Atmospheric Chemistry III

Chapman chemistry, catalytic cycles: reminder

Source of catalysts, transport to stratosphere: reminder

Effect of major (O_2) and minor (N_2O, CH_4) biogenic gases on [O_3]: modulation of concentrations by biota. Note influence of UV **on** biota.

Man's perturbation of stratospheric ozone

Because of *catalytic* nature of cycles, small amounts of material introduced into the stratosphere could destroy much O_3 (and problem compounded by stability of stratosphere).

Reasons for concern:

Human health: skin cancer, immune system
Vegetation, phytoplankton, etc
Climate: radiative forcing
Chemistry: altered UV intensities

Agriculture, use of land, biota

CH_4, NO_x (*via* N_2O) influences

Stratospheric aircraft

Direct injection: initial suggestions concerned H_2O, but soon rejected
Engine emissions (242 kg NO hr^{-1} or 118 000 l hr^{-1})
Return later to more recent analyses of aircraft problem

Chlorofluorocarbons

One of most worrying catalysts: chlorofluorocarbons and Cl_x, Br_x species

$CF_2Cl_2 \rightarrow h\nu \rightarrow Cl \rightarrow CF_2Cl$

{Handout 2 shows: SOURCE; CYCLE; RESERVOIR; RELEASE (gas-phase)}

Constancy in troposphere, drop in stratosphere: photolysis.

stability of CFCs; consumption and uses

CFC-11 concentration 1971 and 1979; CFC-11 and CFC-12 concentrations 1979-87
Controls and "alternatives": HFCs and HCFCs
Actual and projected Cl loadings for several scenarios
CFC emission scenarios and ozone depletions
[More detailed view of response of different Cl and Br species to Copenhagen]

Ozone concentrations and trends

Mid-latitude averages to May 1993; Arosa data
Ozone trends as a function of latitude

Stratospheric ozone hole

BAS observations 1957-88 (+ some TOMS); BAS up to current year
Satellite observations TOMS (Nimbus 7); Octobers 1979–97; current year minima/area

Why not seen earlier by TOMS!

Vertical profiles late August, early September 1987 (H6 is 1989)
1987 expedition: DC8, ER2 (cf balloons of last time)

I Meteorological factors
- Antarctic vortex
- PSCs

II Observations of chemical composition
- Concentration measurements: 23/8/87 and 16/9/87 ClO and O_3
- ClO enhancement, H_2O, NO_x depletion

III Interpretation
- Reservoir chemistry altered in presence of PSCs
- Containment
- Chain regeneration of Cl involves ClO dimer photolysis; also BrO mechanisms
- Summary view of time evolution

Potential for Arctic ozone depletion: chemistry results (AASE and EASOE)
Arctic December 1999 – March 2000: (a) vortex-average ozone profile {blue would be late March profile expected without loss}, and (b) ozone mixing ratio inside vortex.

Importance of bromine
- Br as much as 50 times more destructive than Cl
- Natural and anthropogenic sources of Br: uncertainties
- Reasons for effectiveness of Br
  - Non-occurrence of Br + CH_4 reaction
  - Rapid conversion of reservoirs back to active Br
  - BrO + BrO; BrO + ClO reactions (regeneration of Br *without* intervention of O)

Additional material

Surface reactions
- Stratospheric aerosol layer (H_2SO_4)
- Mount Pinatubo and the Arctic campaigns: signatures of processing
- Effects of heterogeneous chemistry: eg N_2O_5 + H_2O reaction

Aircraft and ozone revisited
- Many aircraft already fly in lower stratosphere; new SSTs
- Impact on stratospheric and tropospheric ozone levels
- Increased importance of HO_x in lower stratosphere with heterogeneous chemistry means that H_2O emission **might** be significant
- H_2O might also increase level of PSCs, and SO_2 and soot lead to increased sulphate aerosol as well as providing CCNs

Ozone and climate
- Greenhouse heating: decreases in lowers stratospheric Ts, offsets
- Increased UV in troposphere may increase [OH]: increases in CH_4 stopped?
- Cooling of lower stratosphere → PSCs → ozone loss; above, losses reduced

Ozone and UV penetration
- UV-B at surface
  - Antarctic: observed
  - Elsewhere: lack of observational data and difficulties - calculations
  - Variation with season and latitude; UK calculations

Atmospheric Chemistry III : Slides

1	G 25	Melanoma deaths v. latitude
2	G 80	Concorde (Gander, Sept 1975)
3	G 10	Concorde (Toulouse)
4	G 81	Stewardess at M2
5	G 82	Concorde in flight (cockpit)
6	G 84	Instruments c/u (altimeter)
7	W 17	Spray cans on globe - CFC introduction
8	RG 16	$CF_2Cl_2 + h\nu$
9	RG 71	Vertical dist. of CFC-11 (N mid-latitude)
10	W 36	Consumption and uses of CFCs to 1991
11	G 24	FC-11 concentrations in 1971 and 1979
12	RG 15 (W 18)	Increase in CFCs 1979-1987
13	W 40	Actual and projected atmospheric chlorine for several scenarios
14	W 43	Daily global ozone with 1993 to May (65N to 65S)
15	RG 27 (W 20)	Decline in October ozone 1956-1988
16	W 23	Ozone—Altitude profiles 15/8/87, 13/10/87
17	RG 31 (W 52)	DC8 (AT)
18	W 53	Instrumentation on DC8
19	RG 32 (W 49)	ER2 (AT)
20	W 51	Instrumentation on ER2
21	RG 38 (W 24)	Vortex over Antarctica
22	RG 36 (W 25)	Polar Stratospheric Clouds
23	W 26	Latitude dependence [O_3], [ClO], late Aug & mid Sept 1987
24	RG 41 (W 18)	Summary of comp. through CPR
25	RG 43 (W 27)	Surface reactions on PSCs

26	W 30	Schematic of time evolution of chlorine chemistry
27	W31	Volume mixing ratios of ClO, HCl and $ClONO_2$: **Arctic**
28	W32	Stratospheric aerosol layer
29	RG 80	Injection of volcanic ash
30	W35	Calculated increase in UV-B % per decade: MAP
31	W34	UV-B as function of season and latitude
32	W41	Stratospheric Cl and Br: Effect of Copenhagen agreement

Atmospheric Chemistry III : Viewgraphs

1	Chapman chemistry; catalytic cycles (CA2-3)
2	Schematic diagram of catalytic processes in stratosphere (CA2-4)
3	Arosa ozone data
4	Ozone trends as a function of latitude
5	BAS Halley observations to current year (2001)
6A	TOMS Maps (Octobers) 1979-1997
6B	Map form minimun of current year (2001)
6C	Antarctic ozone minima 1979 – 2001
plus	AVI movie compilation for current year
7	Antarctic daily ozone minima and ozone hole area 2001 (compared with 1999, 2000)
8	Ozone hole chemistry (Chlorine)
9	Arctic ozone losses, year 2000
10	The importance of bromine
11	Mount Pinatubo
12	Effects of heterogeneous chemistry: relative contributions of cycles
13	Aircraft and ozone
14	Stratospheric ozone: recent observations
15	Mechanisms for mid-latitude ozone decline
16	Ozone trends, global: percent per year, 1978-1990 (**update** to latest)
17	Ozone and climate
18	Reduced ozone and UV penetration
19	Factors affecting UV-B at the surface
20	Ozone and UV-B: anticorrelation, Antarctic (CA2-2)