Atmospheric Chemistry II

Ozone in the atmosphere and its significance

Stratosphere: UV filtering and heating; sources of OH and NO
Troposphere: source of OH; pollution
Most important: UV filtering in stratosphere

Ozone history

Schönbein's 1839 discovery; smell; name
Dobson and Lindemann; Dobson's Boar's Hill laboratory; Lindemann and ChCh; etc.

Chapman chemistry

Scheme
Layer formation
Concept of "odd oxygen": introduction to families (O_x, NO_x, HO_x, Cl_x, etc)
Prediction ("model") and experiment: inadequacy of O-only scheme

Protection afforded by ozone layer

Biological sensitivity
Evolution

Sensitivity of organisms to UV with $\lambda < 300$nm: Ozone only possible <u>atmospheric</u> filter. Atmosphere without O_2 to begin with: almost all O_2 from photosynthesis.
Liquid water as filter:

$<10^{-3}$ PAL ~ 10m water can filter: shallow pools
10^{-2} PAL, few cms water effective: oceans
10^{-1} PAL, life can emerge onto dry land

Connection between evolution of life, O_2, and O_3
Geological & biological evidence for evolution of $[O_2]$
$[O_3]$ then calculated from models
Former belief: evolutionary explosion - dawn of Cambrian.
Evidence for life: to earliest known rocks. Nevertheless, multicelled organisms require ~ 10^{-2} PAL (for cell division: fossil record - 2GYr to 1.4GYr BP); shelly metazoans need 10^{-1} PAL. By then, probably enough O_2 (and thus O_3) for life to emerge onto land, yet did not for another 170 MYr. Possibility exists that adequate screening by ozone may have been available before the Silurian period, and was not directly linked with the spread of life onto land. The connection between the emergence of life out of water and the development of the ozone shield remains a tantalizing one.

Stratospheric ozone: more detailed chemistry

Problem with Chapman O-only scheme is O + O_3 reaction ==> catalytic cycles of type

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

with X = H, OH, NO, Cl, etc

e.g.

$OH + O_3 \rightarrow HO_2 + O_2$ $\quad NO + O_3 \rightarrow NO_2 + O_2$ $\quad Cl + O_3 \rightarrow ClO + O_2$
$O + HO_2 \rightarrow OH + O_2$ $\quad O + NO_2 \rightarrow NO + O_2$ $\quad O + ClO \rightarrow Cl + O_2$

Where do HO_x, NO_x, Cl_x come from? Troposphere (+ lightning): $O(^1D)$ (and OH) reactions. Note, therefore, influence of biosphere. NB N_2O from soil, importance of CH_4 because of "cold trap" at tropopause.

The effects of the catalytic species would be even greater than they are were it not for the existence of `reservoir' species that divert catalytic species away from the odd-O reactions

HNO_3	from OH	+	NO_2	+	M		
HNO_4	from HO_2	+	NO_2	+	M		
HCl	from Cl	+	CH_4				
$ClONO_2$	from ClO	+	NO_2	+	M		
HOCl	from ClO	+	$HO_2 \rightarrow$ HOCl			+	O_2

Note that these reservoirs involve active catalysts from two different families. Cross cycles couple the different catalytic families

$$HO_2 + NO \rightarrow OH + NO_2$$
$$ClO + NO \rightarrow Cl + NO_2$$

Release of active species from reservoirs

Examples:

$$ClONO_2 \xrightarrow{M} ClO + NO_2$$
$$OH + HCl \rightarrow Cl + H_2O$$

Overall pattern for particular families:

NO_x on screen and handout; ClO_x on handout

Relative contributions of the different families to O_3 removal

Dynamics and transport

Importance of atmospheric motions in redistributing trace species

Significance of lifetime: short-lived (eg OH), long-lived (eg CFCs, N_2O) and intermediate species

Examples:

N_2O: overall lifetime ca 170yr, evenly distributed in troposphere, but is photolysed and reacts with $O(^1D)$ above ca. 25km. Transport from troposphere to stratosphere - low latitude → return flow at high latitude depleted in N_2O.

O_3: major source region is equatorial low stratosphere, and highest mole fractions are found there. However, largest column abundance at high latitudes in early spring. Photochemistry alone does not explain distributions - air motions as well.

Therefore need to incorporate the rate equations for the very many chemical reactions, allow for the correct temperatures at different altitudes and latitudes, and then for transport. *Numerical modelling* becomes inevitable.

Models

Numerical models to describe systems of complex interacting non-linear chemical, physical and biological processes.

Zero-dimensional box models

Study individual system interactions in laboratory (laboratory chemistry), numerical mathematical models to comprehend system behaviour as whole. Models are attempts to create computer replicas of system behaviour so that causes and effects may be better understood.

Interesting stage of model development: knowledge sufficient to design reasonable model, but not so far that all factors influencing system are understood. Deviation of model results from what is measured → search for processes not yet understood: example - ozone hole. This is "diagnostic" use. Answers question “Have you understood the science properly?”

"Prognostic" use - ability of models to explore situations not available in reality: eg responses of atmospheres to changes of forcing functions (nb policy implications). Also for exploring the past. Answers question “What can you do with the science?”

Model results must be checked against appropriate simultaneous measurements of as many model variables as possible to discover deficiencies of the model → insufficient understanding, or absence of key processes and understanding. This will lead us to the question of measurements in atmosphere. First:

Different types of model
- Dimensionality; grid size; limited chemical complexity
- Hybrid 3-D / chemical models
- Eulerian and Lagrangian approaches
- Introduction of feedbacks into the models
- "Fast" chemistry and "family" models

Requirements for models:
- Laboratory data on reactions, pathways and kinetics - not for this lecture!
- Measurements of sources, sinks, and **especially** atmospheric concentrations.

Atmospheric measurements

In situ and remote: advantages and disadvantages of each
- Altitude profiles
- Methods as applied to atmospheric O_3 measurements
- Remote (microwave) measurements of ClO
- *In situ* balloon experiments using resonance fluorescence
- [O], [O_3] data; comparison of [O]/[O_3] with model predictions
    - OH resonance fluorescence
    - HO_2 resonance fluorescence + titration
    - ClO resonance fluorescence + titration

Atmospheric Chemistry II : Slides

1.	R 2	Concentrations of neutrals (repeated from lecture 1)
2.	W 5	Ozone concentration as a function of altitude; heating
3.	W 1	Schönbein: full
4.	W 2	Schönbein: face
5.	W 3	Dobson
6.	W 4	Dobson's Boar's Hill laboratory
7.	W 7	Chapman
8.	BG 6	Ozone layer formation
9.	R 3	Ozone profiles: experiment and oxygen-only model
10.	W 9	UV solar flux and biological sensitivity (DNA damage)
11.	BG 34 (NB = W 10)	Atmospheric oxygen deduced from biology; and accompanying ozone
12.	RB 60	Catalytic cycles: scheme
13.	RB 61	Sources of catalytic species
14.	RB 42	Reservoir species
15.	RB 64	Schematic of NO_x reaction scheme
16.	RB 62	Contributions of Chapman and catalytic cycles to O_3 destruction
17.	RG 48	Inflated balloon
18.	RG 49	Rising balloon
19.	RG 50	Parachute/payload
20.	RG 51	Payload recovery
21.	RG 52	Yo-yo arrangement

Probably omitted

22.	RG 66	Vertical profile OH
23.	RG 67	Vertical profile HO_2
24.	RG 68	Vertical profile ClO

Atmospheric Chemistry II : Viewgraphs

“0”. Regions of Earth’s atmosphere

1. Importance of ozone: ozone photolysis and the reactions of excited atomic oxygen

2. Ozone and UV-B: correlations, Antarctic

3. Chapman chemistry; catalytic cycles

4. Chemistry involved in ozone formation and removal by catalysts

5. Some HO_x catalytic cycles

6. Competing reactions in the NO_x cycle

7. Reservoir species; cross cycles

8. Chemical cycles for NO_x species (see slide 14)

9. Chemical cycles for ClO_x species (see slide 15)

10. Percentage contribution to catalytic cycles (see slide 17)

11. Zonal mean mixing ratios for N_2O (October, modelled)

12. Stratospheric ozone distribution; seasonal variation of column O_3 with latitude

13. Box and 1-D models

14. Types of model

15. Methods for measurements in the atmosphere

16. Techniques for measuring stratospheric ozone concentrations

17. Comparison of modelled and measured diurnal ClO

18. Observed [O] and [O_3]; measured and calculated [O]/[O_3]