Chemistry 471/671

Atmospheric Chemistry IV:
Human Impact on the Stratosphere

The Ozone Hole

But where do the X-O species come from?

NO_2 comes from the photolysis of N_2O, a naturally occurring species

HO_2 comes from water, but the stratosphere is very cold, and very dry

BrO comes largely from CH_3Br, which is both a pesticide and a naturally occurring compound

ClO comes from a class of compounds called chlorofluorocarbons, or ***CFC***s

The Role of CFCs

What are CFCs?

- Compounds which contain only C, F, Cl
- Widely used examples: $CFCl_3$ ("F-11"), CF_2Cl_2 ("F-12")
- Nontoxic, nonflammable, nonreactive
- Replaced NH_3 and SO_2 as refrigerants
- Used to create bubbles in plastic foams
- Used as propellants in aerosol spray cans
- Used as residue cleaners in electronic fabrication

So… what's the problem?

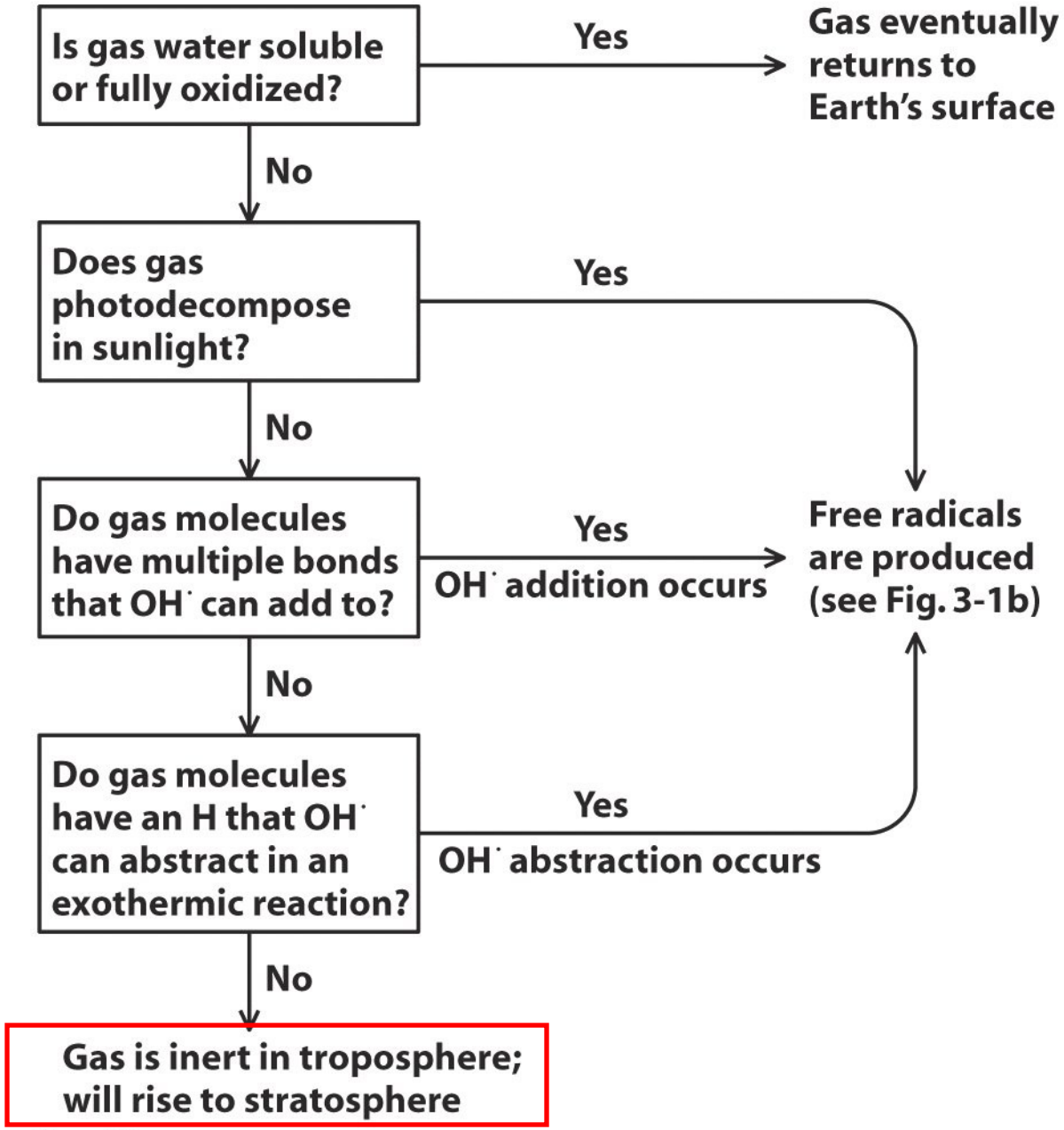


Figure 3-1a
Environmental Chemistry, Third Edition

The Role of CFCs

- The problem: CFCs are *so* nonreactive that they are completely inert in the troposphere
- They diffuse upward to the stratosphere, where they are exposed to shorter wavelength UV light
- Photolysis occurs, and F and Cl are released into the stratosphere, in the heart of the ozone layer

Other problematic compounds:

CCl_4 – widely used as solvent, dry-cleaning

CH_3Br - pesticide

CH_3CCl_3 - metal cleaning agent

Halons - contain Br in addition to C, F, Cl

Used as fire extinguisher

HCFCs – have largely replaced CFCs in developed nations

H abstraction pathways destroy most in the troposphere (and then...?)

BUT – the C-Cl bond is weaker than in CFCs, and its *short term* impact on O_3 is large

Other problematic compounds:

HCFCs – a temporary solution, and regulated as such

The long-term solution appears to be HFCs

Why? HFCs which reach the stratosphere will still release F atoms

But F reacts rapidly with methane to form HF, which is remarkably stable

F atoms form extremely stable reservoir species which are **not** re-activated by photolysis or on PSC surfaces

Regulation of CFCs

The U.S. banned CFCs in spray aerosols in 1978, but international regulation was required

1985 saw the Vienna Convention on the Protection of the Ozone Layer, which led to scientific discussion, but the science wasn't well understood

The Montreal Protocol was signed in 1987, and made sweeping changes

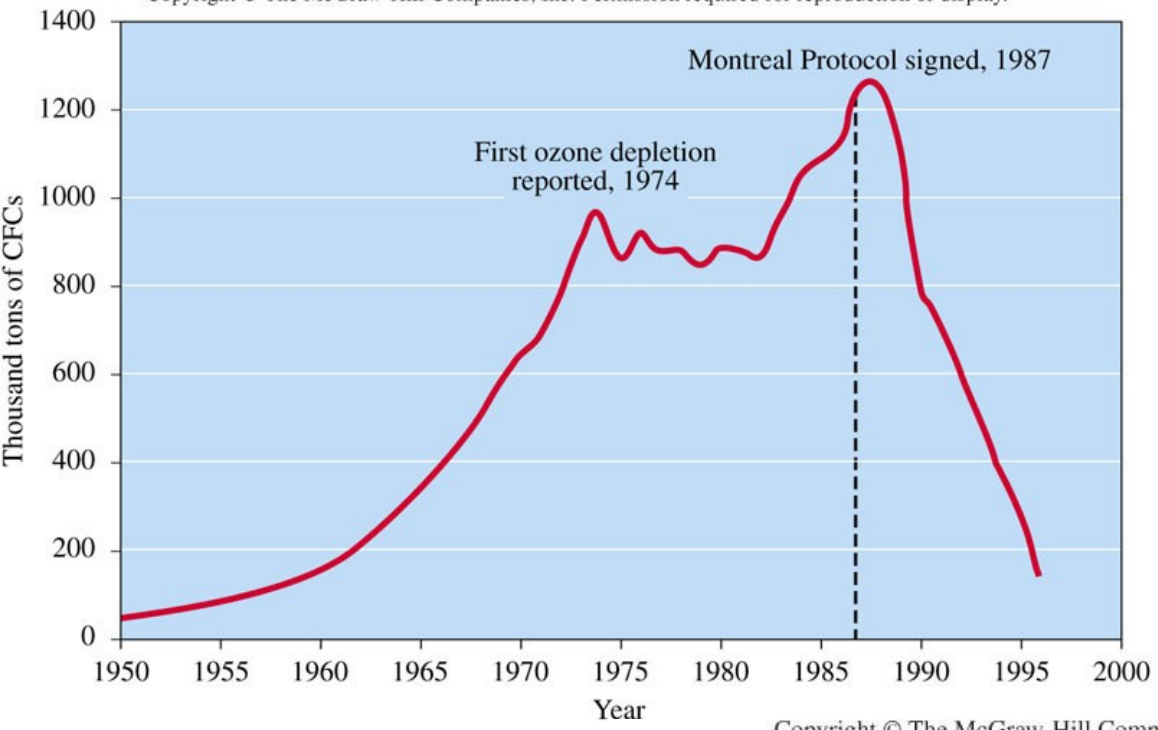
Kofi Annan: "[It is] perhaps the single most successful international agreement to date..."

Regulation of CFCs – The Montreal Protocol

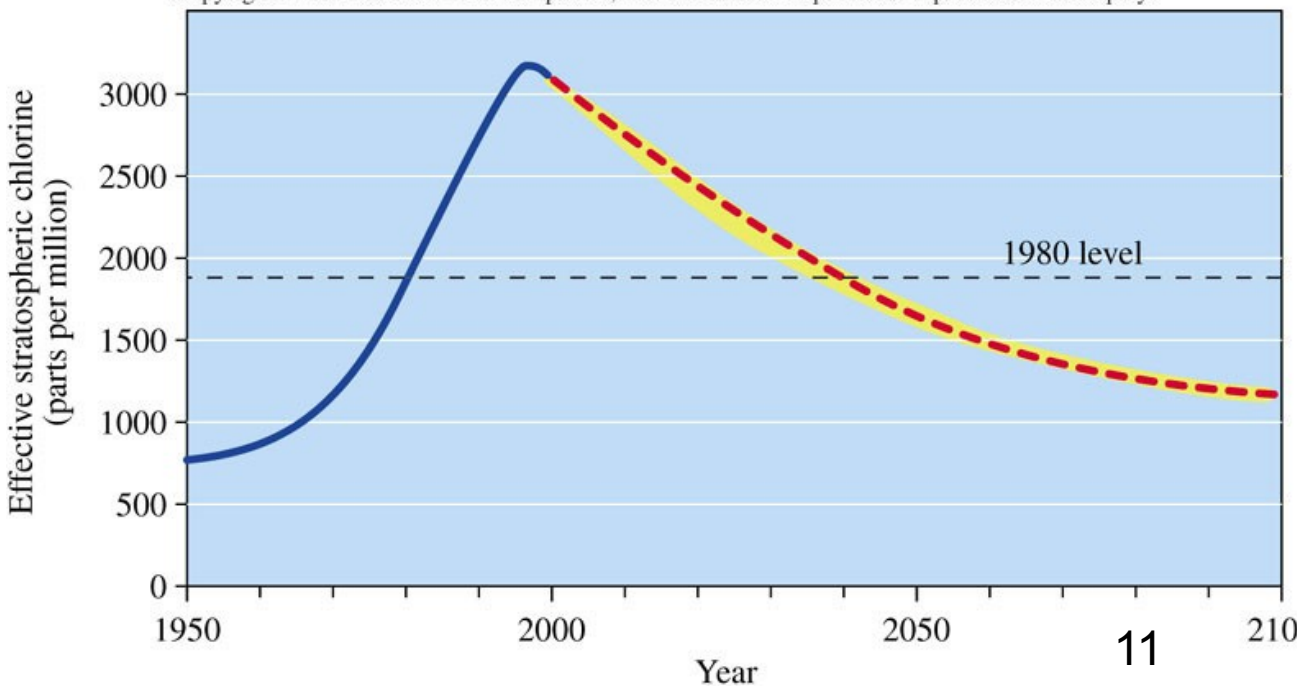
- Developed countries ceased CFC production by 1995, along with CCl_4 and CH_3CCl_3, and agreed to cease HCFC production by 2030
- Developing nations pledged to stop CFC production by 2010 and HCFCs by 2040
- Halon production banned in developed countries in 1994
- Developing countries have until 2010
    - China, Korea have been problematic
- CH_3Br banned in developed countries in 2005
    - Developing countries have until 2015

Regulation of CFCs – The Montreal Protocol

- Bound nations to reduce their CFC output to one half of 1986 levels by 1998
- Required future meetings to revise standards
- In 1990, 100+ nations agreed to halt CFC production altogether by 2000, and this phase-out was accelerated further at later meetings
- The Beijing Amendment of 1999 added bromine-containing “halons” …
- ... AND required the regulation of the short-term replacement HCFCs
- Important provisions were made for developing nations whose economies couldn’t sustain the mandated changes



Global Production of CFCs



Stratospheric concentrations of chlorine

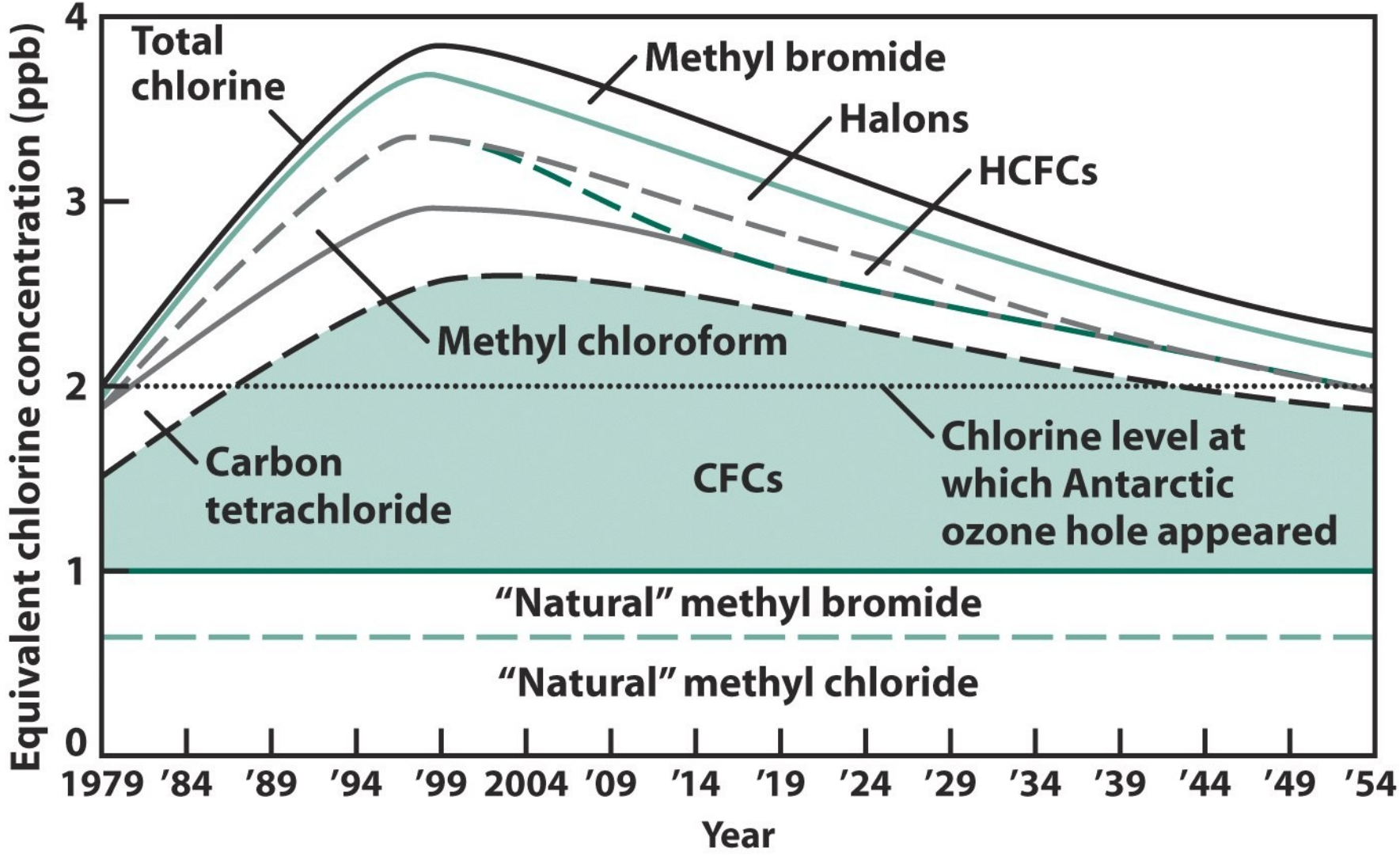


Figure 1-21
Environmental Chemistry, Third Edition

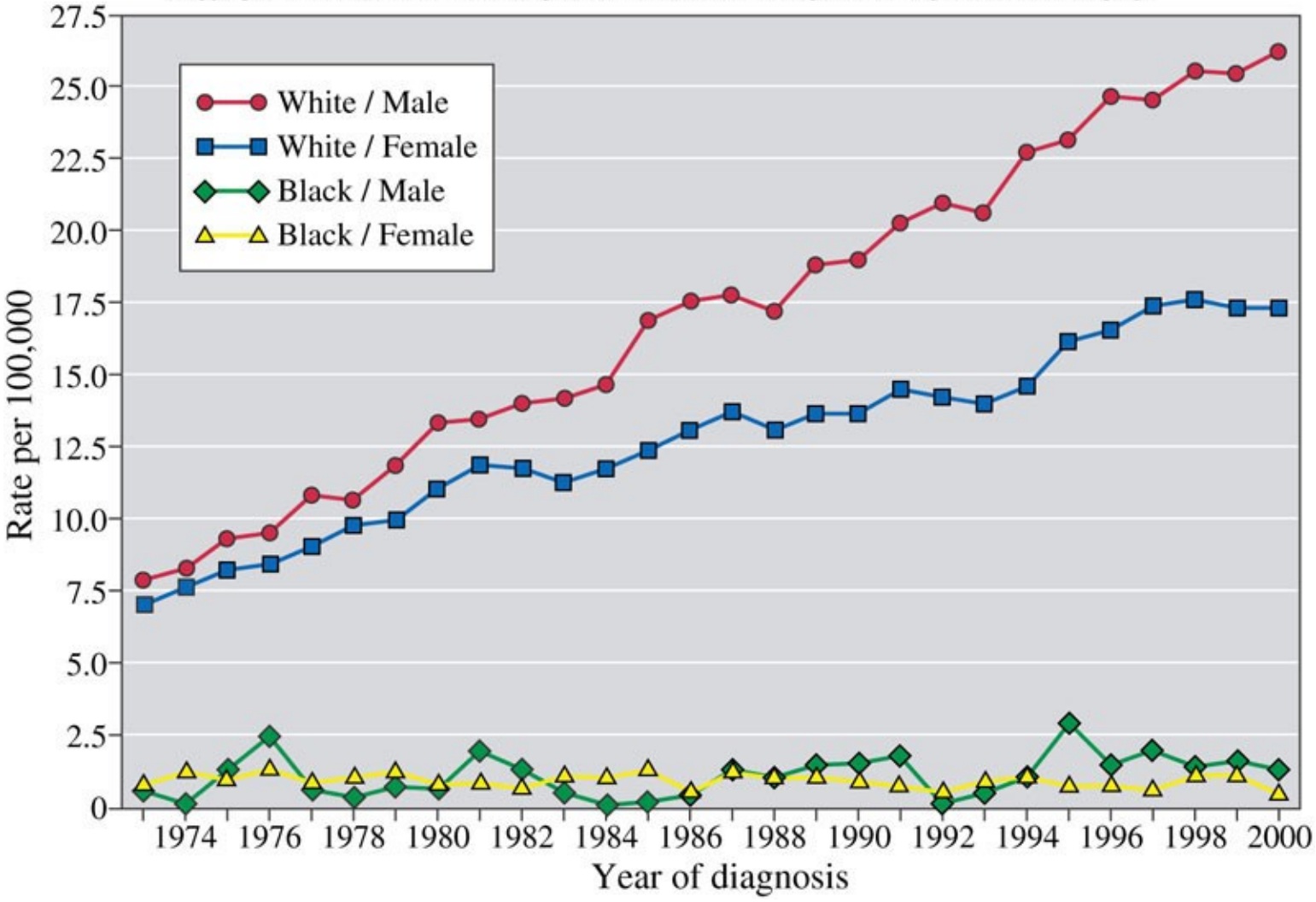
Ozone Depletion

In addition to the isolated and seasonal depletion of ozone over the poles, there has been a steady ~4% per decade decline in stratospheric ozone throughout the world

Halogens? Sulfate aerosols? Meteorology?

Some combination?

Biological Effects of Ultraviolet Radiation



Most reports indicate that a given % reduction in O_3 concentration will produce about twice that % increase in skin cancer

Mid-latitude ozone depletion

There has been recent evidence of sporadic, isolated events where ozone levels at **mid-latitudes** are dramatically reduced

This cannot be explained by the polar vortex or by the presence of PSC particles

There is a lively debate about how this occurs... Which we don't have time to cover

A fine presentation topic?

Unforeseen consequences:

The long-term solution appears to be HFCs

BUT...

1) OH + HFC $\rightarrow \rightarrow \rightarrow CF_3COOH$

   Trifluoroacetic acid (TFA)

   Water soluble – rains out

   What happens then?

2) HFCs have atmospheric lifetimes of decades

   HFCs have strong IR absorptions

   HFCs are almost certainly Greenhouse Gases