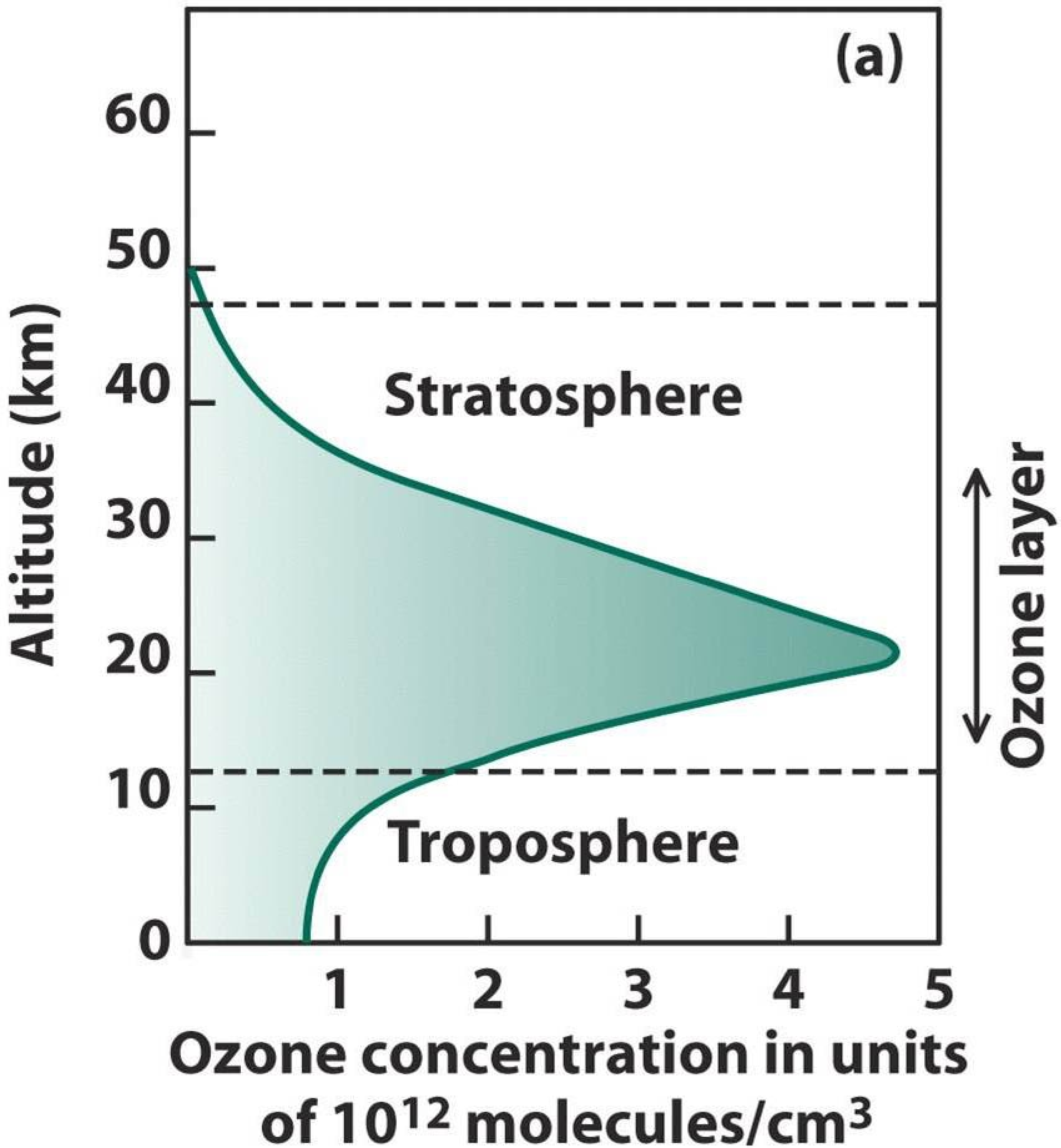
Chemistry 471/671

Atmospheric Chemistry III:
Stratospheric Ozone Depletion


(a)
60
50
40
30
20
10
0
Altitude (km)
Stratosphere
Troposphere
Ozone layer
1
2
3
4
5
Ozone concentration in units
of 10^{12} molecules/cm^3

The Chapman Mechanism

$$O_2 + h\nu \rightarrow 2\ O(^1D)$$

$$O(^1D) + O_2 + M \rightarrow O_3 + M$$ *Exothermic*

$$O(^1D) + O_3 \rightarrow 2\ O_2$$

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta_g)$$ *Exothermic*

How does this mechanism explain the highly localized ozone layer?

Steady State

What does it mean to say that a species is in “Steady State”?

The concentration of the given species doesn’t change significantly with time

Like Equilibrium, this does NOT mean that individual molecules are not being created or destroyed…

… but the *rate of creation* is equal to *the rate of destruction*

OR *sources* = *sinks*

This knowledge can be used to infer important kinetic information about a system

Note: Equilibrium can be seen as a special case of Steady State where the source for one species is the sink of its equilibrium counterpart

Actinic Flux

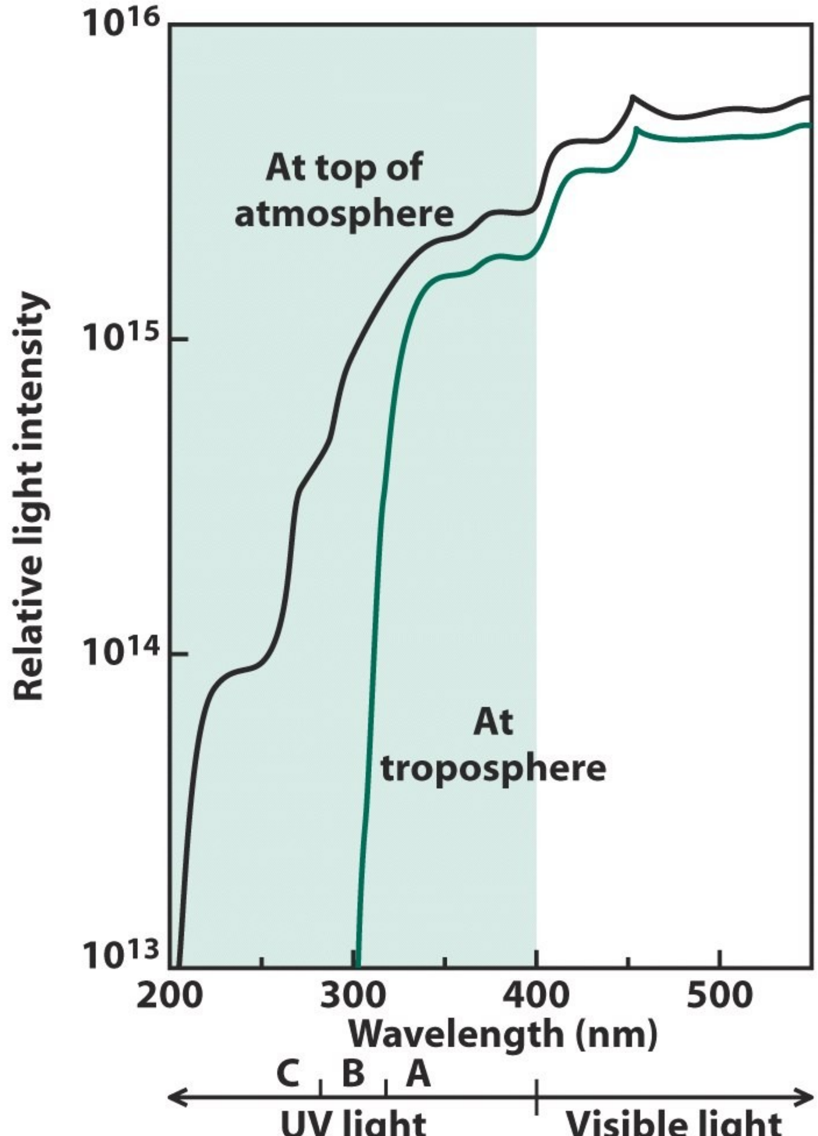


Figure 1-9
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Absorption Spectrum of Human DNA

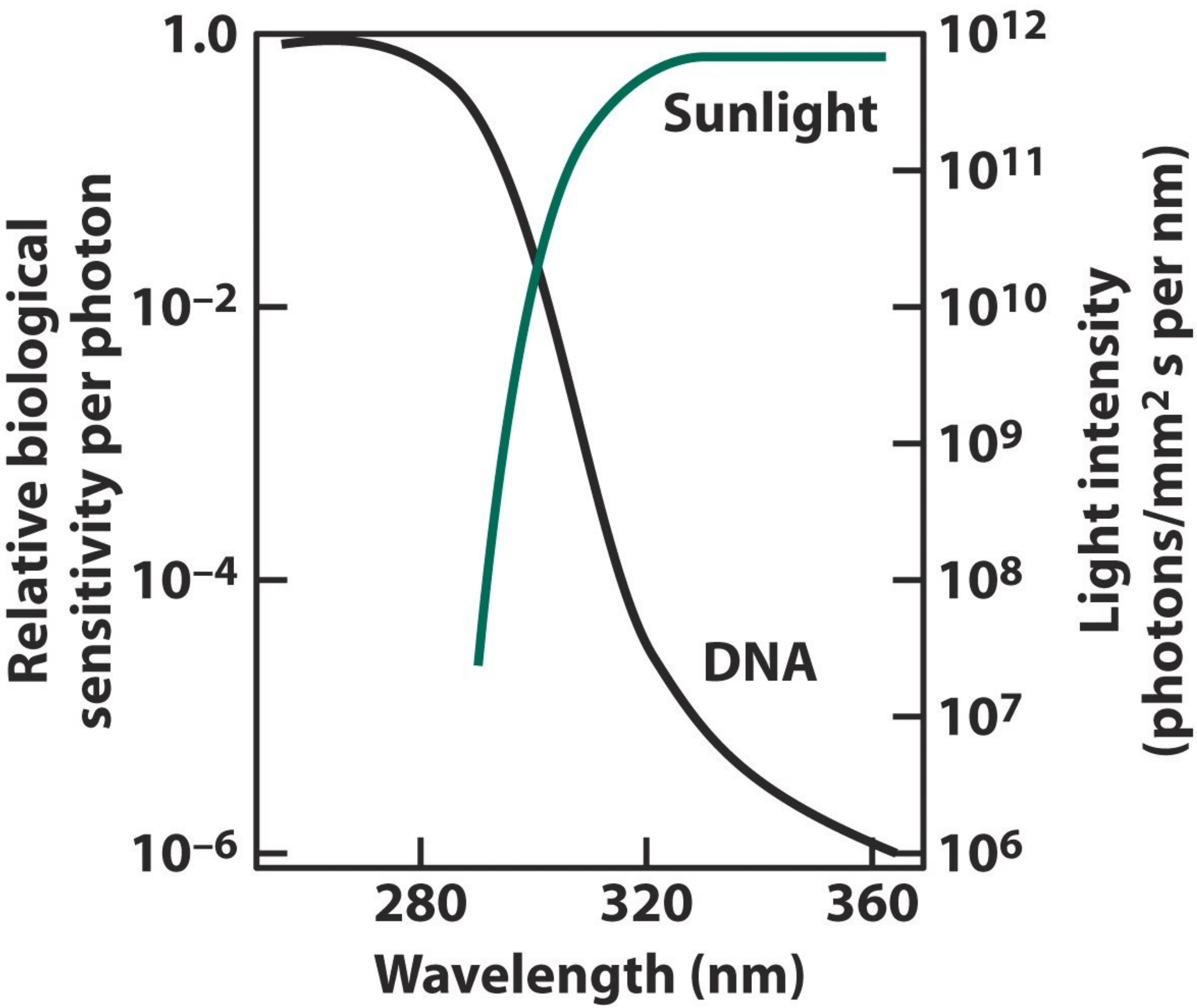

Figure 1-10
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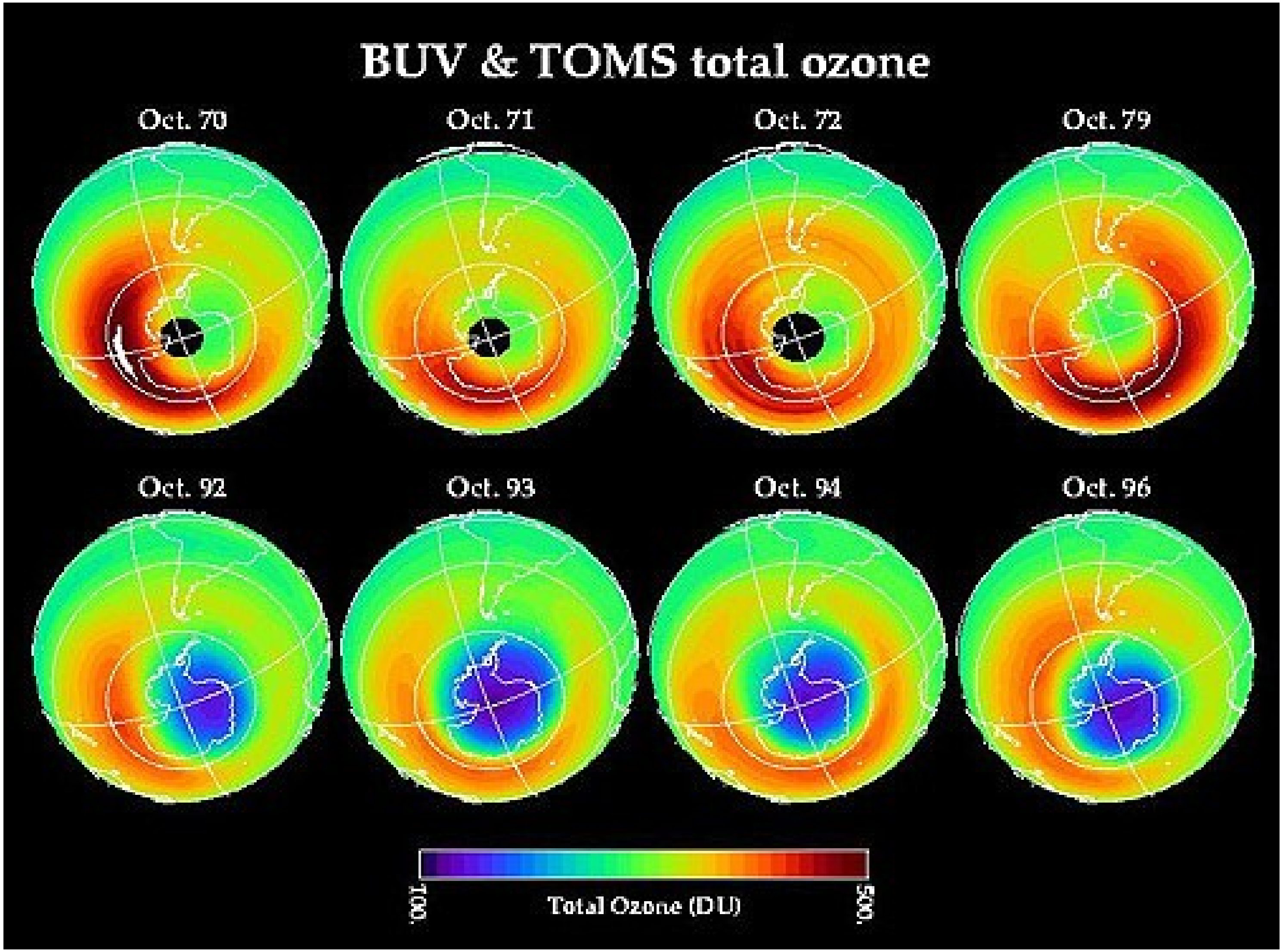
An Aside – Dobson Units (DU)

The total amount of ozone (or any other gas) that lies over a given point can be measured in terms of Dobson units.

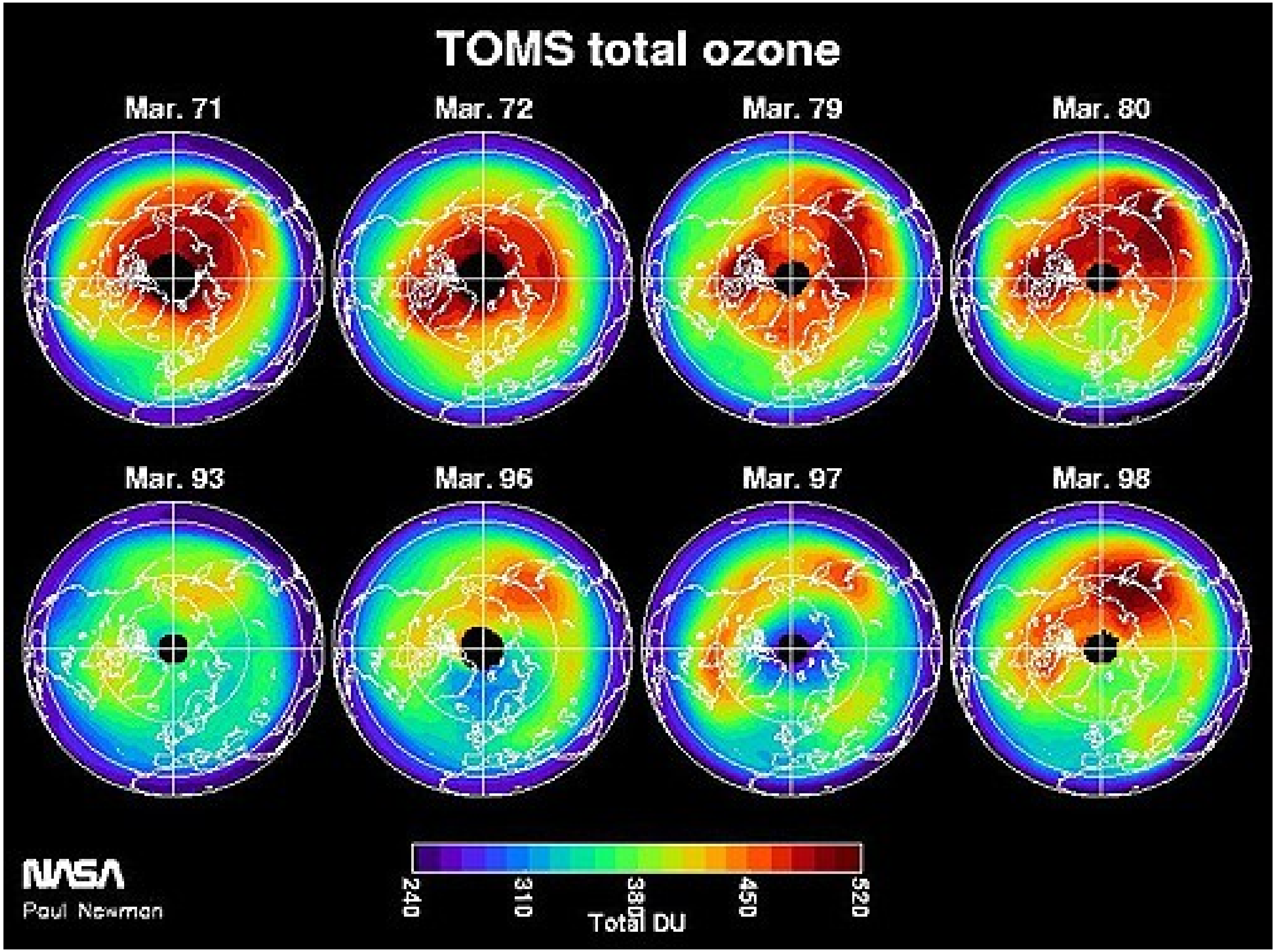
One DU is equivalent to a 0.01 mm thickness of the pure gas at the density it would possess if the entire column were brought to STP: 1 atm of pressure and 273 K.

The global average in temperate latitudes is approximately 350 DU; if all of the ozone above our heads were brought to STP, it would measure only 3.5 mm thick.

Polar Ozone Depletion – The “Ozone Hole”



Polar Ozone Depletion – The "Ozone Hole"



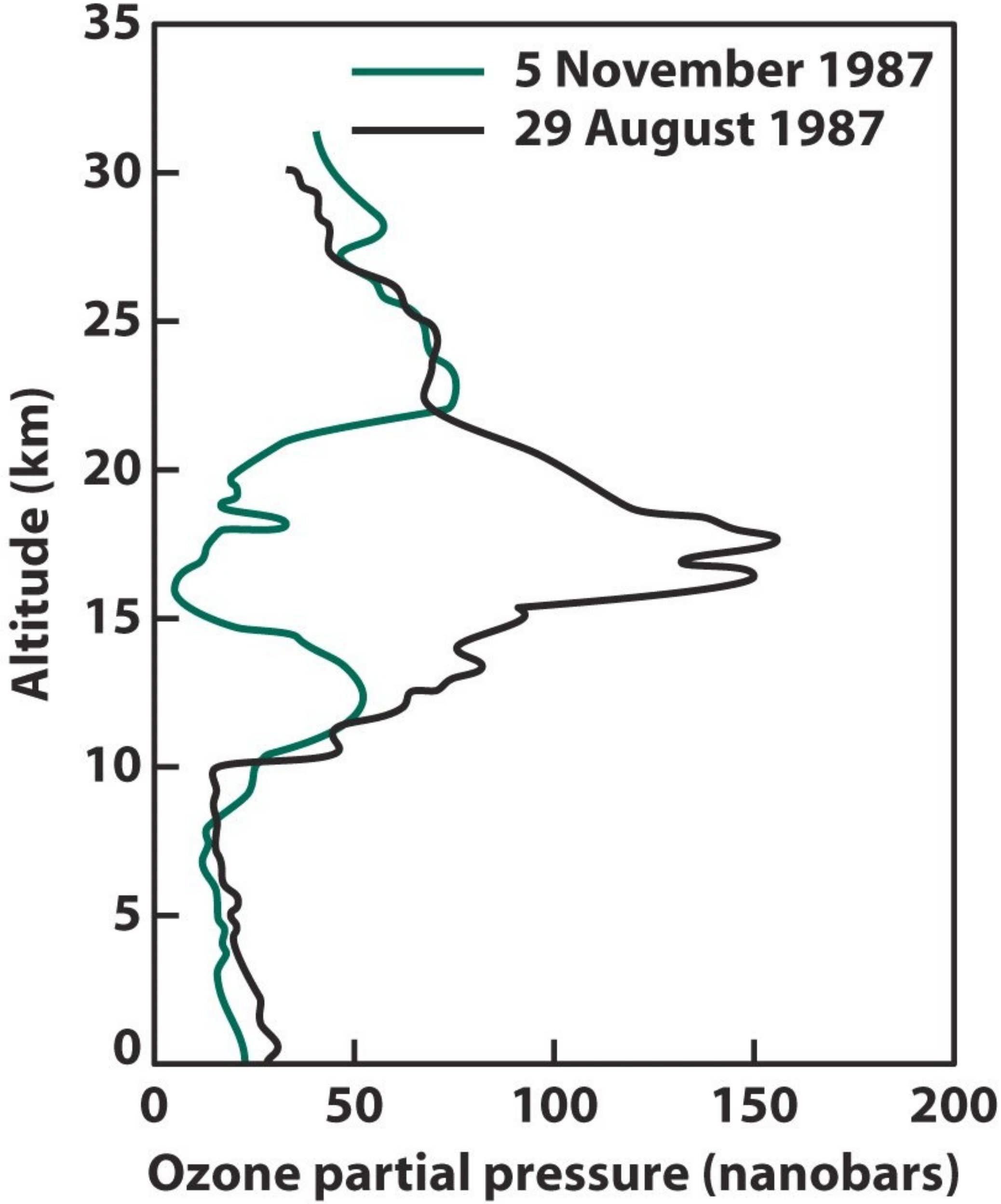


Figure 1-18
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Ozone Depletion

We've shown that the chemistry of the atmosphere is dominated by the reactions of radicals

But what reactions lead to the ozone hole?

Radical-initiated catalysis

What does catalysis mean?

Mechanism I

If X = Cl,
k(298) = 1.2x10^{-11}

$$X + O_3 \rightarrow XO + O_2$$

k(298) = 3.8x10^{-11}

$$XO + O \rightarrow X + O_2$$

$$O_3 + O \rightarrow 2\,O_2 \qquad \textbf{overall}$$

k(298) = 8.0x10^{-15}

Figure 1-15 part 1
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Mechanism II

$$X + O_3 \rightarrow XO + O_2$$

$$X' + O_3 \rightarrow X'O + O_2$$

$$XO + X'O \rightarrow \rightarrow X + X' + O_2$$

$$2\,O_3 \rightarrow 3\,O_2 \qquad \text{overall}$$

Figure 1-15 part 2
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Ozone Depletion – radical catalysis

Driven by molecules with "loosely bound" oxygen

"Loose" oxygens are joined by a single bond to another electronegative atom possessing nonbonded lone pairs

The interaction of nonbonded electron pairs weakens the single bond

Ozone Depletion – radical catalysis

Molecule X-O	X-O Bond Energy(kJ/mol)
O_3	107
BrO	235
HO_2	266
ClO	272
NO_2	305

(For comparison: C-C 348, C-O 358, C-H 413
C=C 614, C=O 799)

The Ozone Hole
Gas Phase Loss Processes

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O_3 \rightarrow OH + 2\ O_2$

Net: $2\ O_3 \rightarrow 3\ O_2$

"HO_x"

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

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

"NO_x"

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

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

"ClO_x"

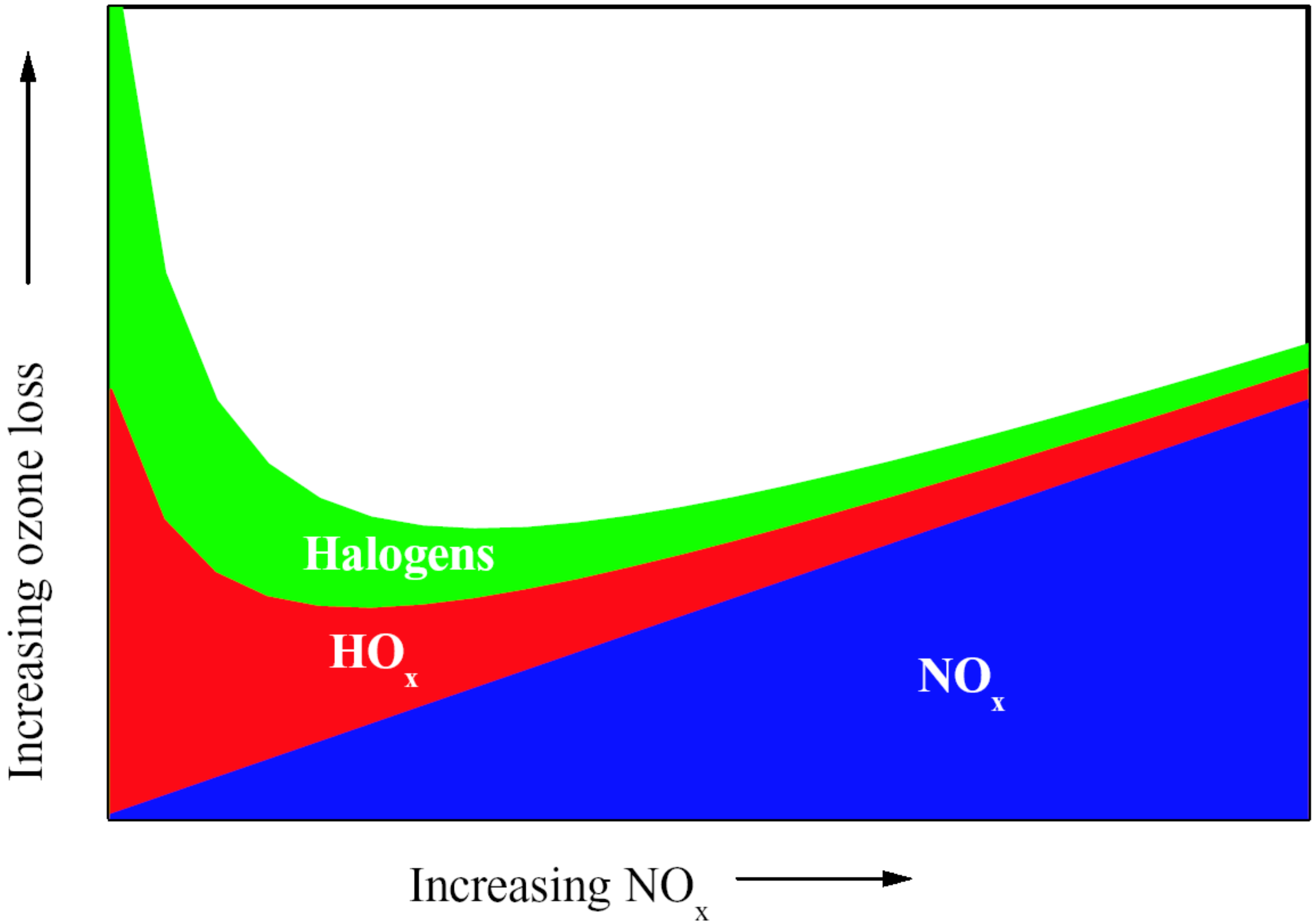
Terminating reactions:

$ClO + NO_2 \rightarrow ClONO_2$

$OH + NO_2 \rightarrow HNO_3$

$OH + ClO \rightarrow HOOCl$

The Ozone Hole
Gas Phase Loss Processes



The Ozone Hole

But…

Why only at the poles?

Why only in the spring?

Well, what’s unique about the poles, particularly when it comes to the seasons?

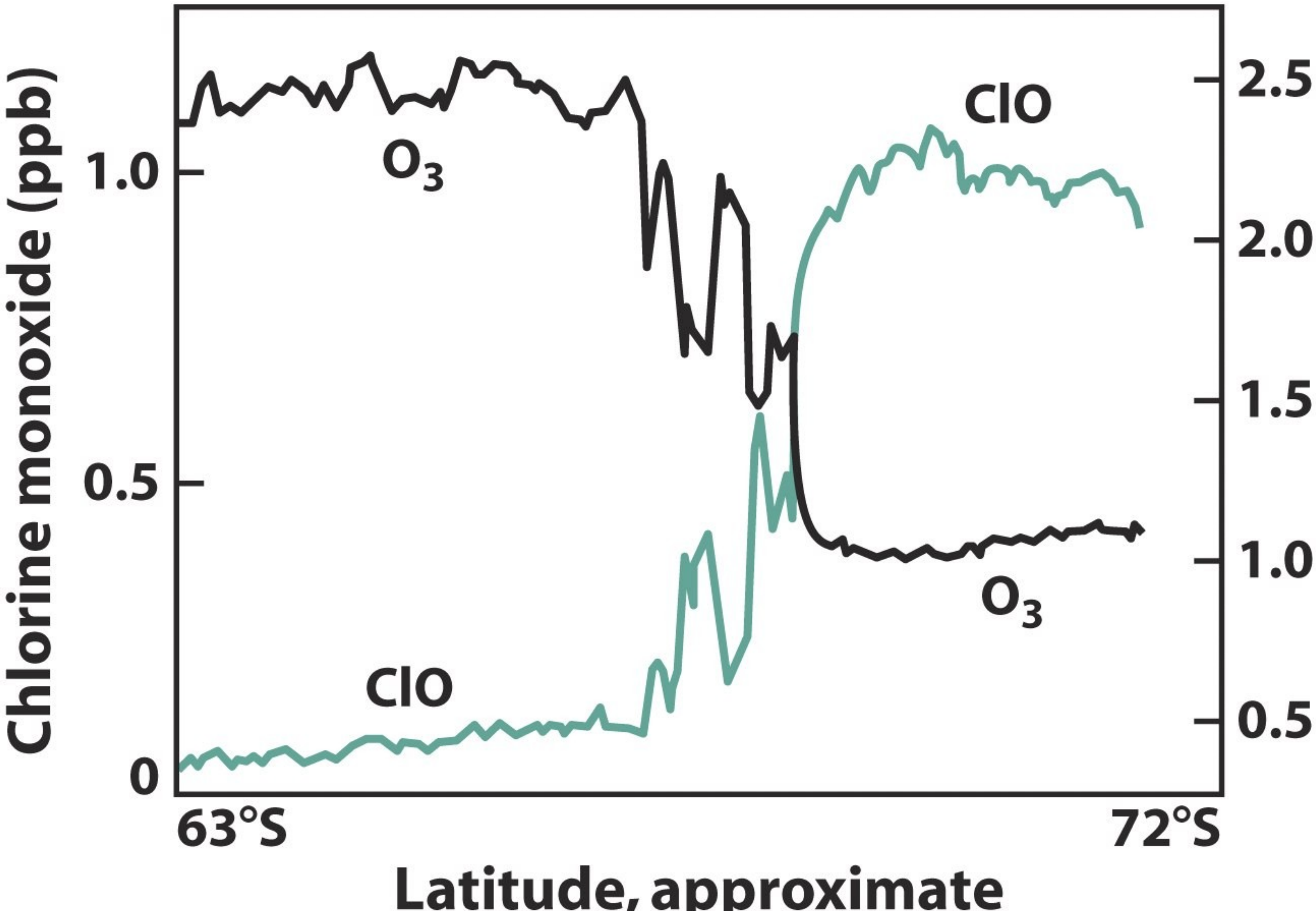


Figure 1-17
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The Ozone Hole
Gas Phase Loss Processes

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

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

"ClO_x"

Mechanism I

$$2 \text{ x } (Cl + O_3 \rightarrow ClO + O_2)$$
$$ClO + ClO \rightarrow ClOOCl$$
$$Cl_2O_2 + h\nu \rightarrow ClOO + Cl$$
$$ClOO \rightarrow Cl + O_2$$

Net: $2\ O_3 \rightarrow 3\ O_2$

"ClO_x"

Mechanism II

But WHY is there such a localized concentration of ClO?

The Ozone Hole

The Antarctic polar vortex

Forms when the sun goes down for 6 months, leading to dramatically cooled air and a descending air mass

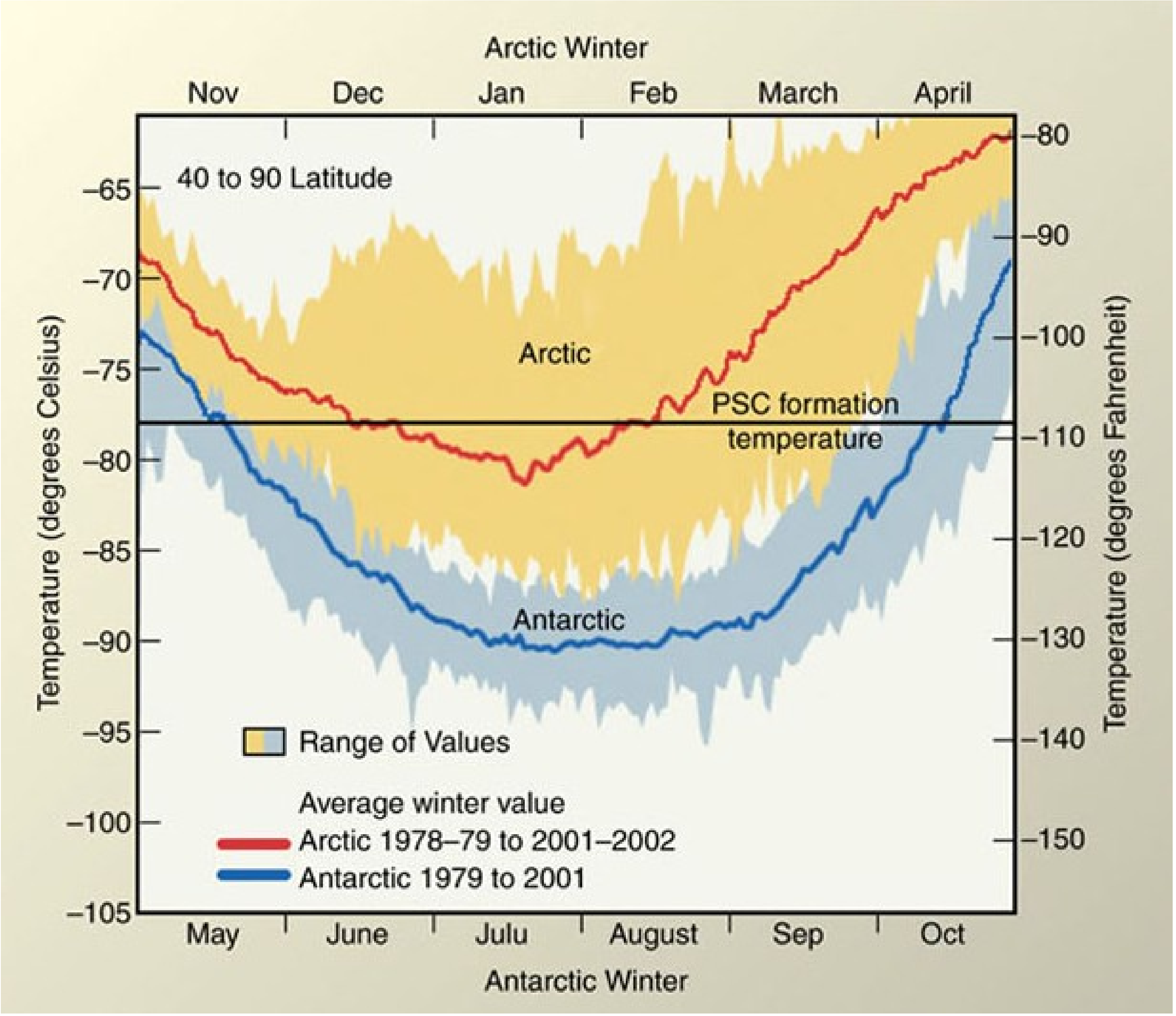
Isolates the pole from the rest of the stratosphere with winds up to 300 km/hr

Strat. temperatures reach as low as 183 K

Under these conditions, Polar Stratospheric Clouds form from gas phase HNO_3, removing NO_x from the gas phase (“denitrification”)

At the same time, the PSCs provide surfaces for *heterogeneous* reactions which activate the Chlorine reservoir

The Antarctic Ozone Hole: A Closer Look



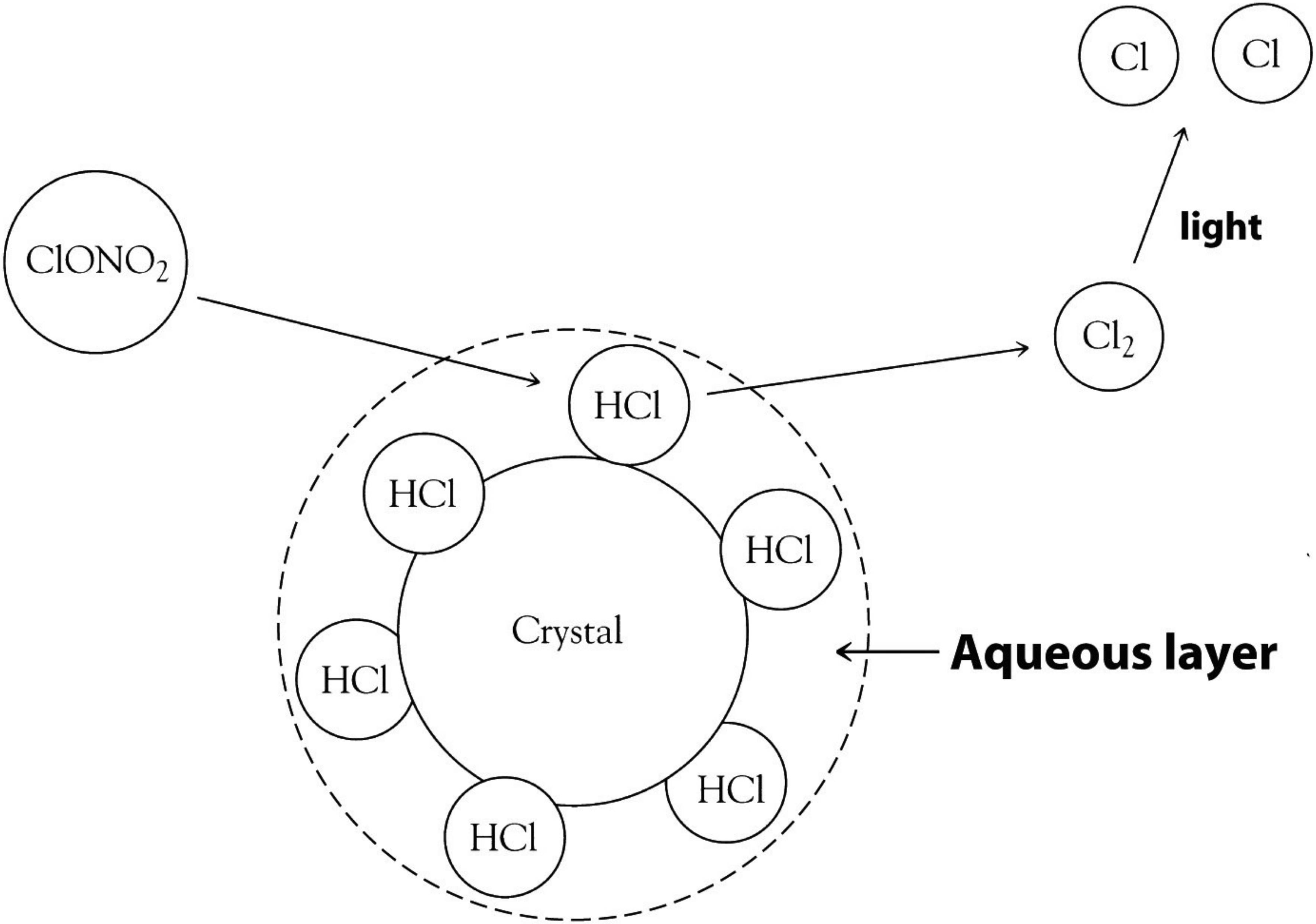


Figure 1-16
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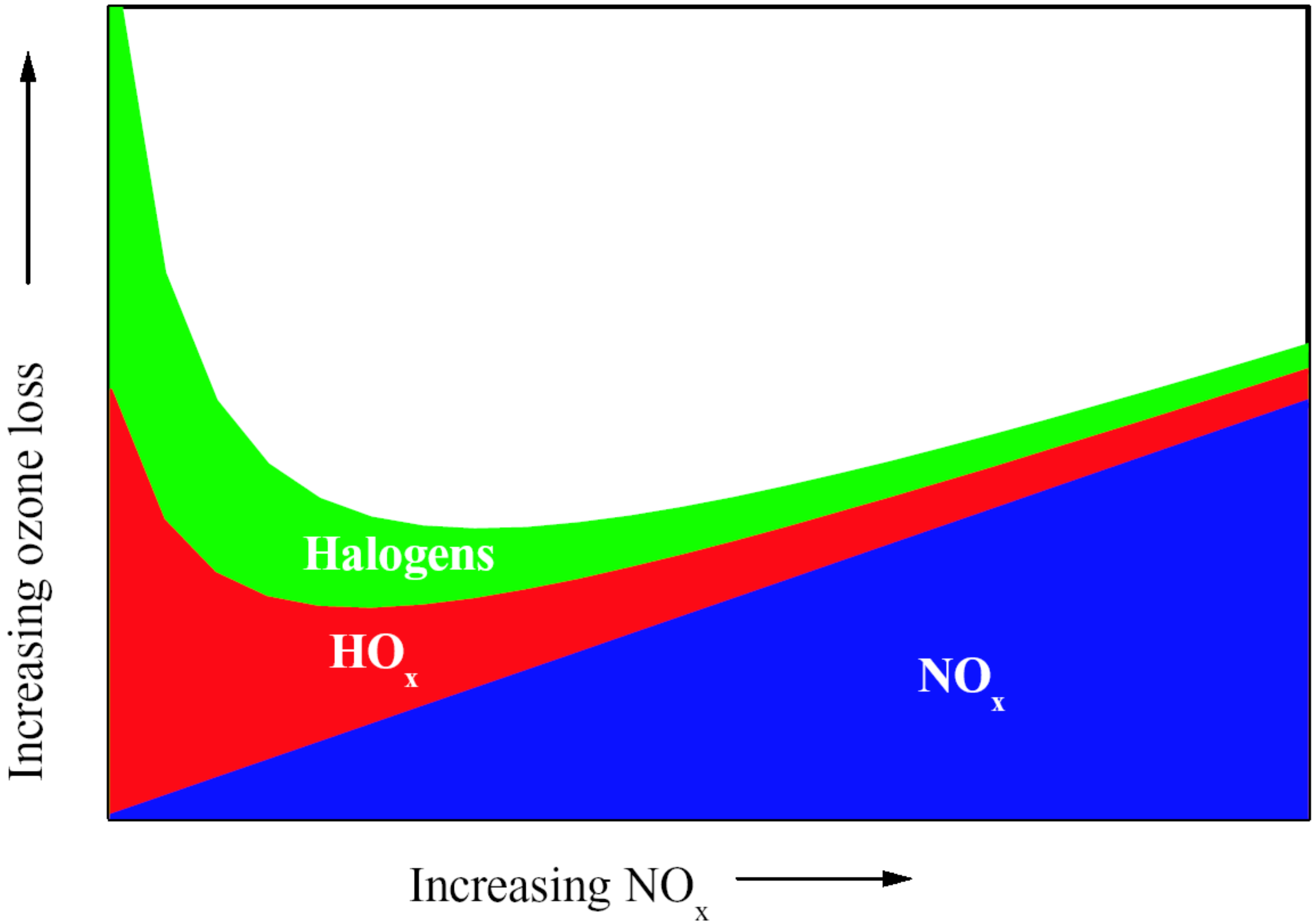
The Ozone Hole
Gas Phase Loss Processes



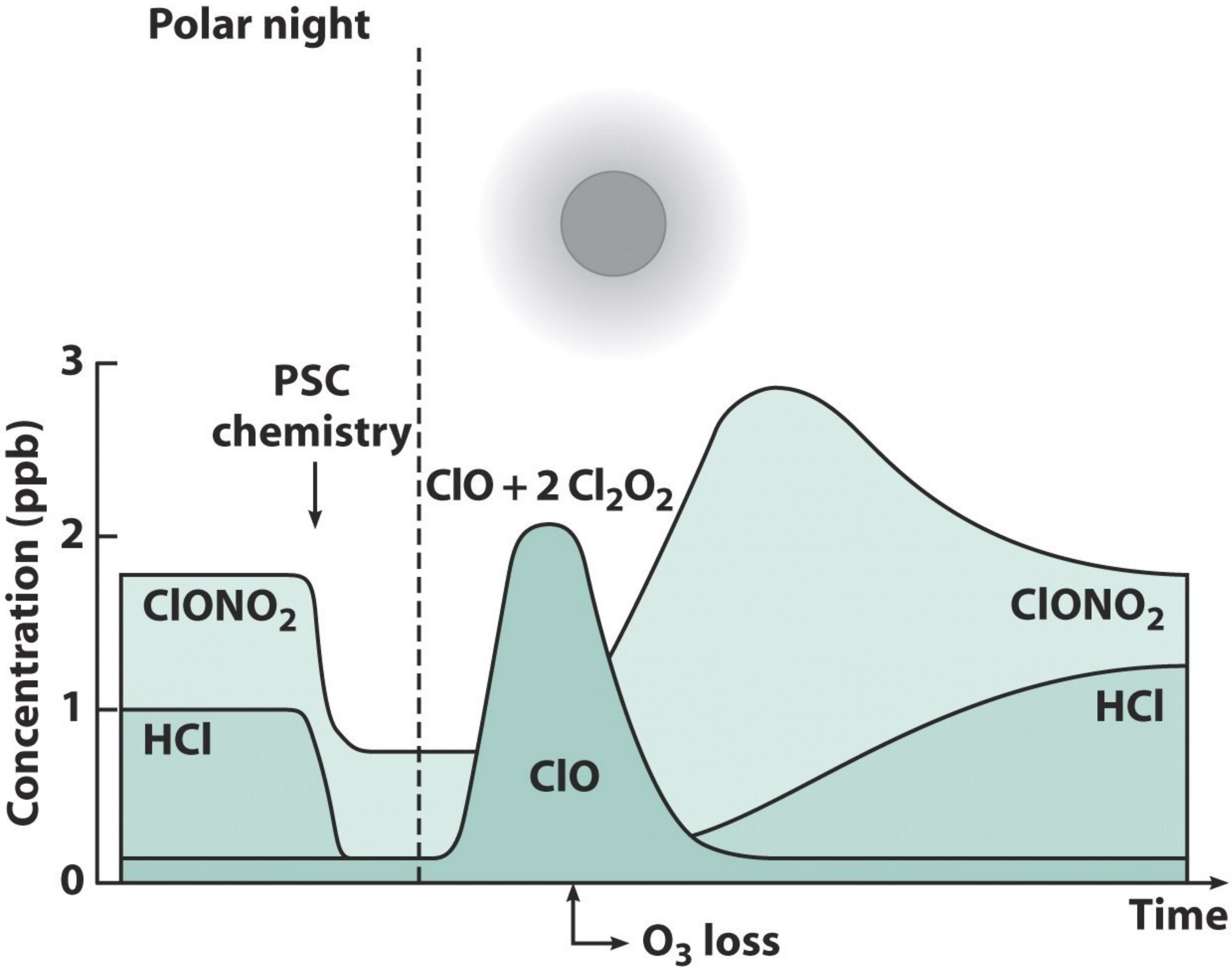


Figure 1-20
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The Ozone Hole

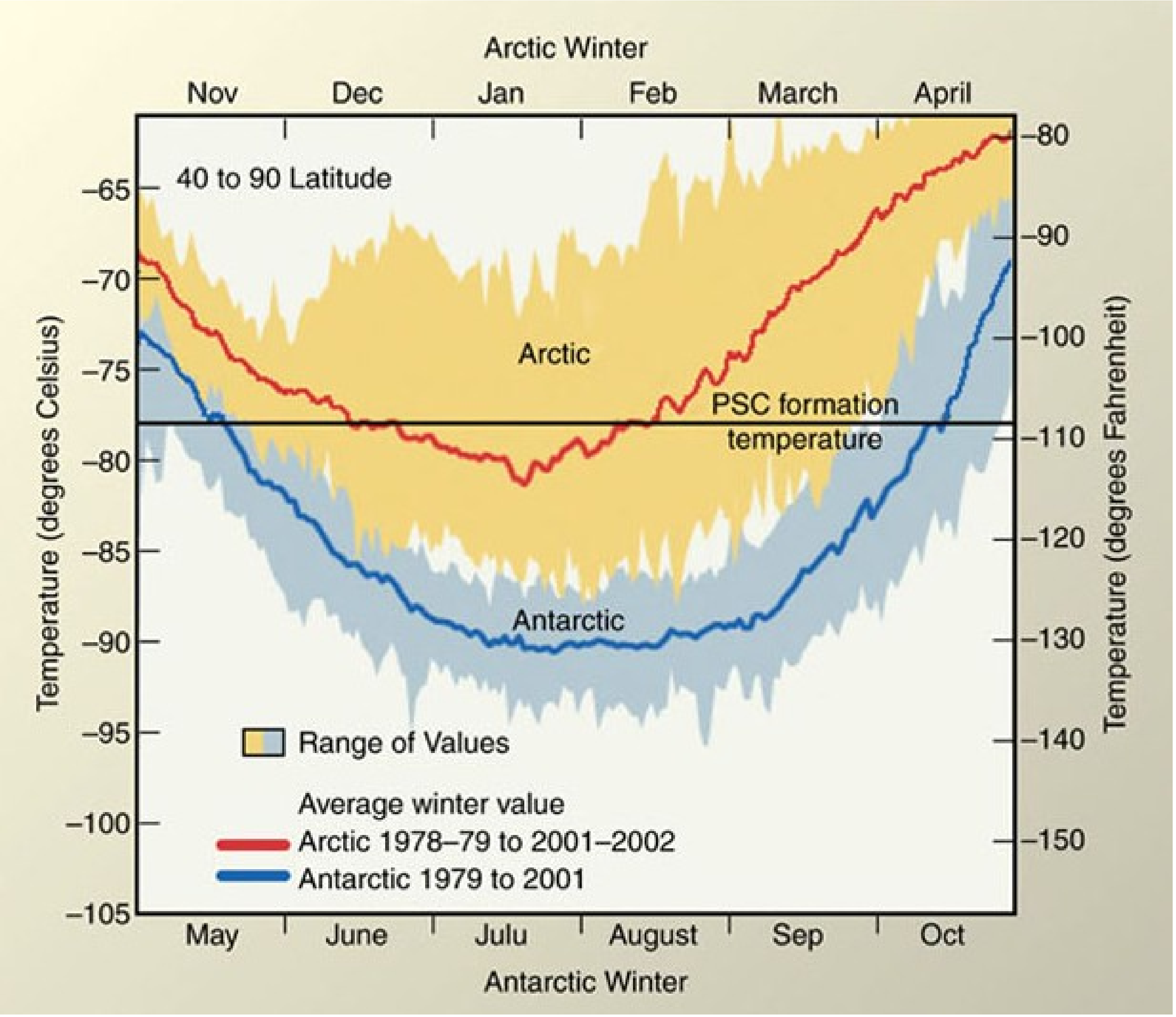
What about northern hemisphere loss?

- Historically, the Arctic vortex is neither as strong nor as long-lived as the Antarctic
- This explains the delayed appearance of the Arctic ozone hole, and the lower levels of depletion
- However, in recent years, the Arctic vortex has lasted longer, and temperatures have grown colder

An important note: increased tropospheric temperatures produce *decreased* temperatures in the stratosphere, as well as higher water content.

This is likely to produce higher concentrations of PSCs later into the season in both hemispheres

The Antarctic Ozone Hole: A Closer Look



The Ozone Hole

But where do the X-O species come from?

NO comes from the photolysis of N_2O, a naturally occurring species

HO comes from water, but the stratosphere is very cold, and thus very dry; also from O* + CH_4

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

ClO comes from two sources:

natural emission of CH_3Cl from plants and decay

a class of compounds called chlorofluorocarbons, or ***CFC***s