Atmos. Chem. Lecture 8, 9/30/13: Stratospheric Chemistry 2

- Review: Ozone chemistry
- Bromine (and other halogens)
- Heterogeneous chemistry of NO_y
- Polar ozone loss
- Montreal Protocol

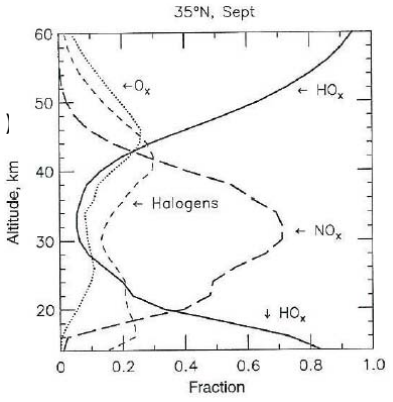
PSet 3 due Wednesday, Oct 9
No lecture Wed Oct 2; guest lecture Mon Oct 7

Review

Chemical families: O_x, HO_x, NO_x, ClO_x (+ BrO_x)

Chemical loss of "odd oxygen" ($[O_x] = [O_3]+[O] \approx [O_3]$)
by numerous channels:
- direct reaction ($O + O_3$)
- catalytic loss by HO_x, NO_x, ClO_x (+ BrO_x) radicals

Important couplings between families
Importance of reservoir species



S&P

Coupling of $HO_x/NO_x/ClO_x/BrO_x$

Removal of Stratospheric O_3 by Radicals: In Situ Measurements of OH, HO_2, NO, NO_2, ClO, and BrO

P. O. Wennberg,* R. C. Cohen, R. M. Stimpfle, J. P. Koplow, J. G. Anderson, R. J. Salawitch, D. W. Fahey, E. L. Woodbridge, E. R. Keim, R. S. Gao, C. R. Webster, R. D. May, D. W. Toohey, L. M. Avallone, M. H. Proffitt, M. Loewenstein, J. R. Podolske, K. R. Chan, S. C. Wofsy

Science 266:398 (1994)

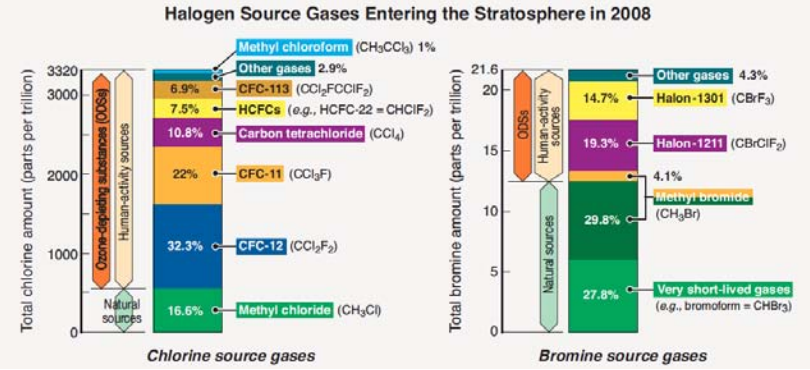
Image removed due to copyright restrictions. See Fig. 7 in Wennberg, P. O., et al. "Removal of Stratospheric O3 by Radicals: In Situ Measurements of OH, HO2, NO, NO2, ClO, and BrO." *Science* 266, no. 5184 (1994): 398-404.

Bromine

$Br + O_3 \rightarrow BrO + O_2$
$BrO + HO_2 \rightarrow HOBr + O_2$
$HOBr + h\nu \rightarrow OH + Br$
$OH + O_3 \rightarrow HO_2 + O_2$

$Br + O_3 \rightarrow BrO + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$BrO + ClO \rightarrow BrCl + O_2$
$BrCl + h\nu \rightarrow Br + Cl$

$Br + O_3 \rightarrow BrO + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$BrO + ClO \rightarrow ClOO + Br$
$ClOO + M \rightarrow Cl + O_2 + M$



WMO: Scientific Assessment of Ozone Depletion: 2010

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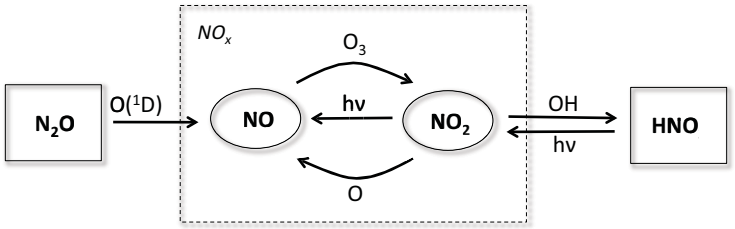
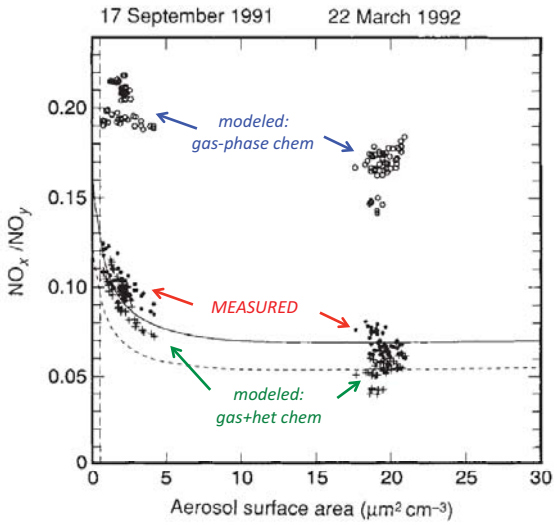
Revisiting NO_y chemistry



[Note: Additional material is discussed here during lecture.]

Overestimate of $[NO_x]/[HNO_3]$



Fahey et al. *Nature* 363:509 (1993)

Effects of N_2O_5 hydrolysis

Images removed due to copyright restrictions. See Fig. 15a and 15b in McElroy, M. B., R. J. Salawitch, et al. "The Changing Stratosphere." *Planetary and Space Science* 40, no. 2-3 (1992): 373-401.

McElroy et al., *Planet. Space Sci.*, 40:373 (1992)

Ozone hole"

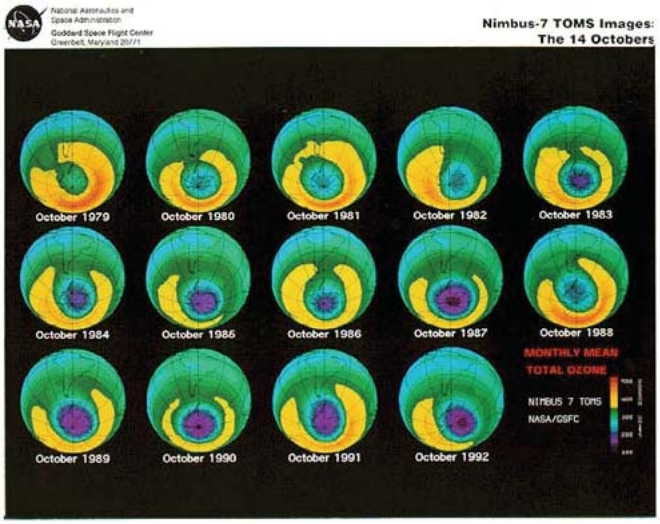
Abstract of the journal article removed due to copyright restrictions.

Nature 315:207 (1985)

Image removed due to copyright restrictions. See Fig. 1 in Jones, A. E., and J. D. Shanklin, "Continued Decline of Total Ozone over Halley, Antarctica, since 1985." *Nature* 376, no. 6539: 371-447.

Nature 376:409 (1995)

TOMS (Total Ozone Monitoring Satellite) Data



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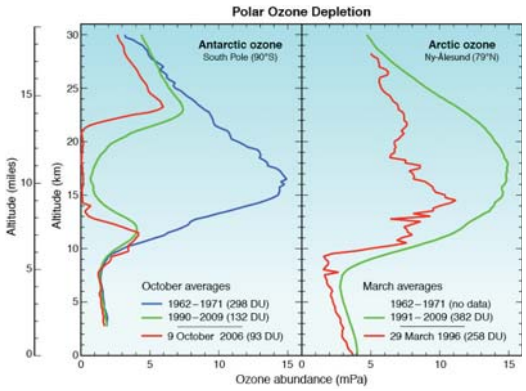
Profile of the "ozone hole"



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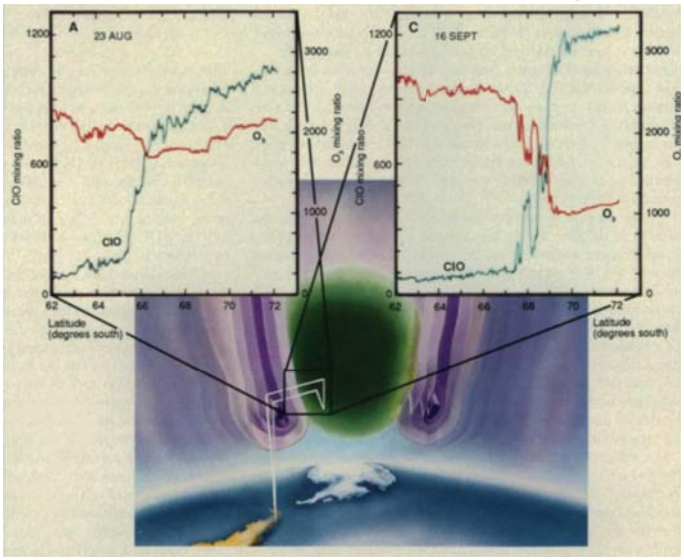
Suggested causes:

- O_3-poor tropospheric air
- solar events: high NO_x
- "Other theories too numerous to mention never made it beyond the popular press." (*Science* 251:39, 1991)

WMO: Scientific Assessment of Ozone Depletion: 2010

In Situ Measurements: ClO and O_3



Anderson et al. JGR 94:11465 (1989)
Anderson et al. *Science* 251:39 (1991)

One more catalytic cycle

[Molina and Molina, *J. Phys. Chem.* 91:433 (1987)]

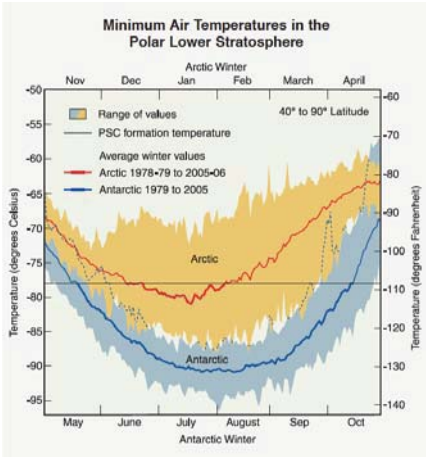
$$ClO + ClO + M \rightarrow ClOOCl + M$$
$$ClOOCl + h\nu \rightarrow ClOO + Cl$$
$$ClOO + M \rightarrow Cl + O_2 + M$$
$$2 \times (Cl + O_3 \rightarrow ClO + O_2)$$

[Note: Additional material is discussed here during lecture.]

Polar vortex

Polar night → air from upper stratosphere cools, descends

Large temperature gradients with lower latitudes → high westerly winds, seals off area



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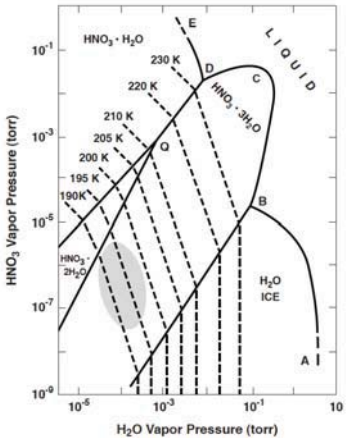
WMO: Scientific Assessment of Ozone Depletion: 2006

Polar Stratospheric Clouds (PSCs)

Binary solutions (H_2O + HNO_3) or ternary solutions (H_2O + HNO_3 + H_2SO_4)



1) HCl (*ads*) + $ClONO_2$ → Cl_2 + HNO_3(*ads*)
Solomon et al., *Nature* 321:755 (1986)

Other heterogeneous reactions also:
$ClONO_2$ + H_2O(*s*) → HOCl +HNO_3(*ads*)

2) Gravitational settling
Voigt et al., Science 290:1756 (2000)
Fahey et al., *Science* 291:1026 (2001)

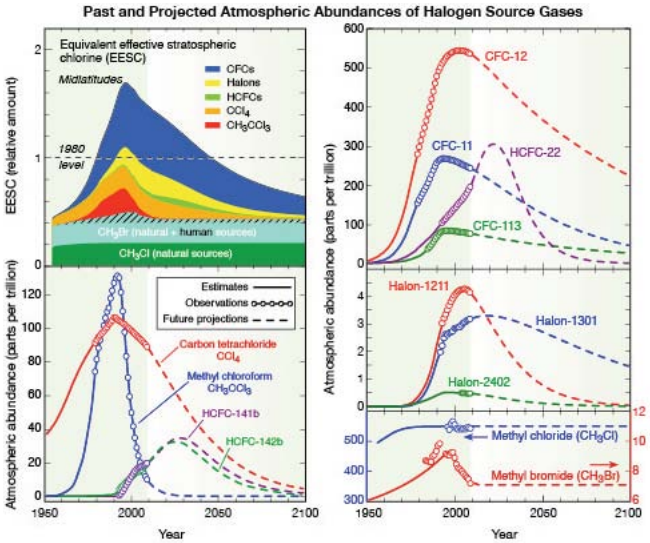
Jacob

Chronology of the "ozone hole"

Image removed due to copyright restrictions. See Figure 10-13 in Jacob, Daniel. *Introduction to Atmospheric Chemistry*. Princeton University Press, 1999.

Jacob

Montreal Protocol (1987, w/amendments)



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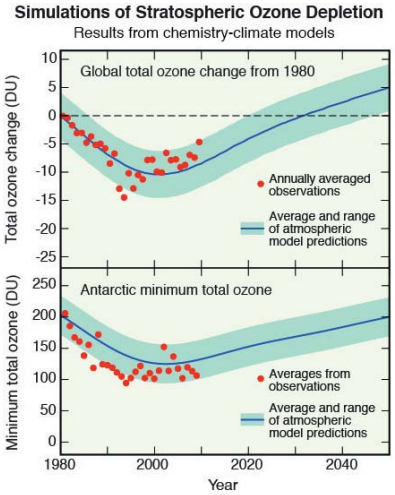
WMO: Scientific Assessment of Ozone Depletion: 2010

Recovery/prospects



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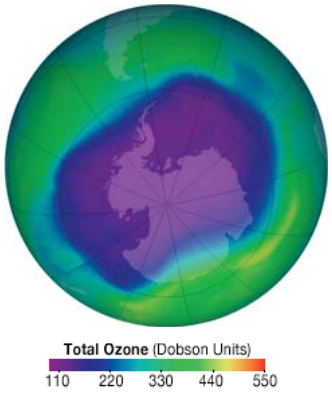
Largest ozone hole *ever*
September 24, 2006



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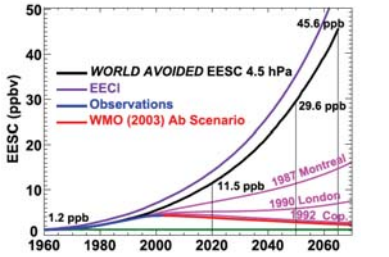
WMO: Scientific Assessment of Ozone Depletion: 2010

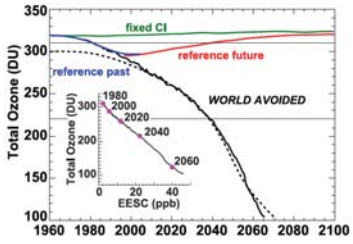
http://ozonewatch.gsfc.nasa.gov/daily.php?date=2006-09-24

"World Avoided"

Counterfactual: No regulation of CFCs [Newman et al, ACP 9:2113, 2009]

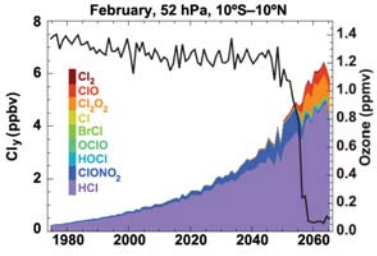
global (EESC=effective equivalent stratospheric chlorine)

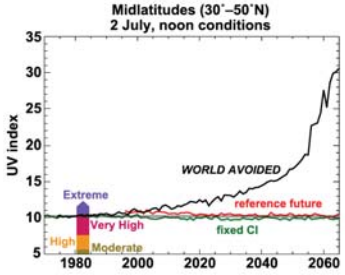




global

tropics





midlatitudes

(also, lower emissions of climate forcers)

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013