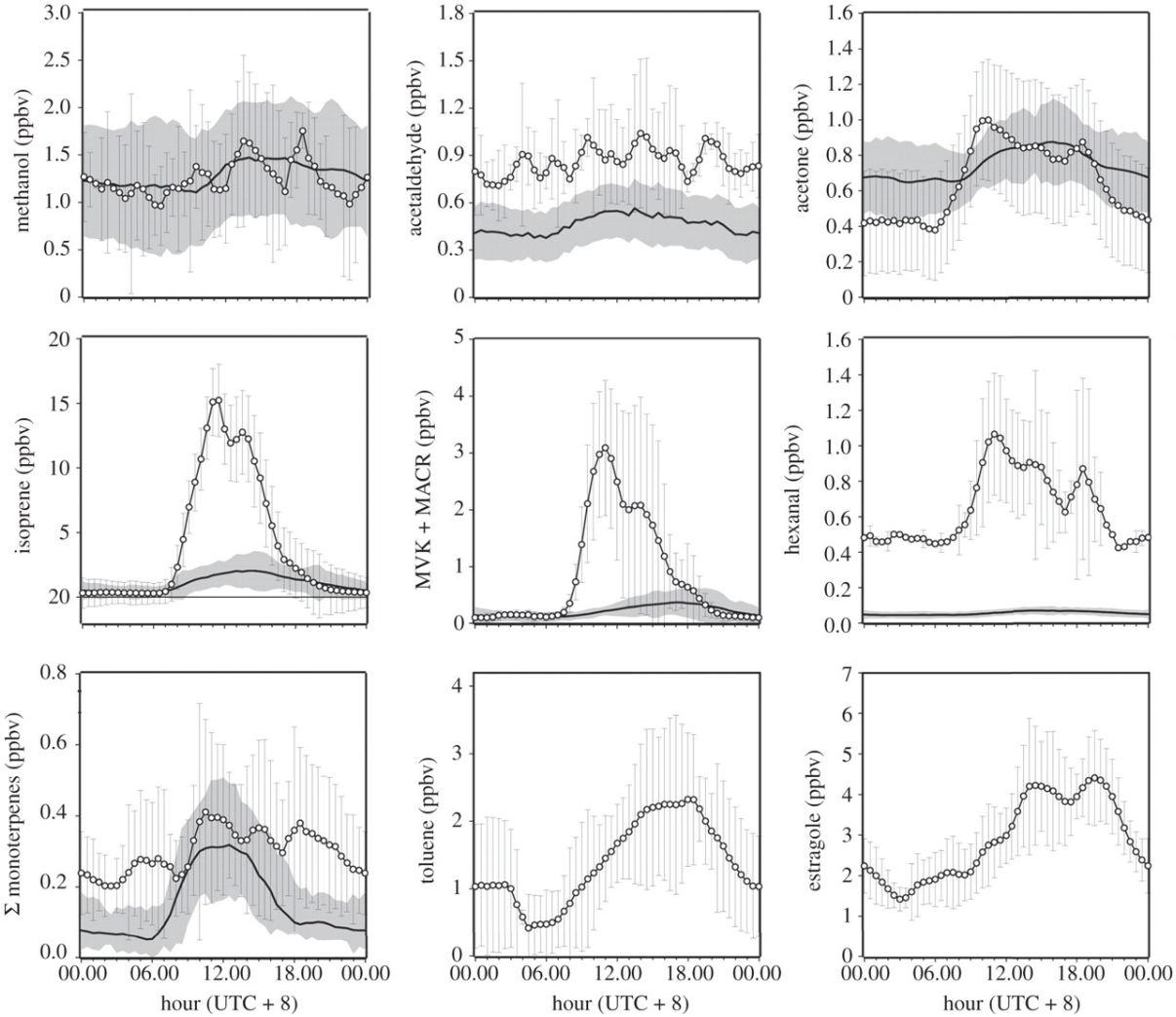
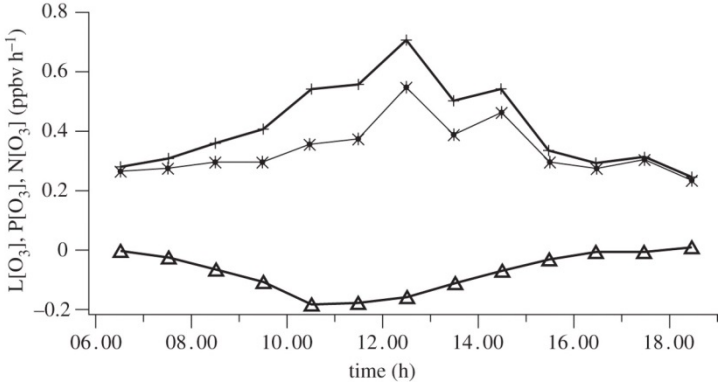
Unit 15

Gasphase chemistry

Nicole Mölders

Behavior of trace species has a diurnal cycle





Mean day-time cycle for net rate of ozone change, $N[O_3]$ (asterisks with solid line), ozone production rate, $P[O_3]$ (plus symbols with solid line), and ozone loss rate, $L[O_3]$ (triangles with solid line), from O^{3P}. Frpm: MacKenzie et al. (2011)

Average diurnal cycles of observed VOCs, measured at 75 m above ground at the Bukit Atur rainforest site, Borneo. Grey shading and error bars show the variability (±1 s.d.) about the mean. Solid line, rainforest; circles with solid line, oil palm. MacKenzie et al. (2011)

Background chemistry in the clean troposphere

$OH + CH_4 \rightarrow CH_3 + H_2O$

$CH_3 + O_2 + M \rightarrow CH_3OO + M$ methylperoxy radical

$CH_3OO + NO \rightarrow NO_2 + CH_3O$ methoxy radical

$CH_3O + O_2 \rightarrow HCHO + HOO$ formaldehyde

$(HOO + NO \rightarrow NO_2 + OH)$

$HCHO + OH \rightarrow HCO + H_2O$

$HCO + O_2 \rightarrow HOO + CO$

$(HOO + NO \rightarrow NO_2 + OH)$

$CO + 2O_2 + h\nu \rightarrow CO_2 + O_2$

$OH + CO \rightarrow CO_2 + H$ (1)

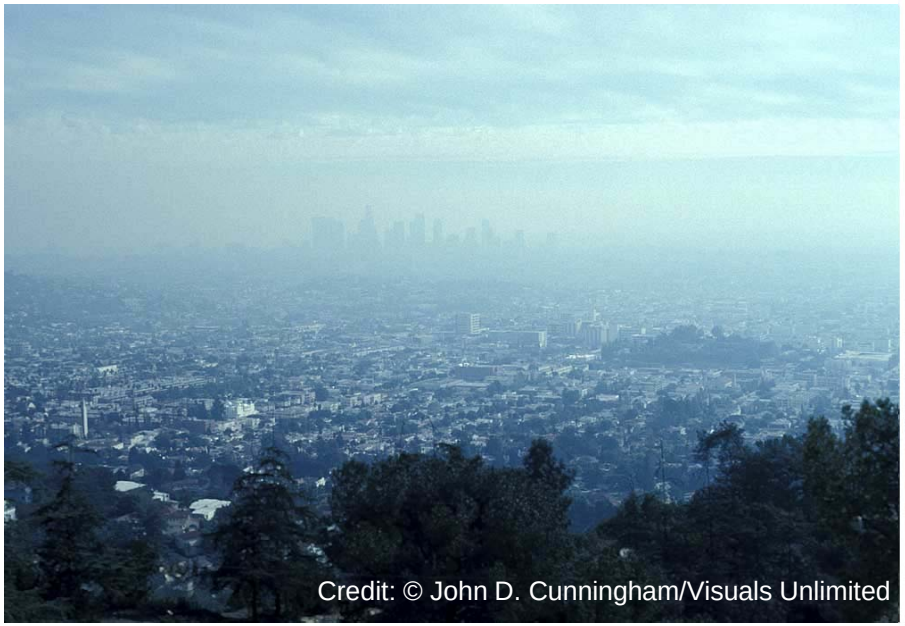
$H + O_2 + M \rightarrow HOO + M$ (2) hydroperoxyl radical

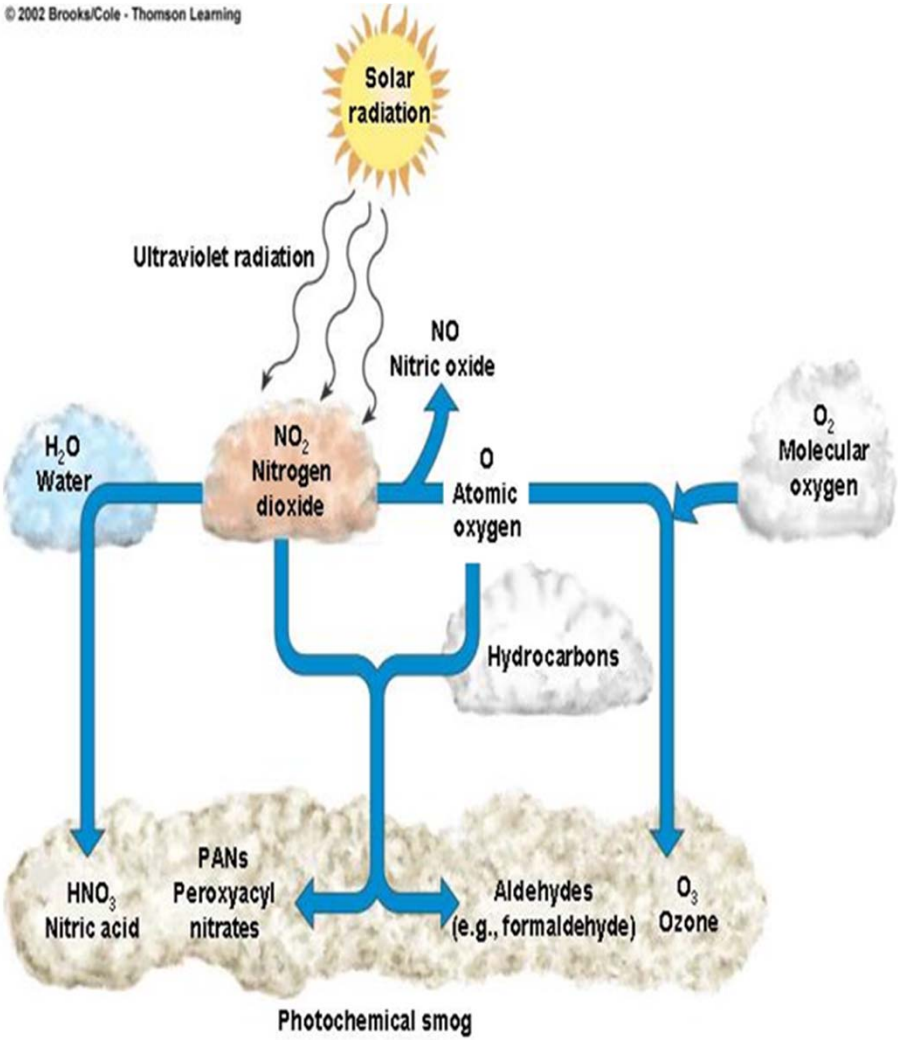
$HOO + NO \rightarrow NO_2 + OH$ (3)

$HOO + O_3 \rightarrow OH + 2O_2$ (4)

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]}$$

Los Angeles smog





Primary photochemical cycle of NO_x & ozone

$2NO + O_2 \rightarrow 2NO_2$

$NO_2 + h\nu \rightarrow NO + O$ (1)

$O + O_2 + M \rightarrow O_3 + M$ (2)

$NO + O_3 \rightarrow NO_2 + O_2$ (3)

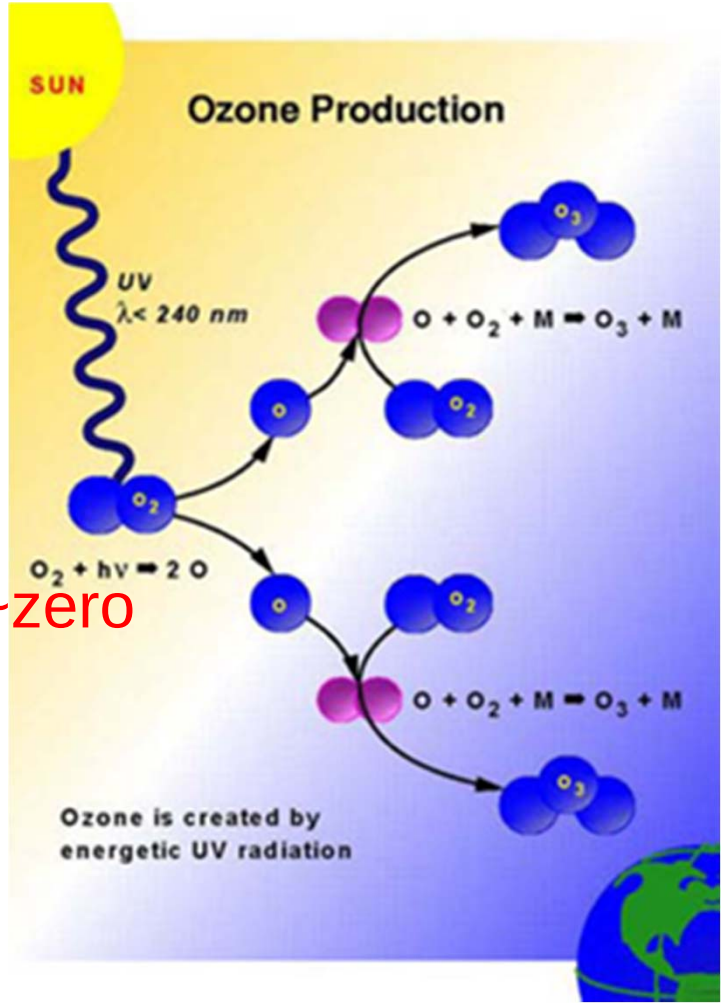
$$\frac{d[O_3]}{dt} = -k_3[NO][O_3] + k_2[O][O_2][M]$$ ~zero

$$\frac{d[O]}{dt} = k_1[NO_2] - k_2[O][O_2][M]$$ ~zero

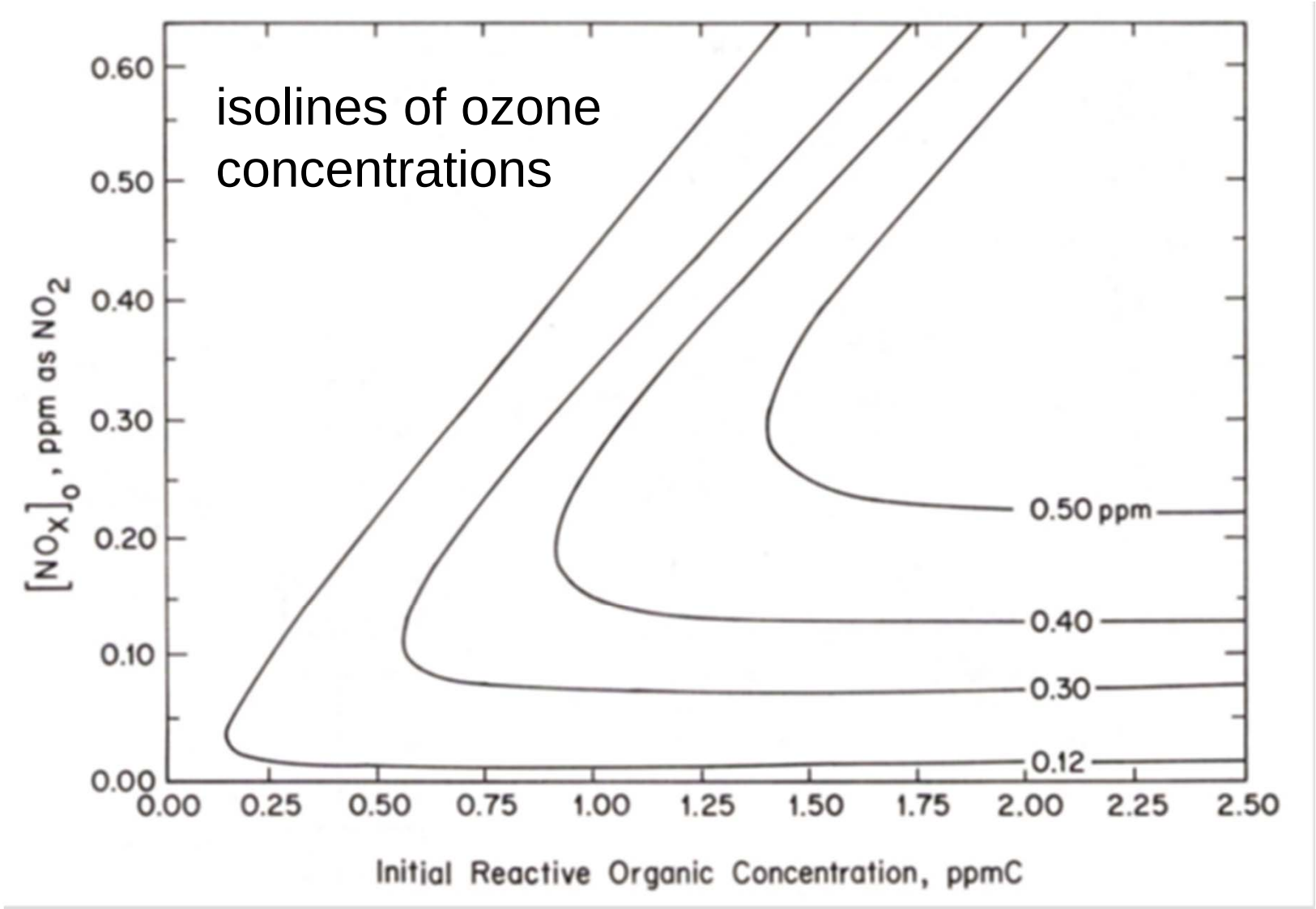
PSSA

$$\boxed{k_1[NO_2] = k_2[O][O_2][M]}$$

$$\boxed{[O_3] = \frac{k_1[NO_2]}{k_3[NO]}}$$



Urban air pollution: photo-smog



Comparison of tropospheric O_3 photochemistry

Clean air

$O_3 + h\nu \rightarrow O_2 + \cancel{O^{1D}}$ (1)

$\cancel{O^{1D}} + H_2O \rightarrow 2OH$ (2)

$\cancel{OH} + O_3 \rightarrow \cancel{HO_2} + O_2$ (3)

$\cancel{HO_2} + O_3 \rightarrow 2O_2 + \cancel{OH}$ (4)

$2O_3 + H_2O \rightarrow 3O_2 + 2OH$ net reaction

$2O_3 \rightarrow 3O_2$ net reaction (3-4)

Polluted air

$OH + CO \rightarrow H + CO_2$ (3')

$H + O_2 + M \rightarrow HO_2 + M$ (4')

$HO_2 + NO \rightarrow NO_2 + OH$ (5')

$NO_2 + h\nu \rightarrow NO + O$ (6')

$O + O_2 + M \rightarrow O_3 + M$ (7')

$CO + 2\,O_2 \rightarrow CO_2 + O_2$ net reaction (3-7‘)

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Polluted air

$\cancel{OH} + CO \rightarrow \cancel{H} + CO_2$ (3')

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$\cancel{HO_2} + \cancel{NO} \rightarrow \cancel{NO_2} + \cancel{OH}$ (5')

$\cancel{NO_2} + h\nu \rightarrow \cancel{NO} + \cancel{O}$ (6')

$\cancel{O} + O_2 + M \rightarrow O_3 + M$ (7')

$CO + 2\,O_2 \rightarrow CO_2 + O_2$ net reaction (3-7‘)

Reaction sequence for alkenes illustrated by the example of methane

$CH_4 + OH \rightarrow CH_3 + H_2O$

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$CH_3O_2 + NO \rightarrow NO_2 + CH_3O$

$CH_3O + O_2 \rightarrow H_2CO + HO_2$

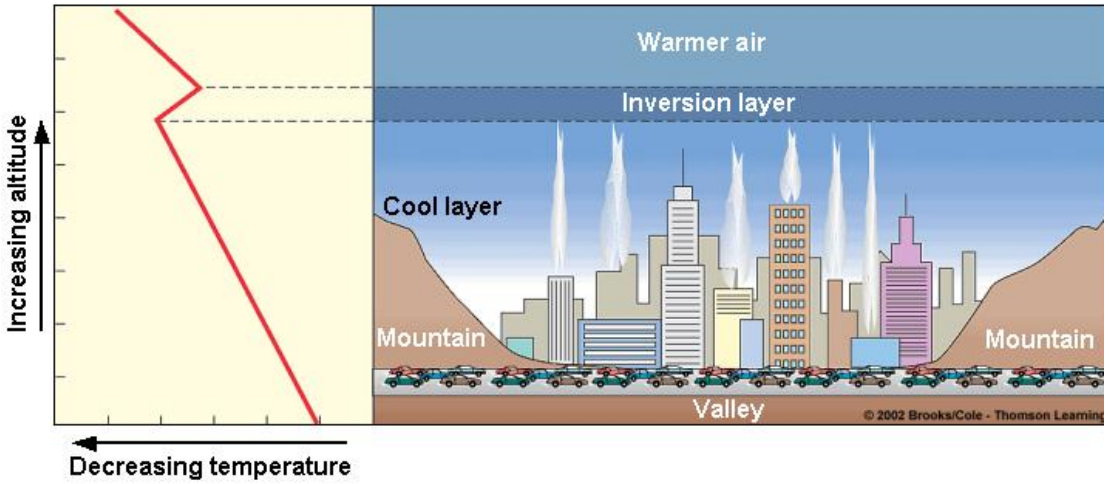
$HO_2 + NO \rightarrow NO_2 + OH$

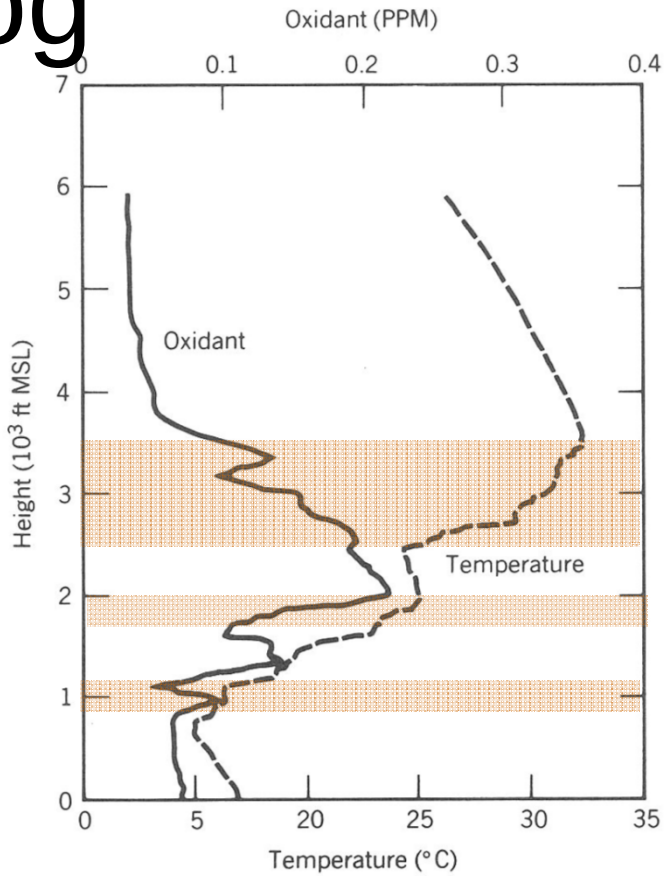
$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

$CH_4 + 4\,O_2 + h\nu \rightarrow 2\,O_3 + H_2CO + H_2O$ net reaction

Photo-smog


Warmer air
Inversion layer
Cool layer
Mountain
Mountain
Valley
© 2002 Brooks/Cole - Thomson Learning
Increasing altitude
Decreasing temperature

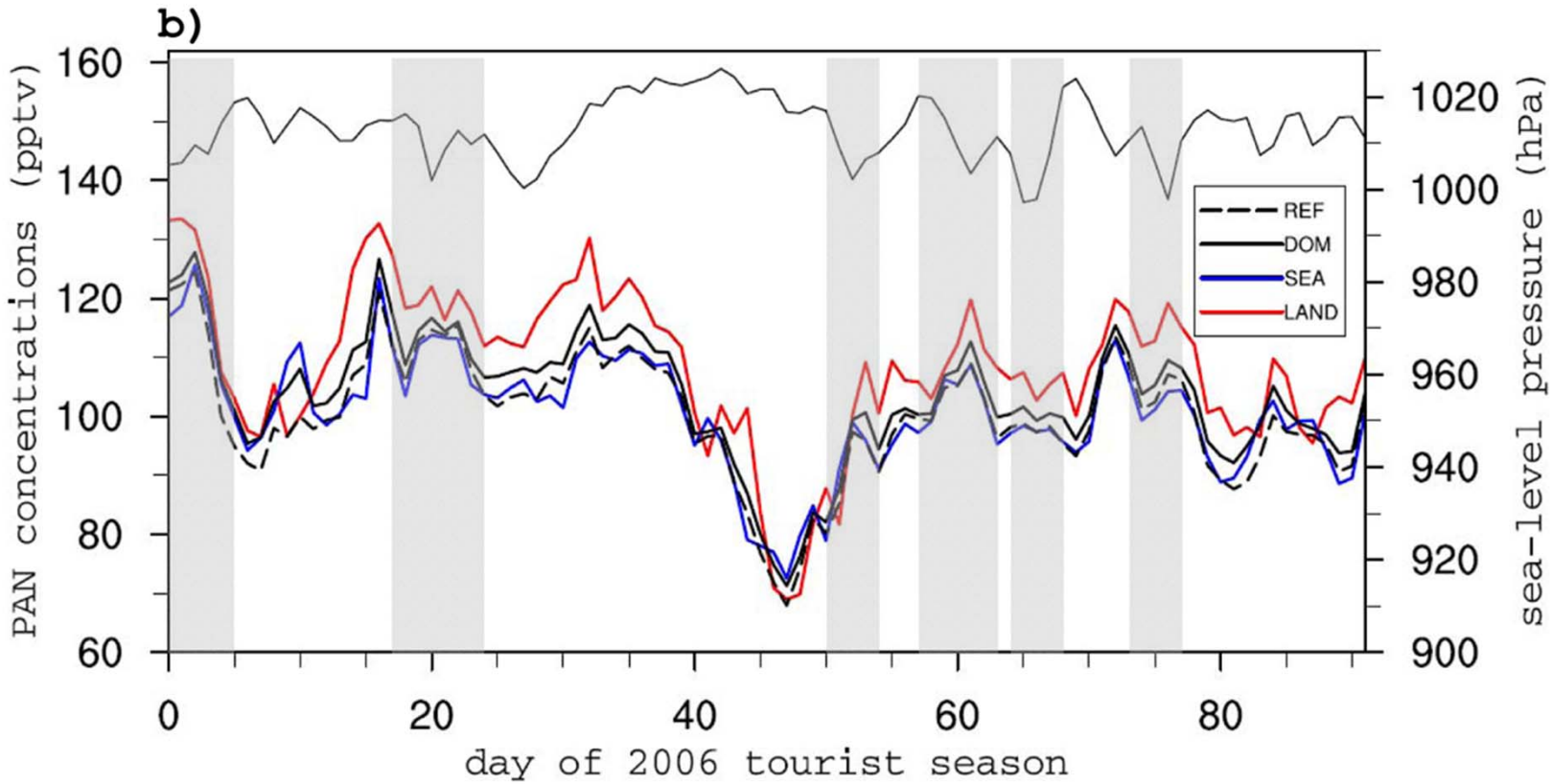

Oxidant (PPM)
0
0.1
0.2
0.3
0.4
Height (10^3 ft MSL)
7
6
5
4
3
2
1
0
Oxidant
Temperature
0
5
20
25
30
35
Temperature (°C)

Formation of peroxyacetyl nitrates (PAN) from oxidation of acetaldehyde

$CH_3CHO + OH \rightarrow CH_3CO + H_2O$

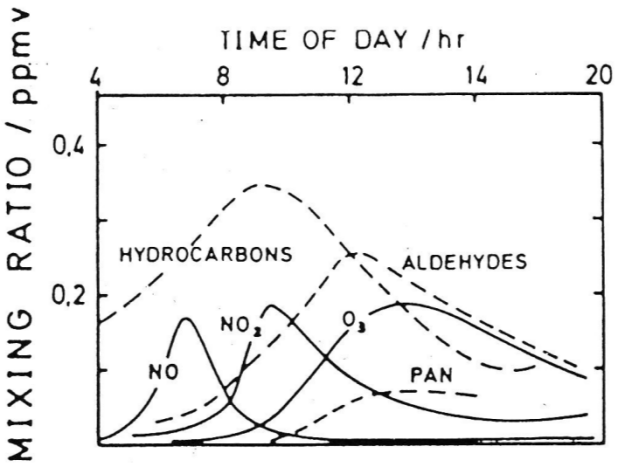
$CH_3CO + O_2 \rightarrow CH_3C(O)OO$

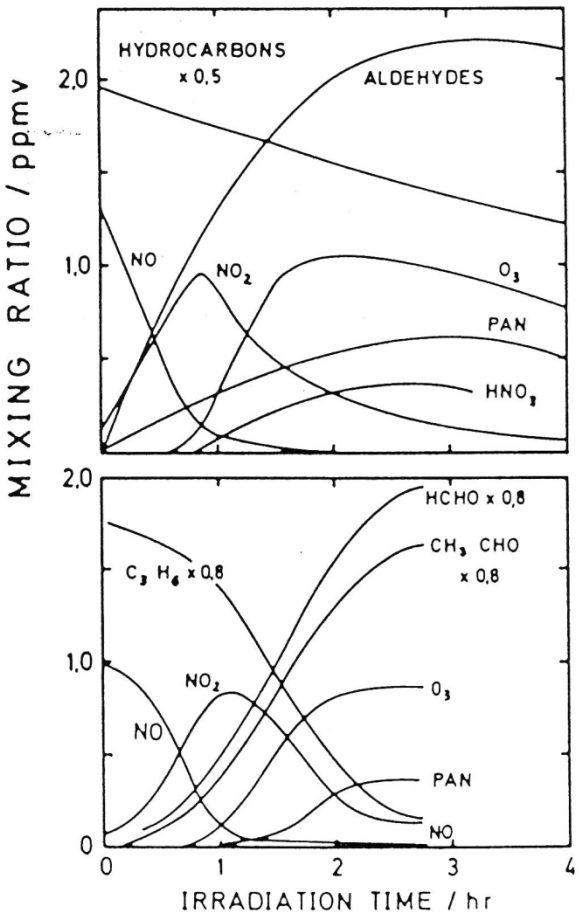
$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)O_2NO_2$ (PAN!)



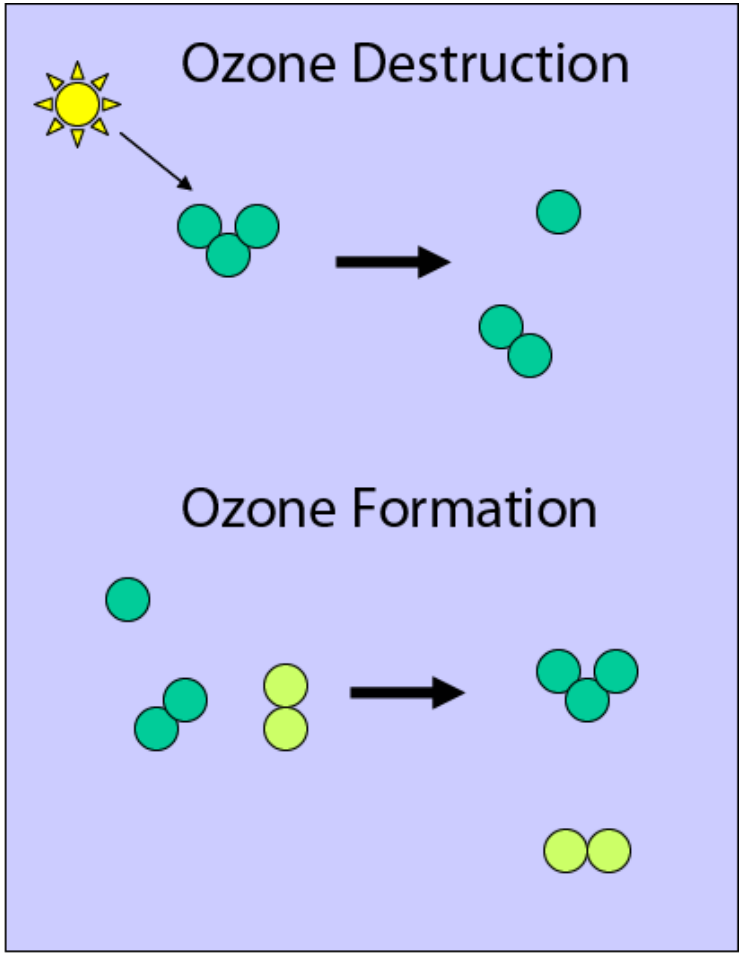
PAN in the Gulf of Alaska from May 21 to August 21, 2006 as obtained by WRF/Chem
Gray p<1000hPa, thin black line = SLP. From: Porter 2009

Dynamics of pollutant formation





Chapman cycle



Chapman cycle

$$O_2 + h\nu \longrightarrow^{j_1} 2O$$

$$O + O_2 + M \longrightarrow^{k_1} O_3 + M$$

$$O_3 + h\nu \longrightarrow^{j_2} O + O_2$$

$$O + O_3 \longrightarrow^{k_2} 2O_2$$

$$3O_2 \longrightarrow \qquad 3O_2$$

$$\frac{d[O_3]}{dt} = k_1[O][O_2][M] - j_2[O_3] - k_2[O][O_3]$$

$$\frac{d[O]}{dt} = 2j_1[O_2] + j_2[O_3] - k_1[O][O_2][M] - k_2[O][O_3]$$

$$\frac{d[O_x]}{dt} = \frac{dO}{dt} + \frac{dO_3}{dt} = 2j_1[O_2] - 2k_2[O][O_3]$$

$$[O_3] = [O_2]\sqrt{(\frac{j_1 k_1[M]}{j_2 k_2})}$$

$$k_1[O][O_2][M] = j_2[O_3] + k_2[O][O_3] \qquad j_1[O_2] = k_2[O][O_3]$$

$$j_2 >> k_2[O] \qquad k_1[O][O_2][M] \approx j_2[O_3]$$

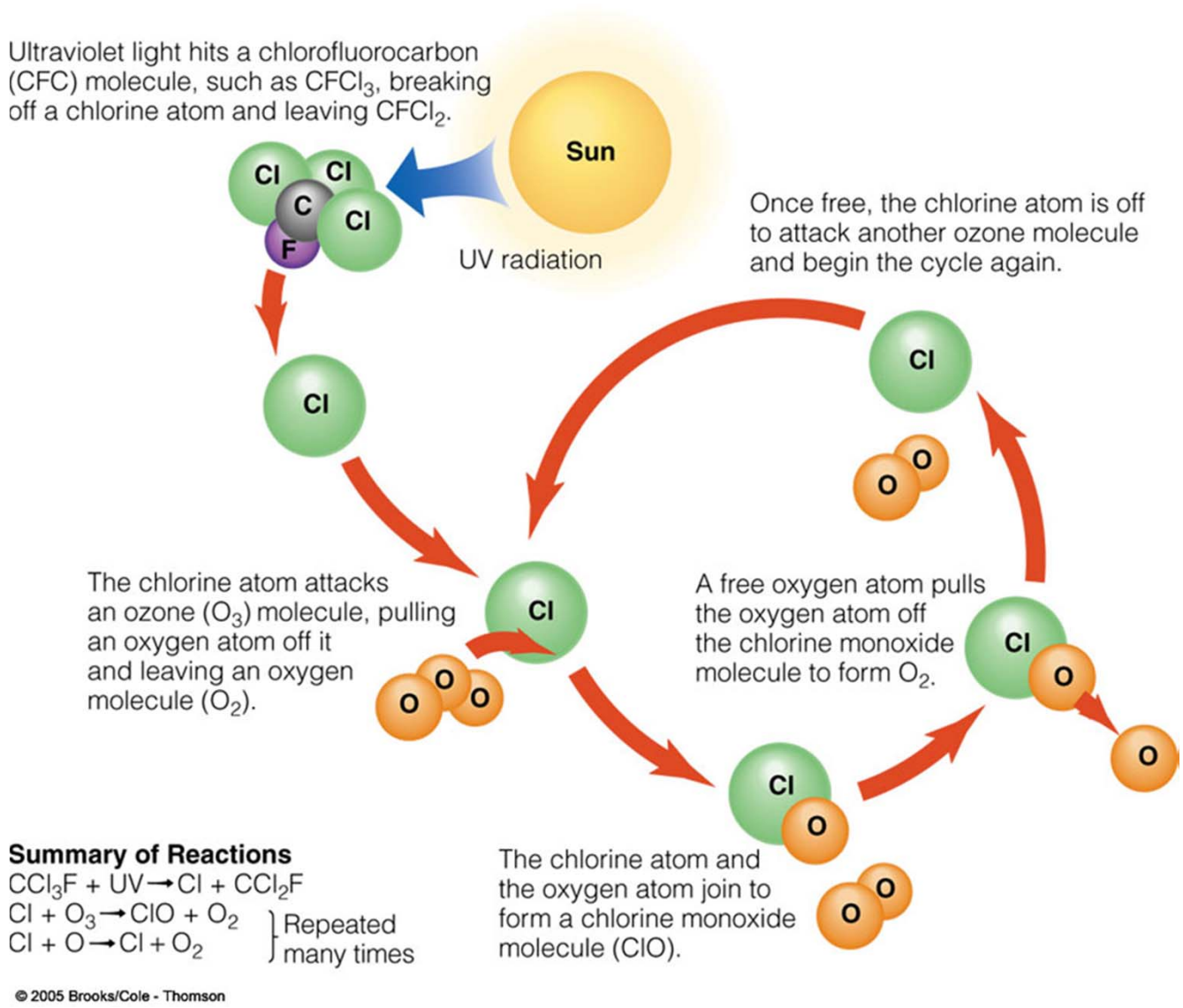
$$\frac{[O]}{[O_3]} = \frac{j_2}{k_1[O_2][M]}$$

Catalytic destruction of stratospheric ozone

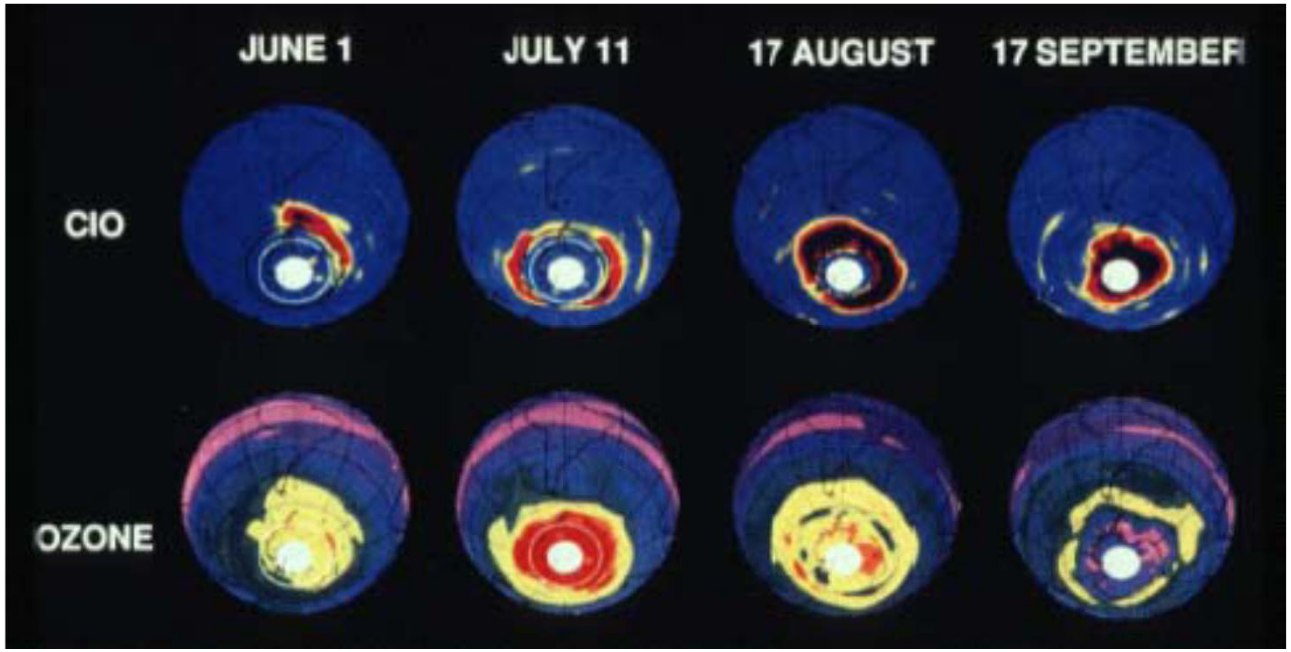
$$\cancel{X} + O_3 \longrightarrow^{k_3} \cancel{XO} + O_2$$

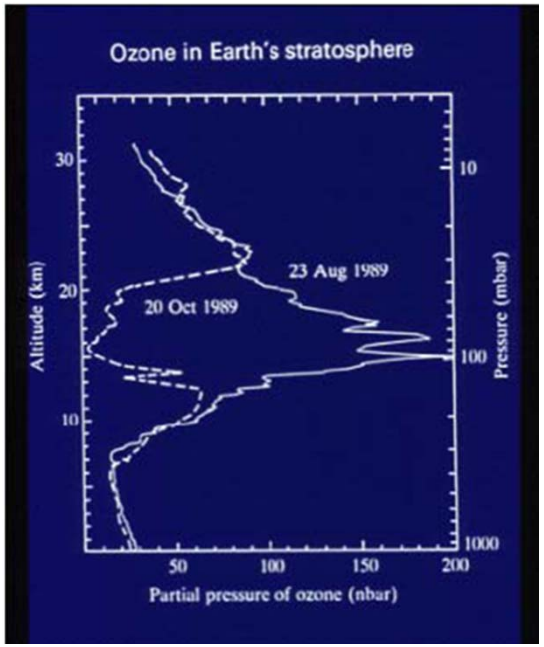
$$\cancel{XO} + O \longrightarrow^{k_4} \cancel{X} + O_2$$

$$O + O_3 \longrightarrow 2O_2$$



Ozone hole


JUNE 1
JULY 11
17 AUGUST
17 SEPTEMBER
ClO
OZONE


Ozone in Earth's stratosphere
Altitude (km)
Pressure (mbar)
23 Aug 1989
20 Oct 1989
Partial pressure of ozone (nbar)
30
20
10
10
100
1000
50
100
150
200

References

Material shown here partly stems from:

- www.atmos.uiuc.edu/courses/atmos348.../Atmos348Lecture17.pdf
- www.ees.ufl.edu/homepp/cywu/.../Equilibrium%20&%20Kinetics.ppt
- http://ua.acd.ucar.edu/Presentations/lecture2.pdf
- http://www.atmos.uiuc.edu/courses/atmos348-sp04/documents/Atmos348Lecture5.pdf
- www.authorstream.com/.../aSGuest8996-131504-smog-chemistry-project-science-technology-ppt-powerpoint/
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