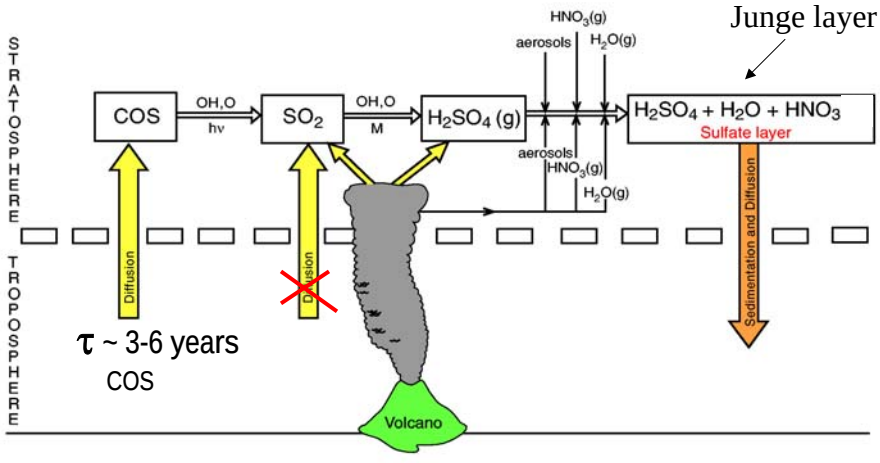
STRATOSPHERIC CHEMISTRY

1. **Stratospheric ozone: distribution**
2. **Chapman mechanism**
3. **Catalytic loss cycles**
   - **Hydrogen oxide radicals (HO_x)**
   - **Nitrogen oxide radicals (NO_x)**
   - **Chlorine oxide and bromine oxide radicals (ClO_x, BrO_x)**
4. **Polar ozone loss**
5. **Role of aerosol chemistry in the stratosphere**

Sources of aerosols in the stratosphere



Wallace & Hobbs

Aerosol chemistry on sulfate aerosols

Role of N_2O_5 hydrolysis:

$$N_2O_5 + H_2O \xrightarrow{\text{aerosol}} 2\ HNO_3$$

→ Converts active nitrogen (NO_x) to long-lived reservoir (HNO_3) [NO_x/NO_y ratio increases], and slows down O_x loss through NO_x cycles.

But at the same time it enhances O_x loss through ClO_x, BrO_x, and HO_x cycles. Lower NO_x result in:

- Slower deactivation of ClO_x through $ClO+NO_2+M \rightarrow ClONO_2+M$
- Slower deactivation of BrO_x through $BrO+NO_2+M \rightarrow BrONO_2+M$
- Slower deactivation of HO_x through $OH+NO_2+M \rightarrow HNO_3+M$

➔ Concentrations of ClO_x, BrO_x, and HO_x increase!

➔ Ozone becomes more sensitive to human-induced increases in chlorine and bromine species in the lower stratosphere.

Hydrolysis of N_2O_5 in aerosols increases the sensitivity of ozone to chlorine

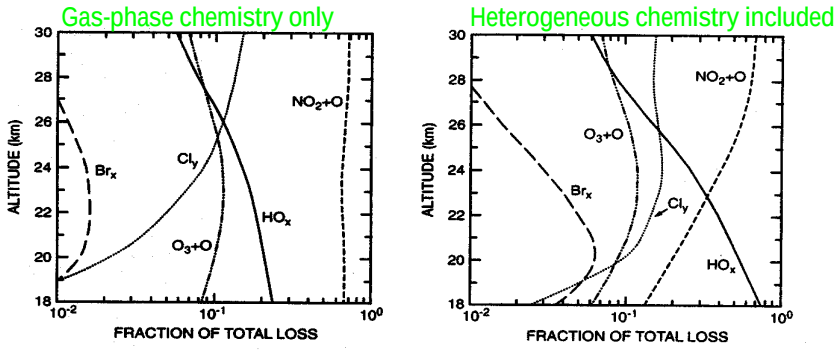


Fig. 10-16 Effect of N_2O_5 hydrolysis in aerosols on model calculations of ozone loss in the lower stratosphere at midlatitudes. The figure shows the fractional contributions of individual processes to the total loss of O_3 in model calculations conducted without (left panel) and with (right panel) hydrolysis of N_2O_5 in aerosols. From McElroy, M. B., et al. The changing stratosphere. *Planet. Space Sci.* 40:373–401, 1992.

Vertical distribution of ozone trends at midlatudes

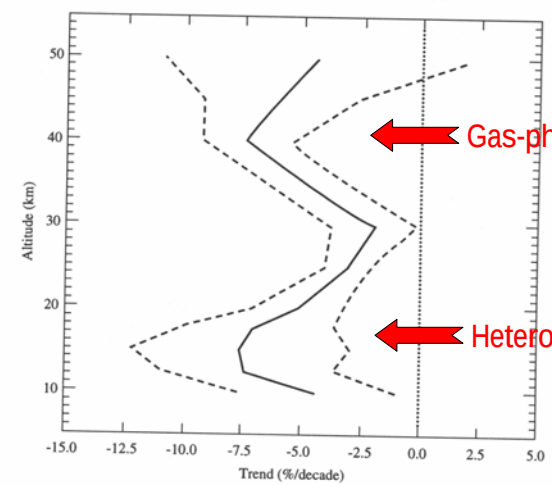
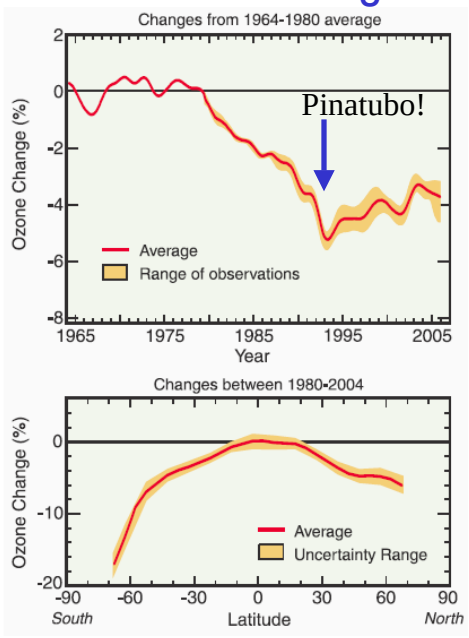


Fig. 10-15 Vertical distribution of the O_3 trend at northern midlatitudes for the period 1980–1996: best estimate (solid line) and uncertainties (dashed lines). Adapted from *Scientific Assessment of Ozone Depletion: 1998*. Geneva: WMO, 1999.

Global total ozone change:1964-2005



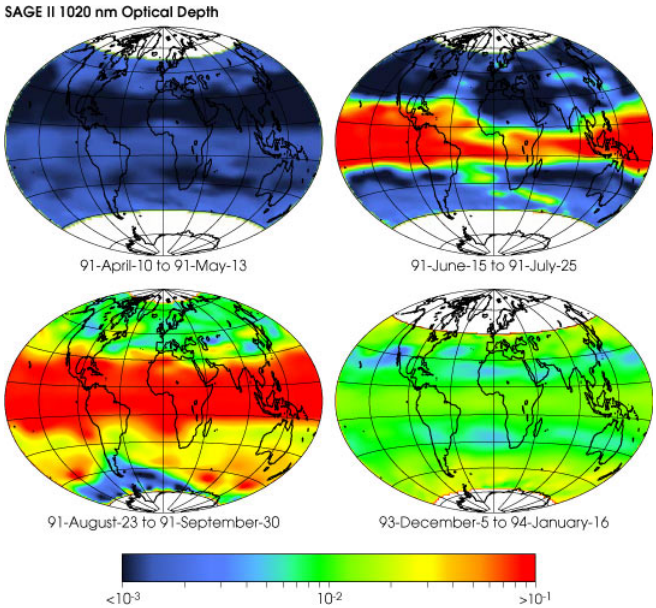
WMO, 2006

Heterogeneous chemistry in action: VOLCANO!!

Figure 13. Eruption of Mount Pinatubo in the Phillipines in 1991. This type of explosive eruption injects large amounts of material into the stratosphere to altitudes of greater than 30 km.

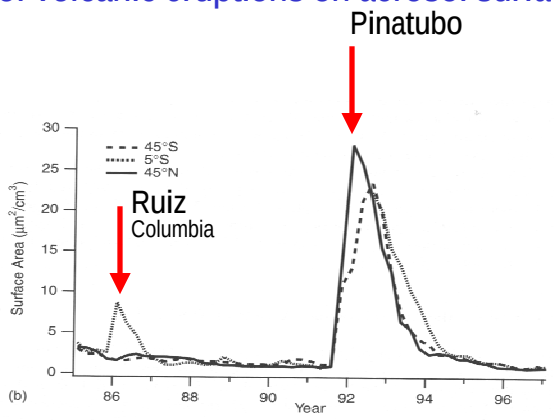
Pinatubo, Philippines. Location: 15.13N, 120.35E Elevation: 5248 ft .

Global effects of Mt. Pinatubo: Satellite optical depth observations



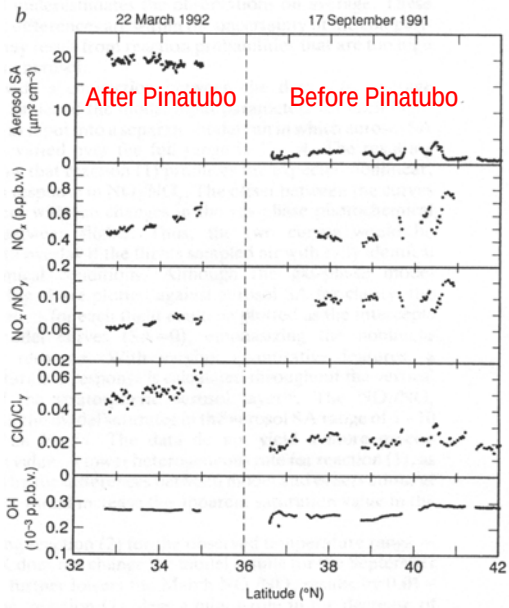
http://earthobservatory.nasa.gov/Newsroom/NewImages/images.php3?img_id=4952

Effect of volcanic eruptions on aerosol surface area



Following the eruption of Mt. Pinatubo (June 1991) aerosol surface area increased within months by a factor of 30! (1→30 $\mu m^2/cm^3$), and then slowly decreased. By 1999 aerosol levels were back to normal.

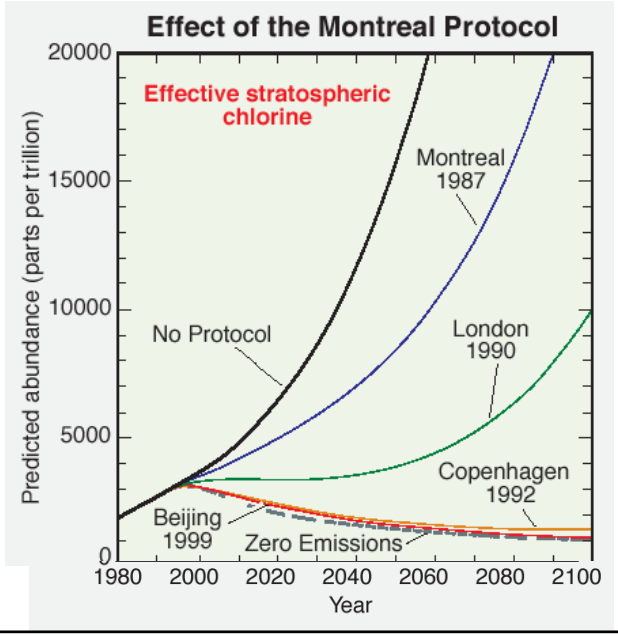
Observed effect of Mt Pinatubo on stratospheric chemistry



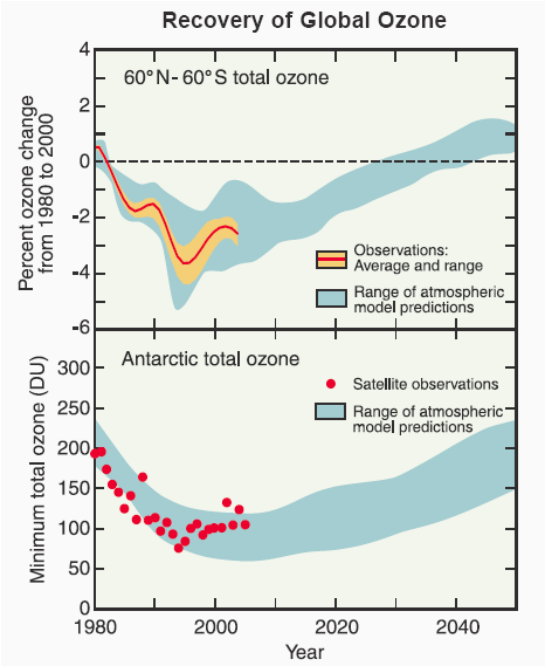
NASA's ER-2 aircraft

Fahey et al., Nature, 363, 509, 1994.

Projected evolution of stratospheric chlorine



WMO, 2004



WMO, 2006