hydrogen and chlorine radicals, etc.

ATMOS on the Space Shuttle

Measurements prior slide were recorded by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer during the third flight of the Atmospheric Laboratory for Applications and Sciences payload (ATLAS-3) on the space shuttle in November 1994

N_2O and Stratospheric Ozone



Revell *et al.*, *ACP*, 2012

Stratospheric O_3 difference in the 2090s found for a computer simulation run using N_2O from RCP 8.5 minus that of a simulation using N_2O from RCP 2.6

Rising N_2O leads to:

a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO_2 (NO_x) mediated loss cycles.

b) speeds up the rate of $OH+NO_2+M \rightarrow HNO_3+M$ & $ClO+NO_2+M \rightarrow ClNO_3+M$ in the lowermost stratosphere, leading to slower ozone loss by these cycles & therefore more O_3 where these cycles dominate total loss of O_3

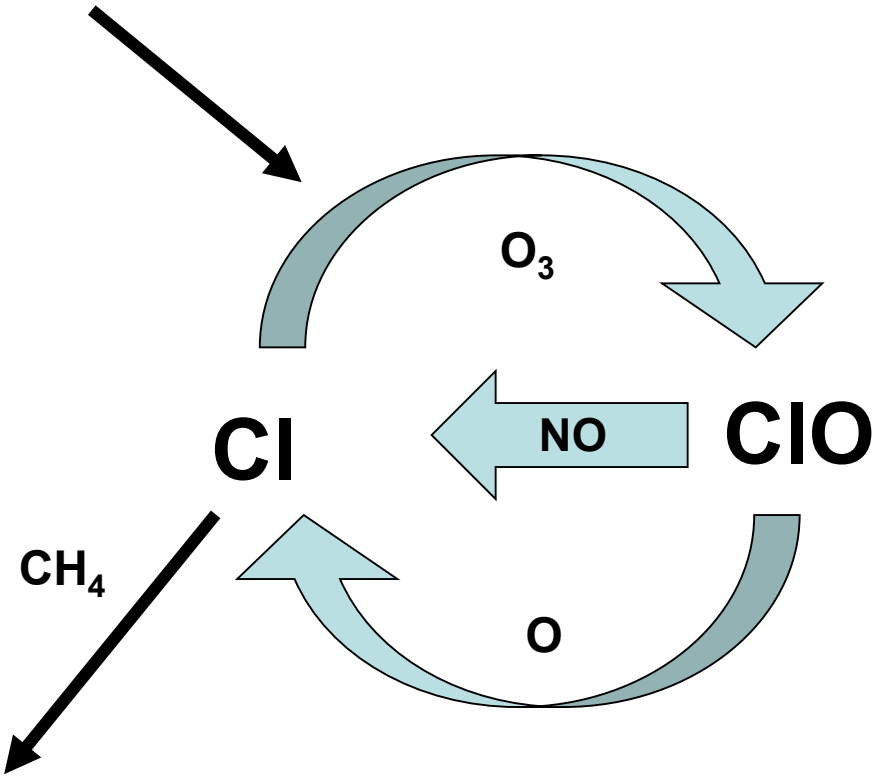
Computer models project stratospheric column O_3 will decline as N_2O rises

Lecture 6, Slide 69

ClO_x : ClO and Cl

ClO is central to stratospheric photochemistry, at mid-latitudes and polar regions

Production : CFCs +hν→ Inorganic chlorine



Final sinks : HCl solubility & rainout (lowermost stratosphere)

ClO_x : ClO and Cl

ClO is central to <u>stratospheric</u> photochemistry, at mid-latitudes and polar regions:

Rapid inner cycle:

ClO formation:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$

ClO loss:

$$ClO + NO \rightarrow Cl + NO_2 \qquad (2)$$

or $$ClO + O \rightarrow Cl + O_2 \qquad (3)$$

ClO loss step (2):

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + NO \rightarrow Cl + NO_2$$

Net: $O_3 + NO \rightarrow NO_2 + O_2$

Followed by: $NO_2 + h\nu \rightarrow NO + O$

Final net: $O_3 + h\nu \rightarrow O + O_2$

ClO loss step (3):

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

Net: $O_3 + O \rightarrow 2\,O_2$

Can show:

$$\frac{dO_3}{dt} + \frac{dO}{dt} = \frac{d\,(\text{Odd Oxygen})}{dt} = -2\,k_3\,[ClO][O]$$

As a convenient short hand, **we consider ClO to be odd oxygen**

ClO_x : ClO and Cl

ClO is central to stratospheric photochemistry, at mid-latitudes and polar regions:

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Net: $O_3 + NO \rightarrow NO_2 + O_2$

Followed by: $NO_2 + h\nu \rightarrow NO + O$

Final net: $O_3 + h\nu \rightarrow O + O_2$

According to Chemistry and Context, what two chemical reactions were first proposed by Rowland and Molina as a mechanism for *ozone destruction* and if these two chemical reactions occur in sequence, what is the net effect?

ClO loss step (3):

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

Net: $O_3 + O \rightarrow 2\,O_2$

Can show:

$$\frac{dO_3}{dt} + \frac{dO}{dt} = \frac{d\,(\text{Odd Oxygen})}{dt} = -2\,k_3\,[ClO][O]$$

As a convenient short hand, **we consider ClO to be odd oxygen**

Proof Halocarbons Reach The Stratosphere

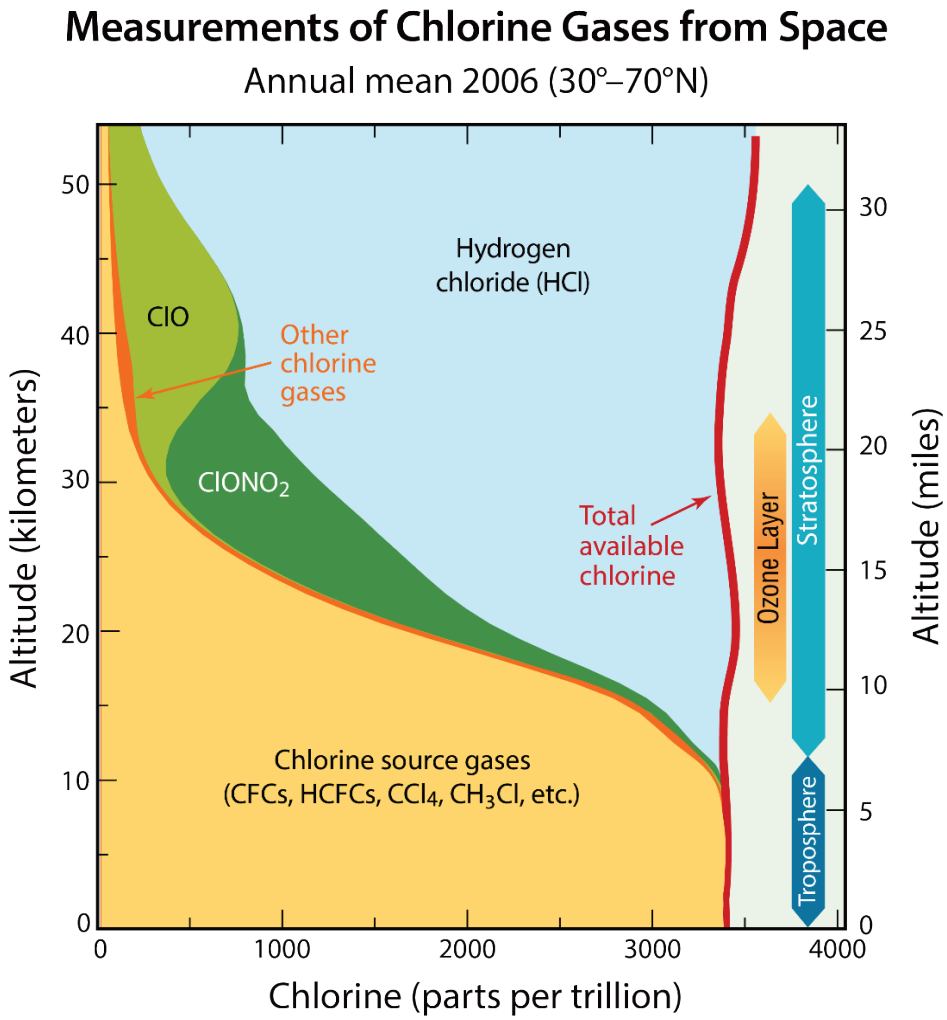


Fig Q7-2, *WMO/UNEP Twenty QAs Ozone*

Proof Halocarbons Reach The Stratosphere

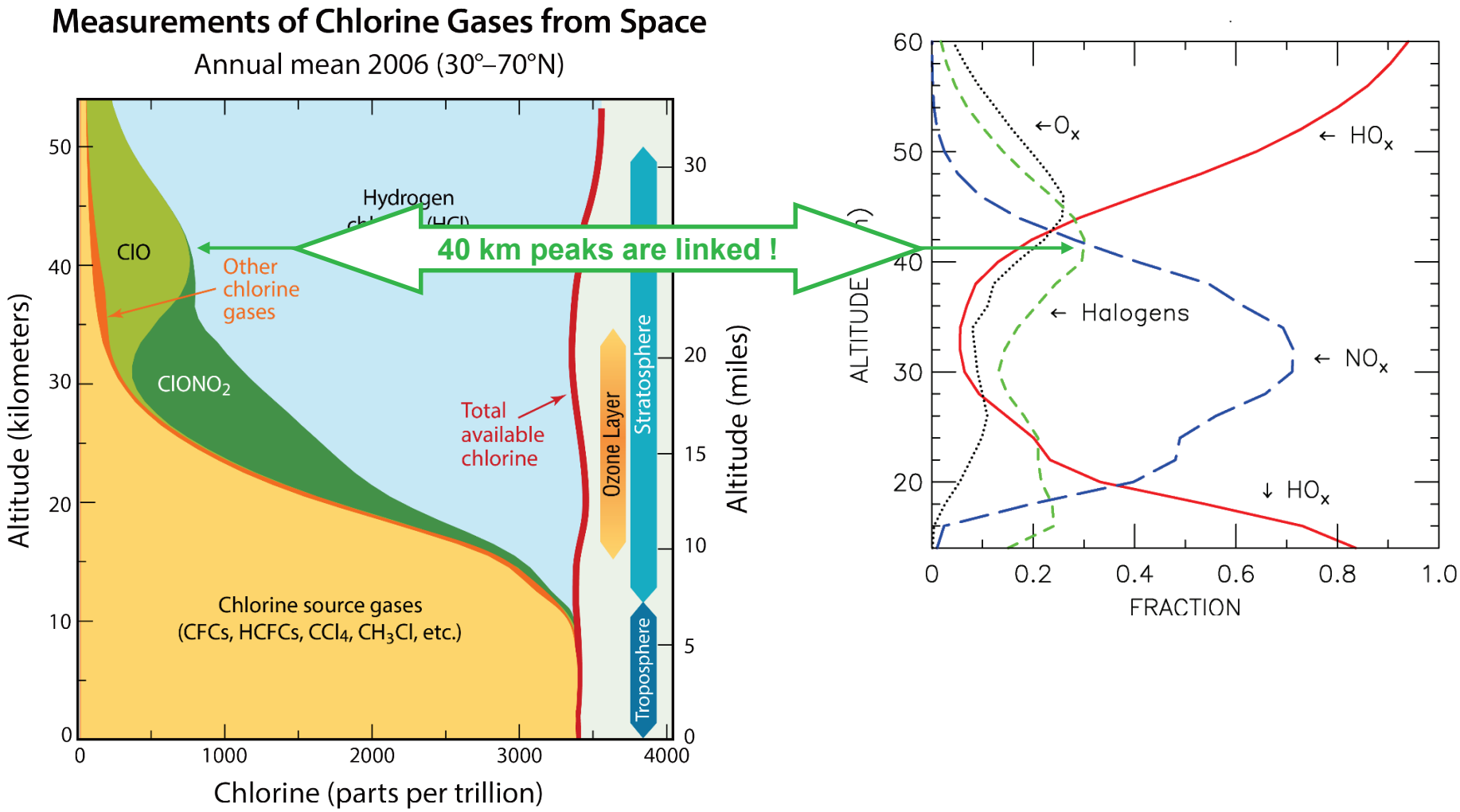
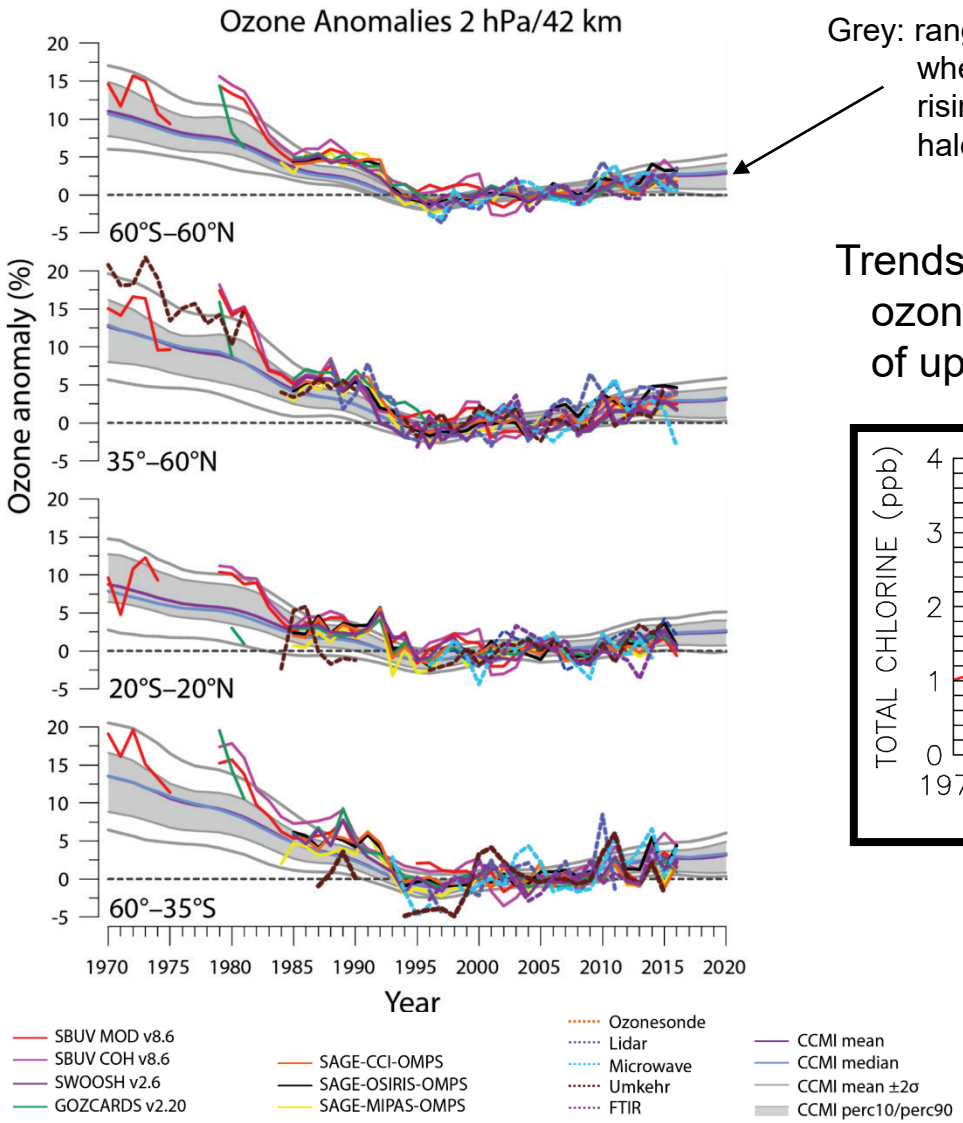


Fig Q7-2, *WMO/UNEP Twenty QAs Ozone*

Trends in Ozone, ~40 km



Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens

Trends in ozone at 40 km are "well understood"
ozone generally *anti-correlates* with time history of upper stratospheric chlorine loading

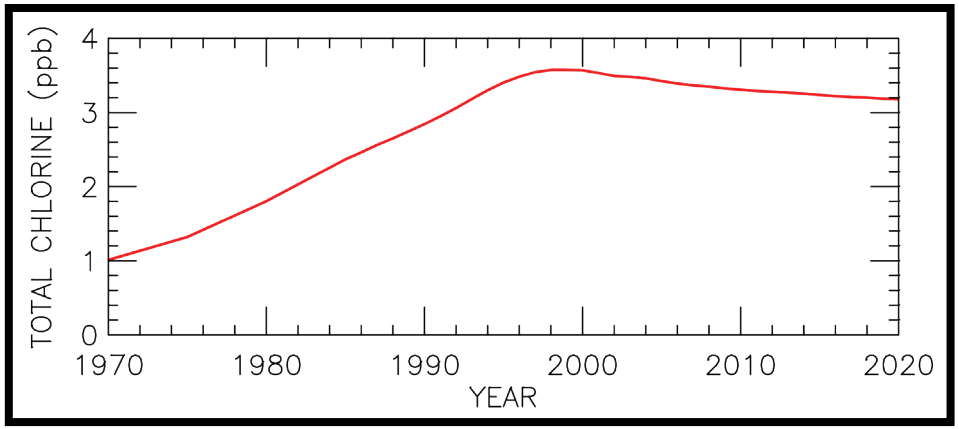
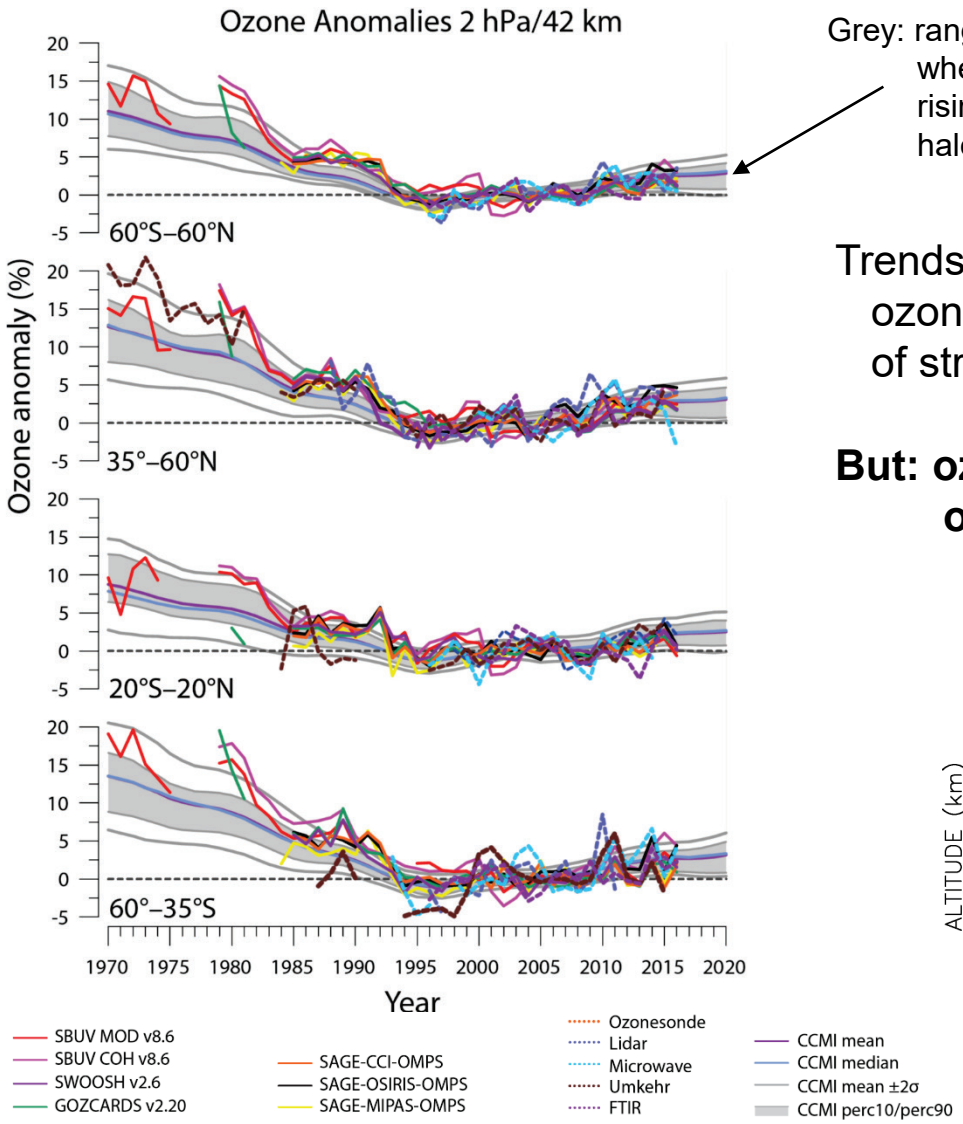


Fig 3-15, *WMO/UNEP Ozone Report*

Trends in Ozone, ~40 km



Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens

Trends in ozone at 40 km are "well understood"
ozone generally anti-correlates with time history of stratospheric chlorine loading

But: ozone at 40 km has little effect on surface UV radiation

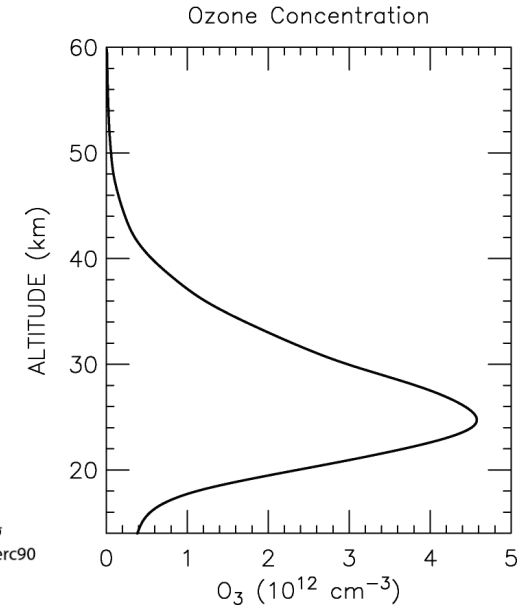


Fig 3-15, *WMO/UNEP Ozone Report*

Trends in Ozone vs Altitude

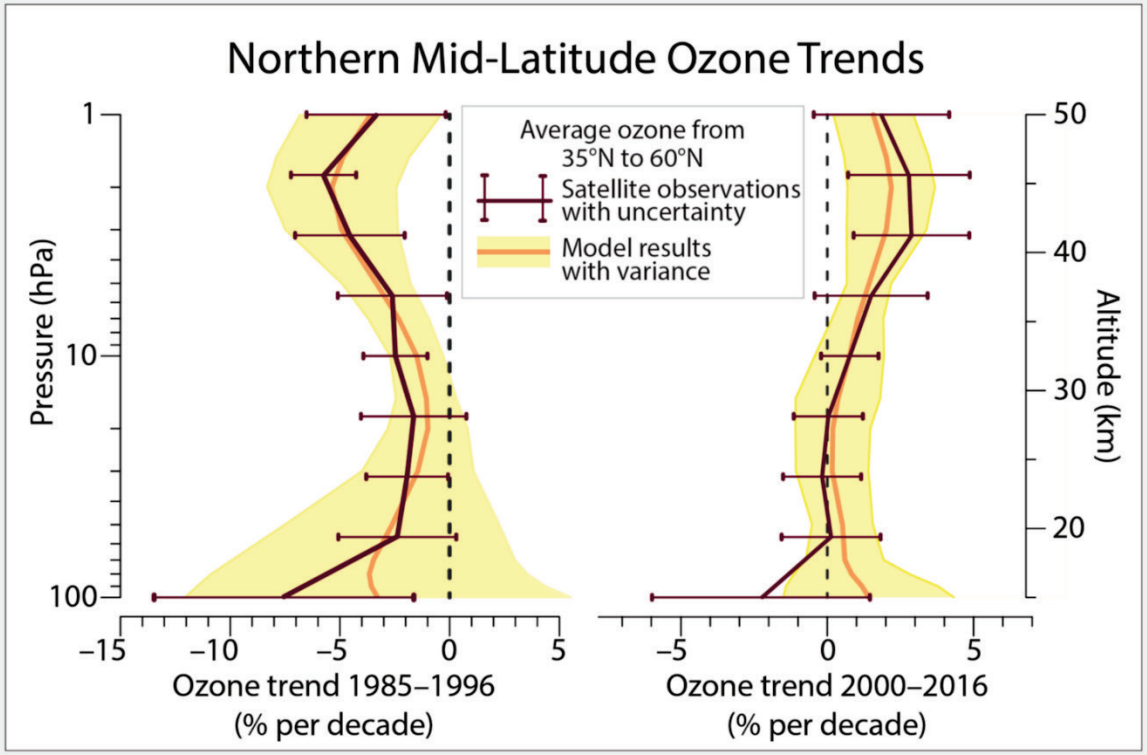


Figure ES-7. Ozone trends in the stratosphere. The largest relative depletion of ozone outside the polar regions occurred prior to 1997 in the northern mid-latitude, upper stratosphere *(left panel)*. The largest recovery has occurred in the same region, with an upward trend of about 3% per decade since 2000 above 40-km altitude *(right panel)*. Ozone trends derived from satellite observations are shown in brown, with uncertainty ranges given by horizontal lines. Ozone trends derived from a set of chemistry-climate models are shown in orange, with the model variance given by the yellow envelope. Ozone trends from chemistry-climate models agree very well with the measured trends. [See also Figure 3-23]

Fig ES-7, *WMO/UNEP Ozone Report Executive Summary*

Trends in Ozone vs Altitude

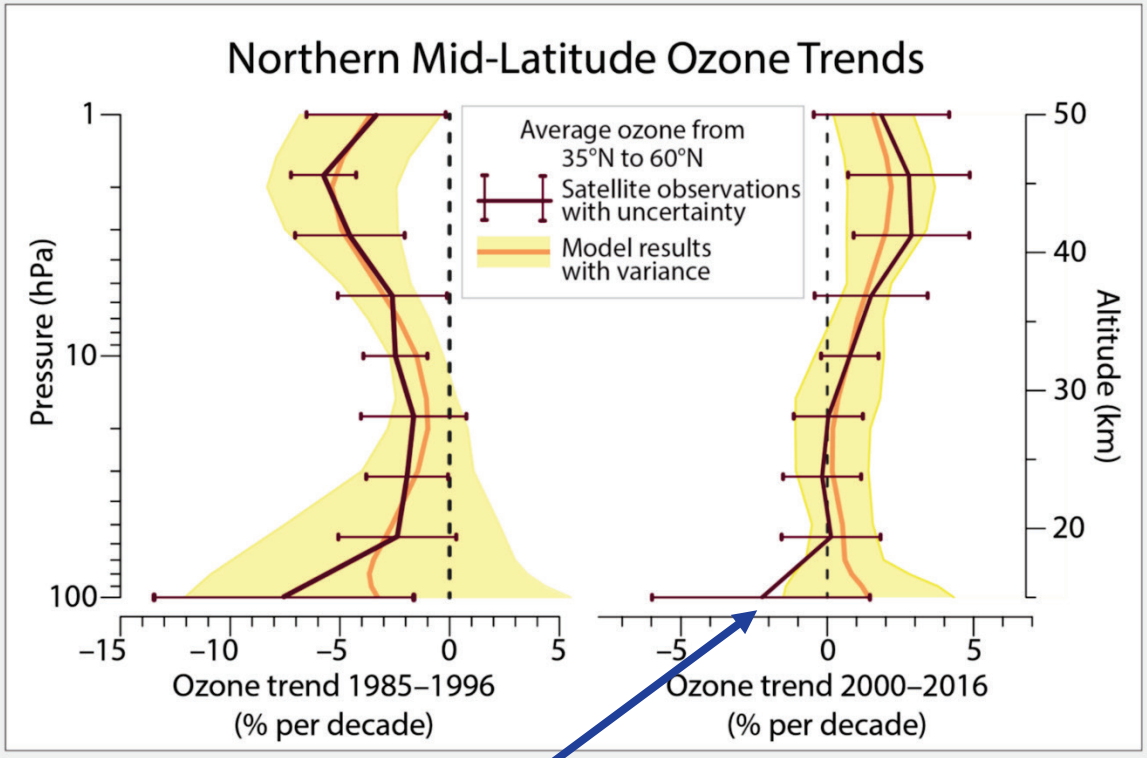
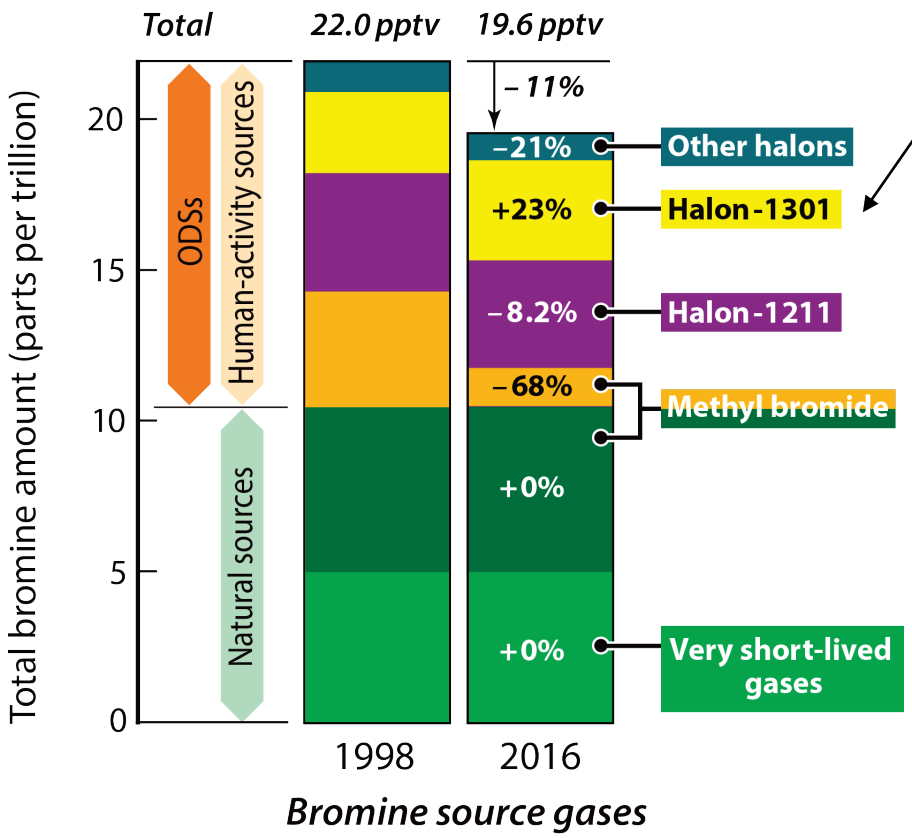


Figure ES-7. Ozone trends in the stratosphere. The largest relative depletion of ozone outside the polar regions occurred prior to 1997 in the northern mid-latitude, upper stratosphere *(left panel)*. The largest recovery has occurred in the same region, with an upward trend of about 3% per decade since 2000 above 40-km altitude *(right panel)*. Ozone trends derived from satellite observations are shown in brown, with uncertainty ranges given by horizontal lines. Ozone trends derived from a set of chemistry-climate models are shown in orange, with the model variance given by the yellow envelope. Ozone trends from chemistry-climate models agree very well with the measured trends. [See also Figure 3-23]

Fig ES-7, *WMO/UNEP Ozone Report Executive Summary*

Three complications to understanding ozone trends in the lower stratosphere:
1) aerosol surface area; 2) bromine; 3) very short lived halogens not currently regulated

Bromine Source Gases



Halons:

- fire extinguishing agents
- production in developed world halted by Montreal Protocol
- present emissions primarily from "banks"

CH_3Br:

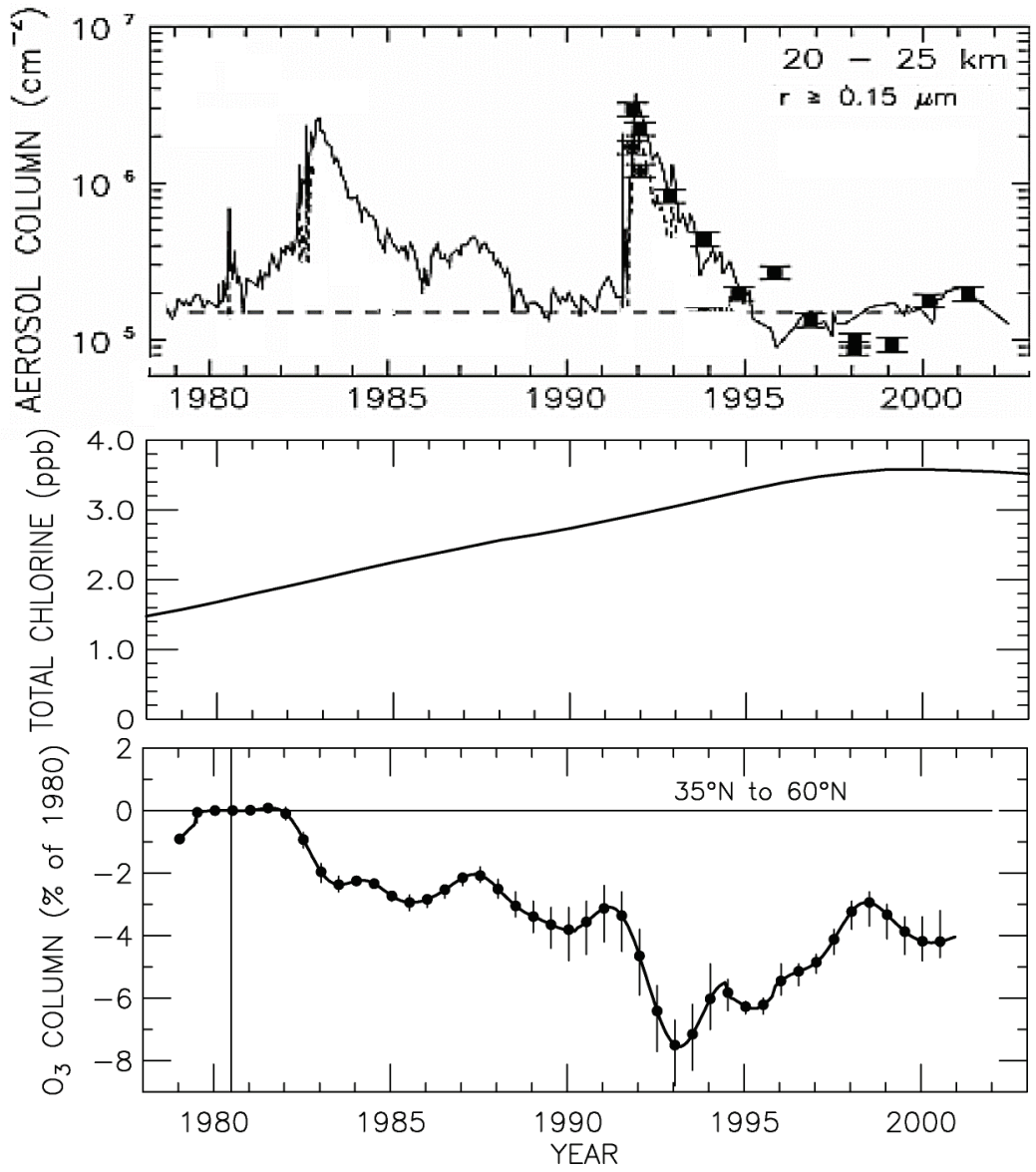
- fumigant; released by biomass burning
- production halted by Montreal Protocol
- significant natural & human sources

VSL Gases (e.g., $CHBr_3$, CH_2Br_2):

- emitted mainly by ocean biology
- not considered in many ozone calcs
- chemistry of decomposition products subject of active research

Fig Q6-1, *WMO/UNEP Twenty QAs Ozone*

Total Column Ozone Time Series, NH



Stratospheric aerosol loading,

Deshler et al., 2003.

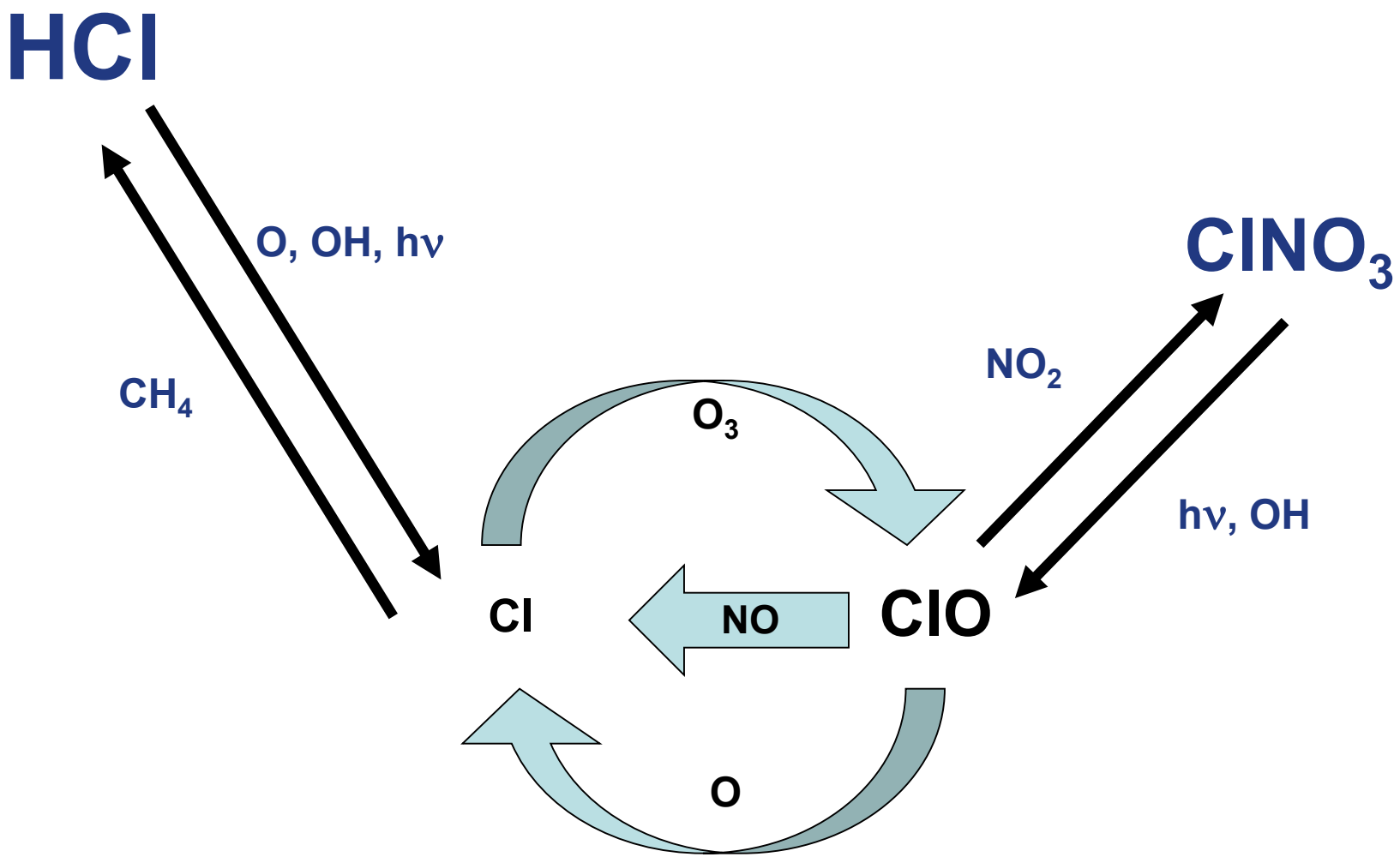
Stratospheric chlorine

Change in ozone column relative to 1980, 35 to 60°N

WMO/UNEP 2006 Ozone Report

Chemical reaction on surface of volcanic aerosol couples NO_2 and HNO_3

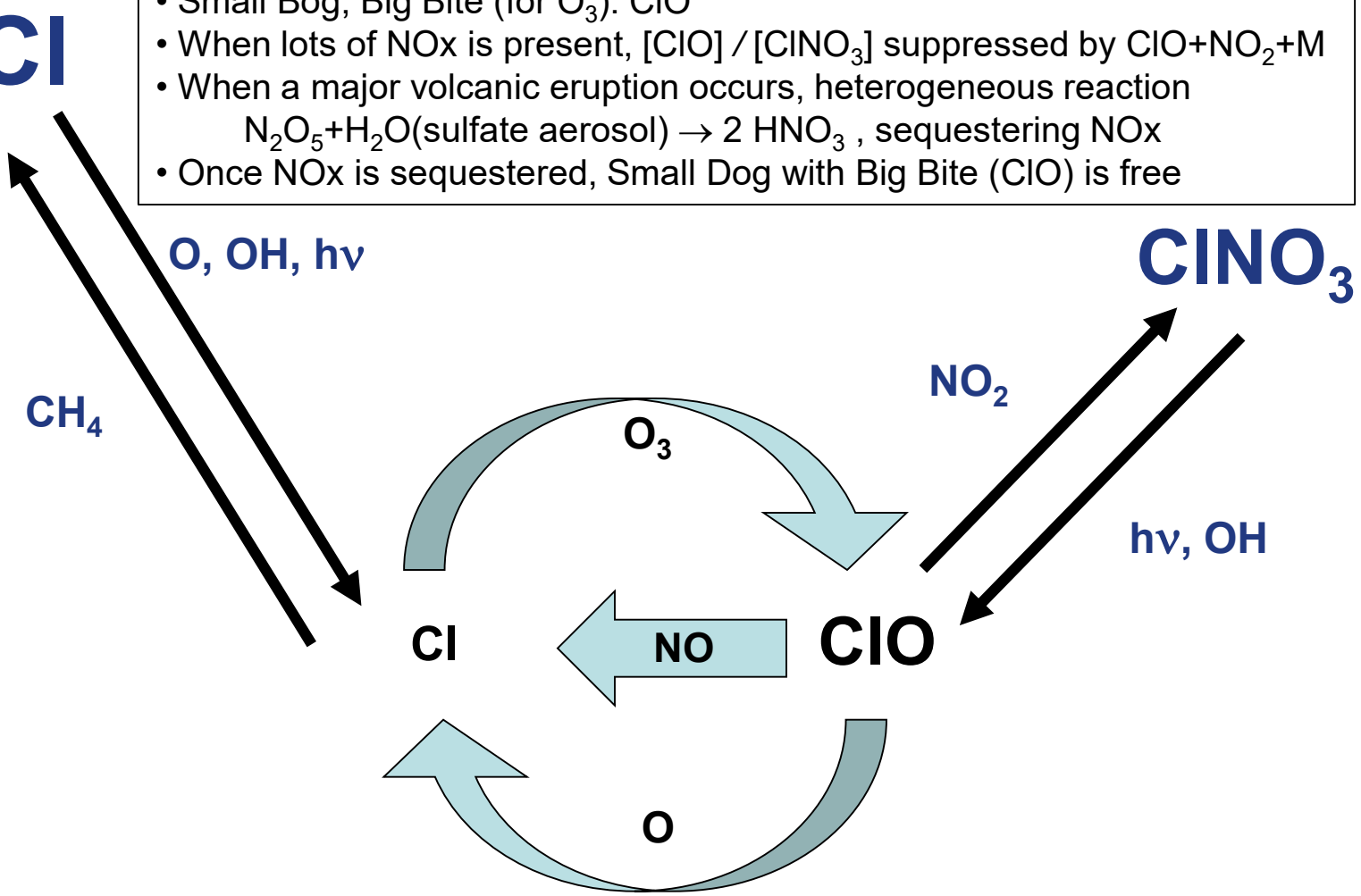
- As sulfate aerosol rises, NO_x (NO and NO_2) falls
- As NO_2 drops, $ClNO_3$ falls and ClO rises

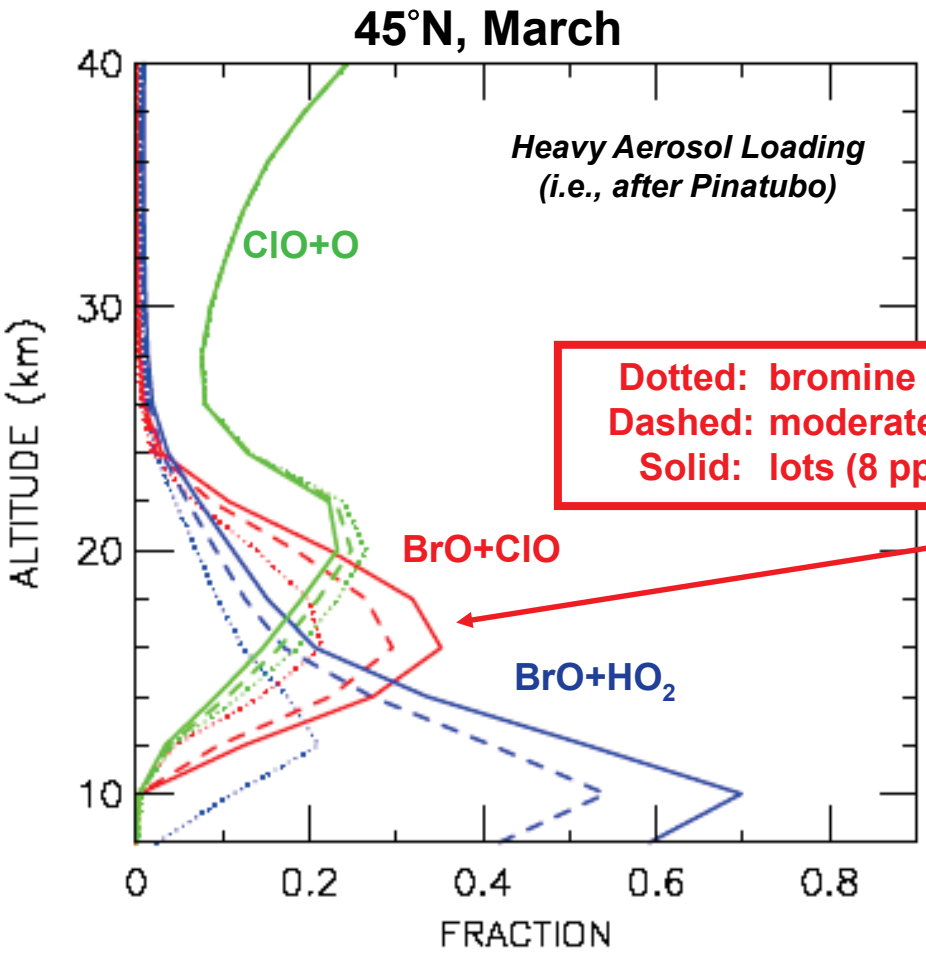


Chemical reaction on surface of volcanic aerosol couples NO_2 and HNO_3

- **As sulfate aerosol rises, NO_x (NO and NO_2) falls**
- **As NO_2 drops, $ClNO_3$ falls and ClO rises**

- Big Dogs in Chlorine Family: HCl & $ClNO_3$
- Small Bog, Big Bite (for O_3): ClO
- When lots of NOx is present, [ClO] / [$ClNO_3$] suppressed by ClO+NO_2+M
- When a major volcanic eruption occurs, heterogeneous reaction
  $N_2O_5+H_2O$(sulfate aerosol) → 2 HNO_3 , sequestering NOx
- Once NOx is sequestered, Small Dog with Big Bite (ClO) is free





Dotted: bromine from CH_3Br & halons only
Dashed: moderate (4 ppt) extra bromine from $CHBr_3$, CH_2Br_2, etc
Solid: lots (8 ppt) extra bromine from $CHBr_3$, CH_2Br_2, etc

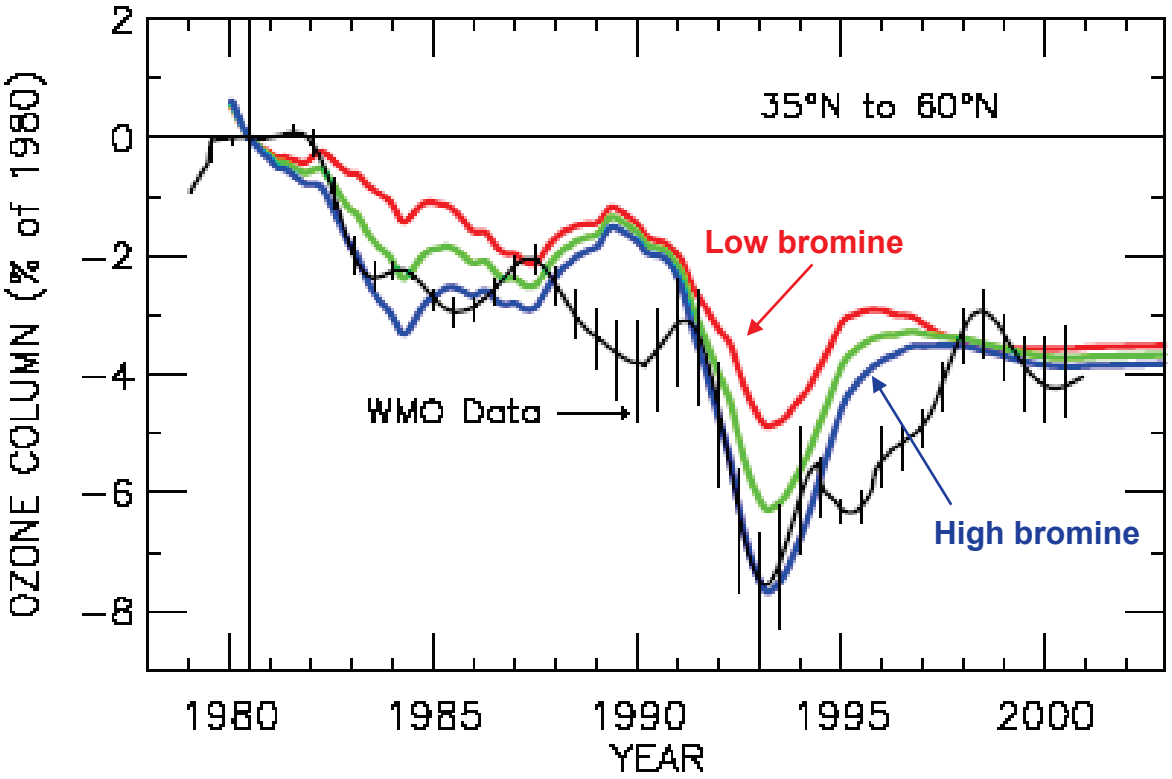
After Salawitch *et al.*, *GRL*, 2005

Ozone responds to:

a) rise and fall of chlorine

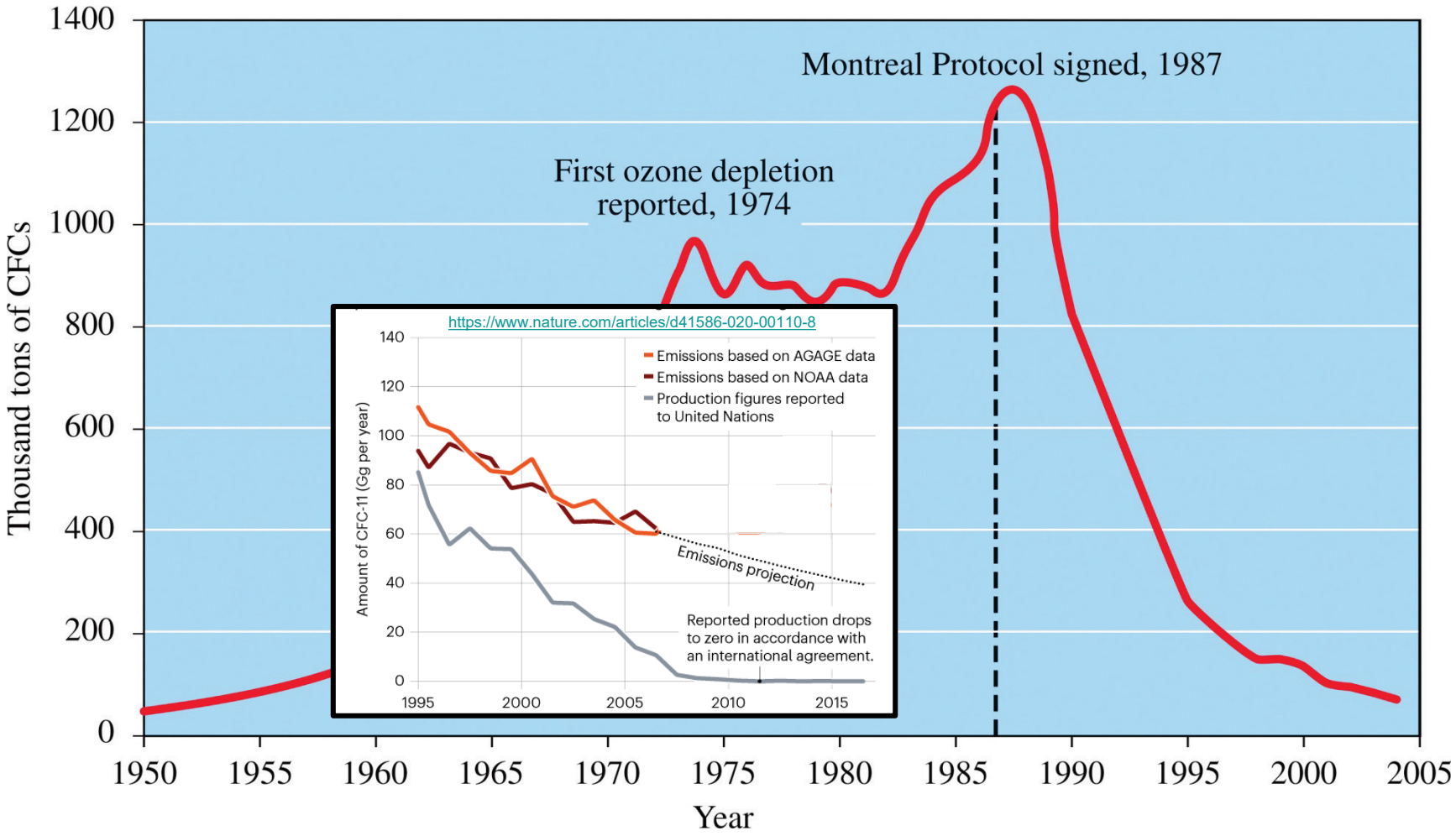
b) volcanic perturbations to aerosol loading

c) amount of bromine in lowermost stratosphere



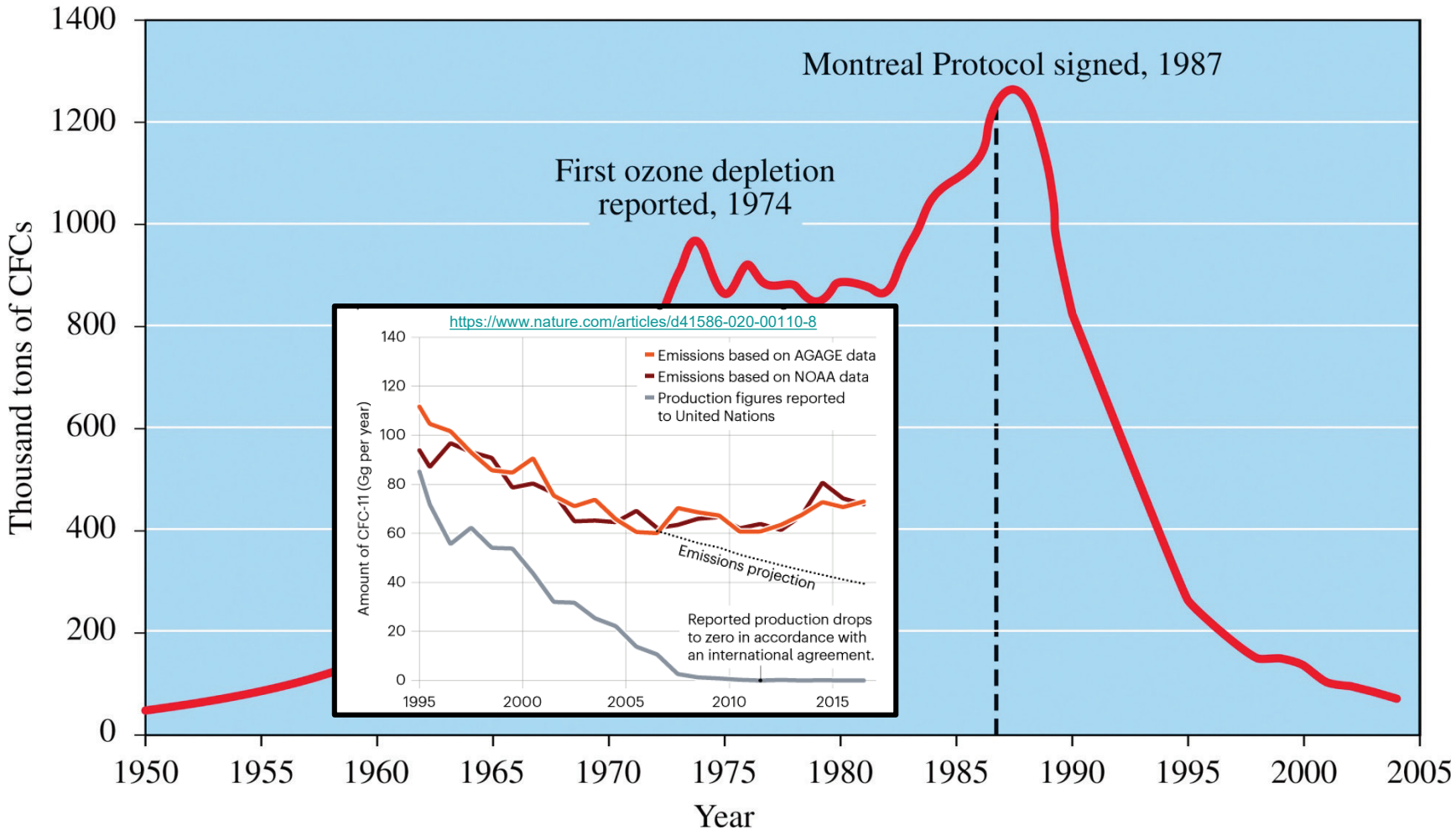
Salawitch *et al.*, *GRL*, 2005

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons



Global Production of CFCs, Fig. 2.19, Chemistry in Context

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons



Global Production of CFCs, Fig. 2.19, Chemistry in Context

Montreal Protocol Had Banned Most Industrial Production of CFCs & Other ODS

The New York Times

In a High-Stakes Environmental Whodunit, Many Clues Point to China

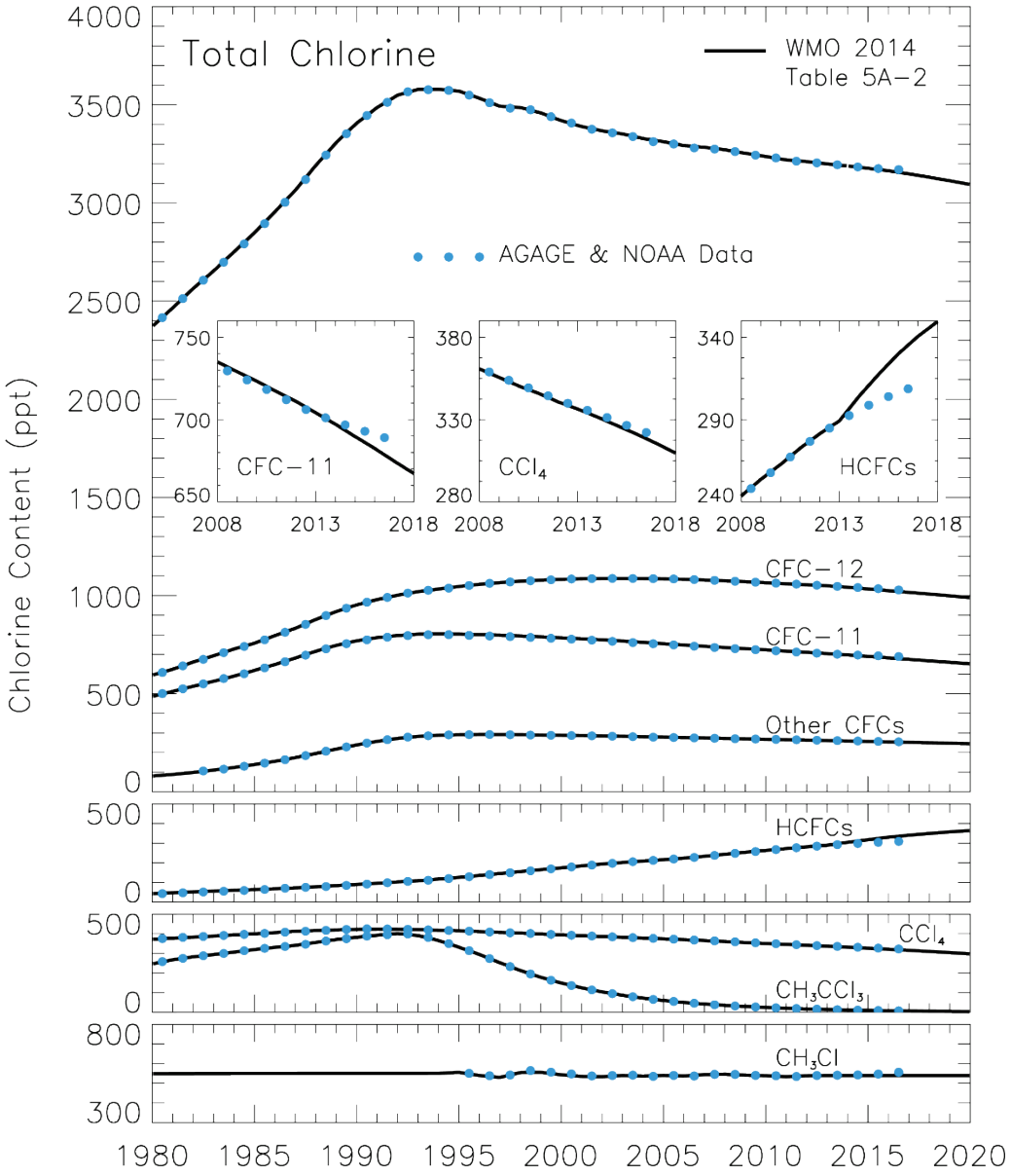
Interviews, documents and advertisements collected by The New York Times and independent investigators indicate that a major source — possibly the overwhelming one — is factories in China that have ignored a global ban and kept making or using the chemical, CFC-11, mostly to produce foam insulation for refrigerators and buildings.

"You had a choice: Choose the cheaper foam agent that's not so good for the environment, or the expensive one that's better for the environment," said Zhang Wenbo, owner of a refrigerator factory here in Xingfu, in Shandong Province, where he and many other small-scale manufacturers said that until recently, they had used CFC-11 widely to make foam insulation.

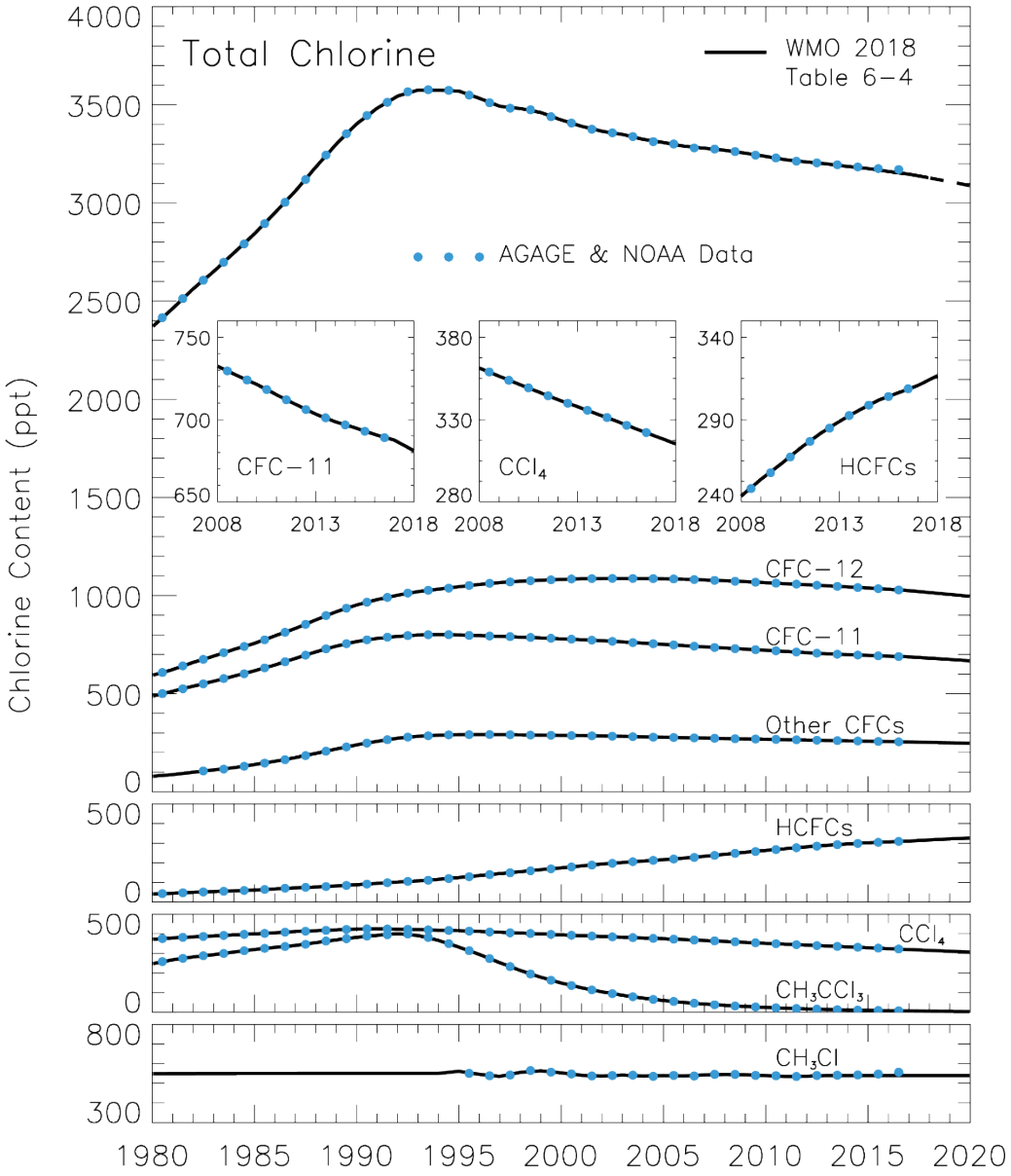
Billboards in Xingfu, China, promoting locally made refrigerators. The city has around 1,700 businesses involved in the production of cooking and refrigeration equipment. Gilles Sabrié for The New York Times

https://www.nytimes.com/2018/06/24/world/asia/china-ozone-cfc.html

Organic Halogens Versus Time



Organic Halogens Versus Time



Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons

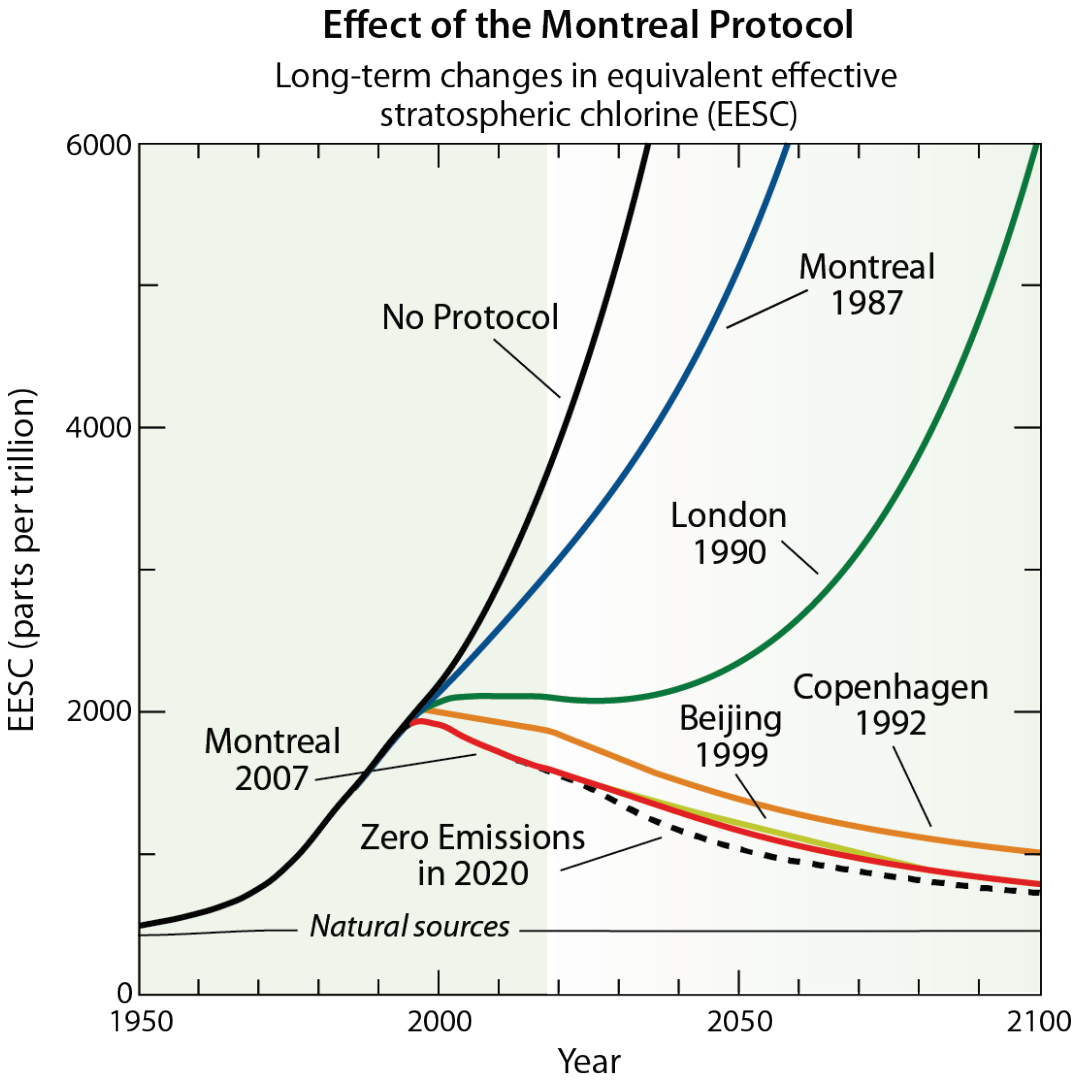
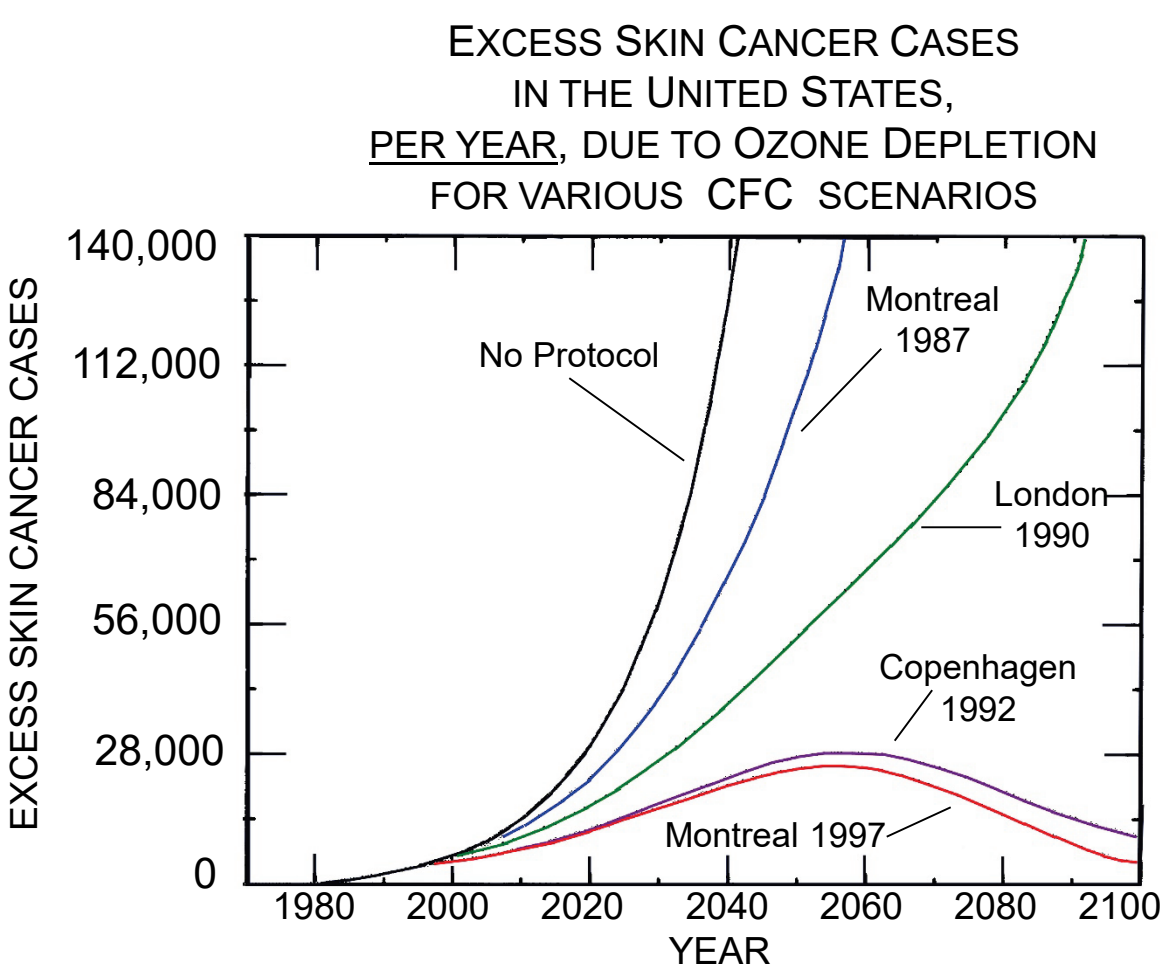


Fig Q14-1, *WMO/UNEP Twenty QAs Ozone*



Longstreth *et al.*, *J. of Photochemistry and Photobiology B*, 46, 20–39, 1998.

See also Slaper *et al.*, Estimates of ozone depletion and skin cancer incidence to examine the Vienna Convention achievements, *Nature*, *384*, 256–258, 1996, who state:

> The no-restrictions and Montreal Protocol scenarios produce a runaway increase in skin cancer incidence, up to a quadrupling and doubling, respectively, by year 2100.