Prof. Dudley Shallcross Atmospheric Chemistry Research Group 2024

Aircraft and Climate, the good, the bad and the downright difficult

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A bit of background atmospheric chemistry

Troposphere and air pollution

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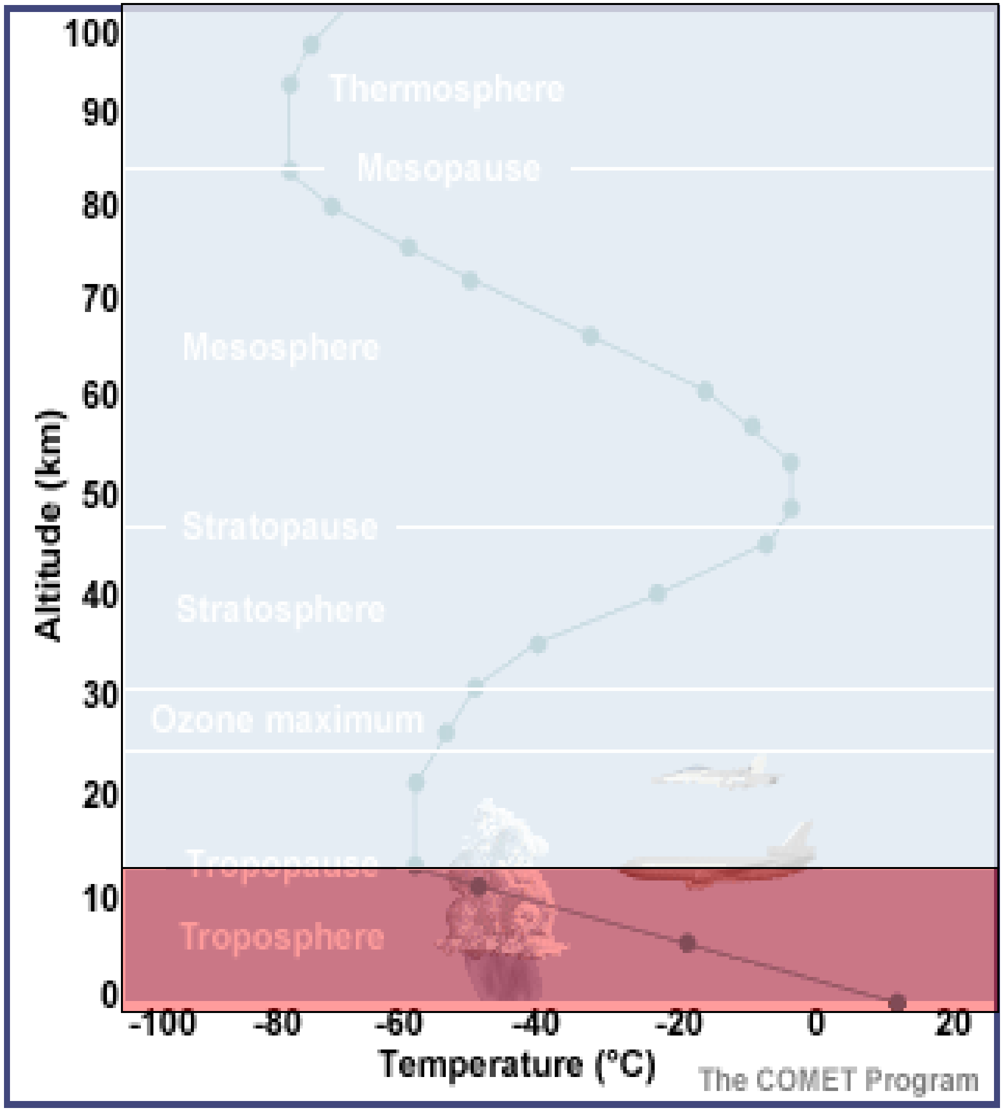

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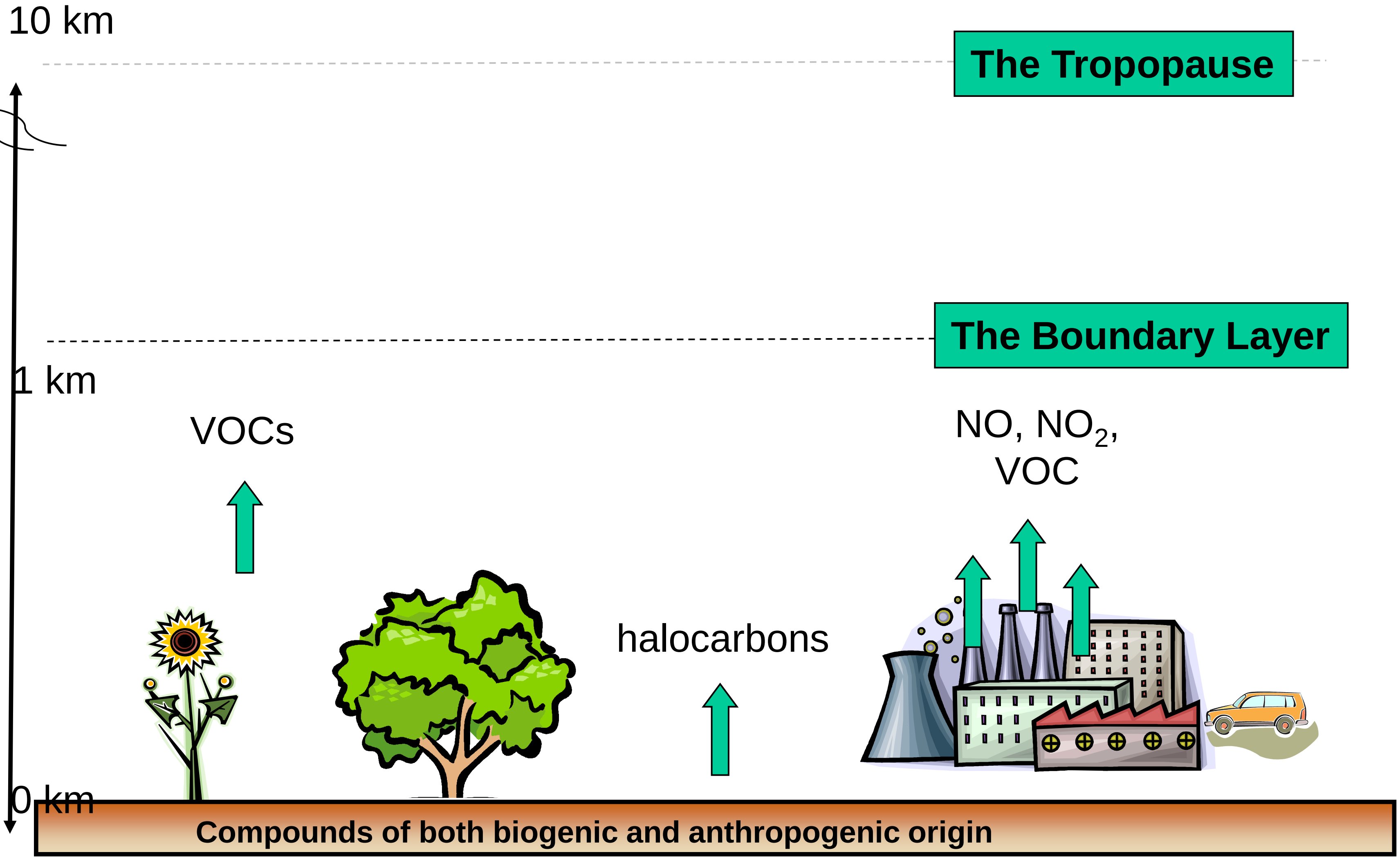
Air Pollution and the Troposphere



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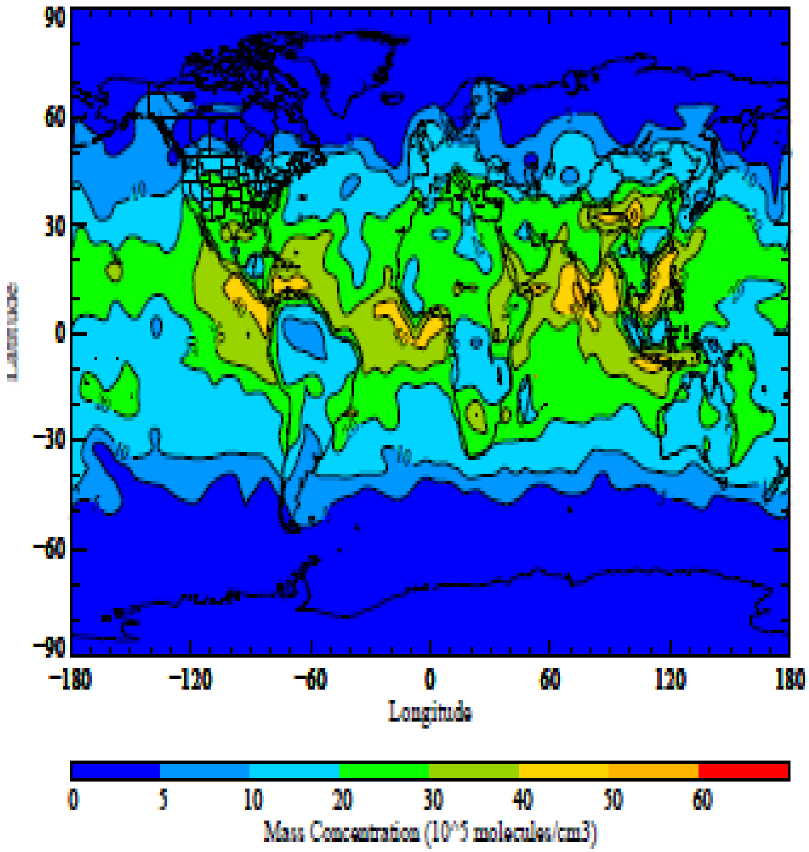
VOCs broken down by the OH radical, generated by sunlight

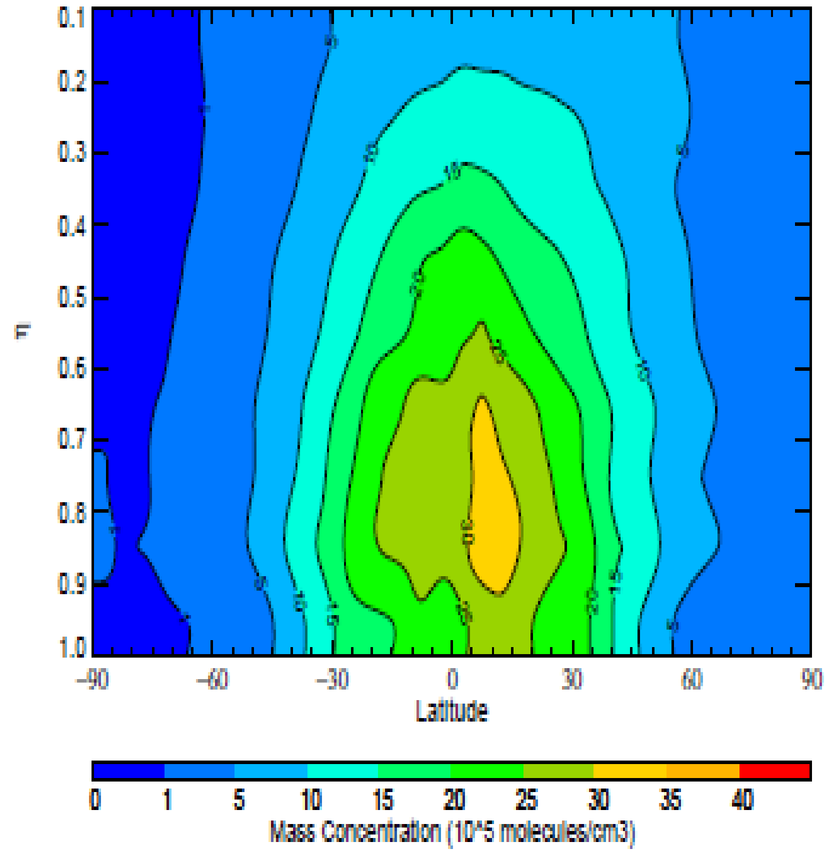
$$O_3 + \text{sunlight} \rightarrow O^* + O_2 \quad \lambda < \sim 330 \text{ nm}$$

$$O^* + H_2O \rightarrow \bullet OH + \bullet OH$$

$$\bullet OH + R\text{-}H \rightarrow \bullet R + H_2O$$

OH surface and altitude distribution





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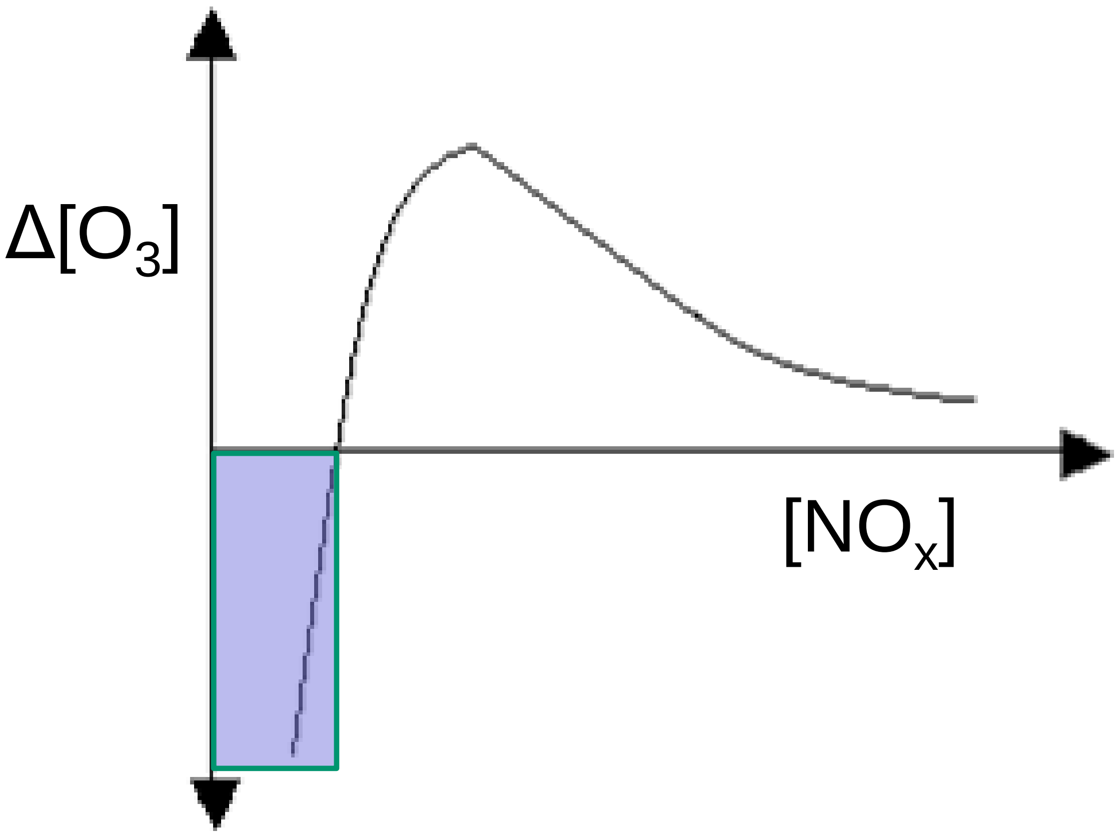
Ozone Chemistry- low NOx environment



Examples: Marine boundary layer, remote free troposphere

Ozone Chemistry- low NO_x environment

$O_3 + h\nu \rightarrow O(^1D) + O_2$ $\lambda \leq \sim 330$ nm

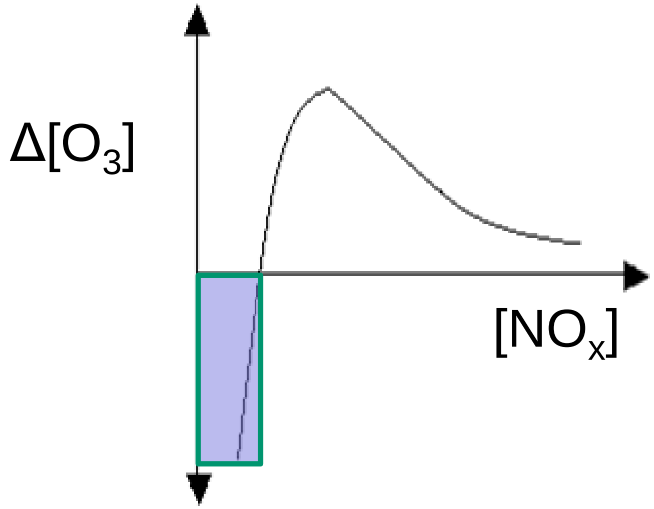
$O(^1D) + M \rightarrow O(^3P) + M$

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

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + O_3 \rightarrow OH + 2O_2$



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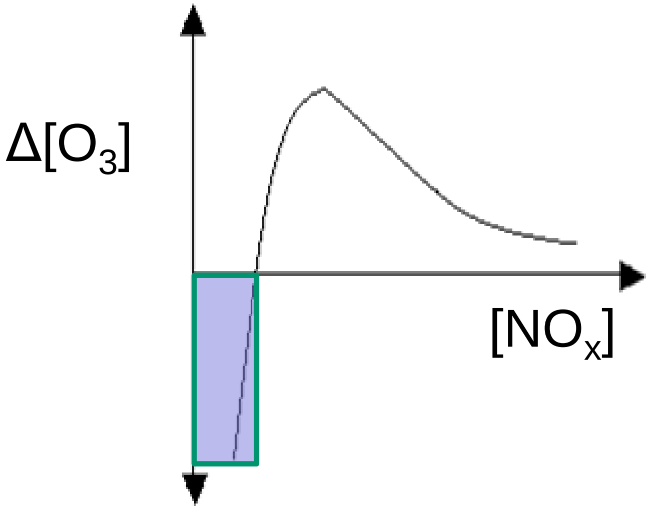
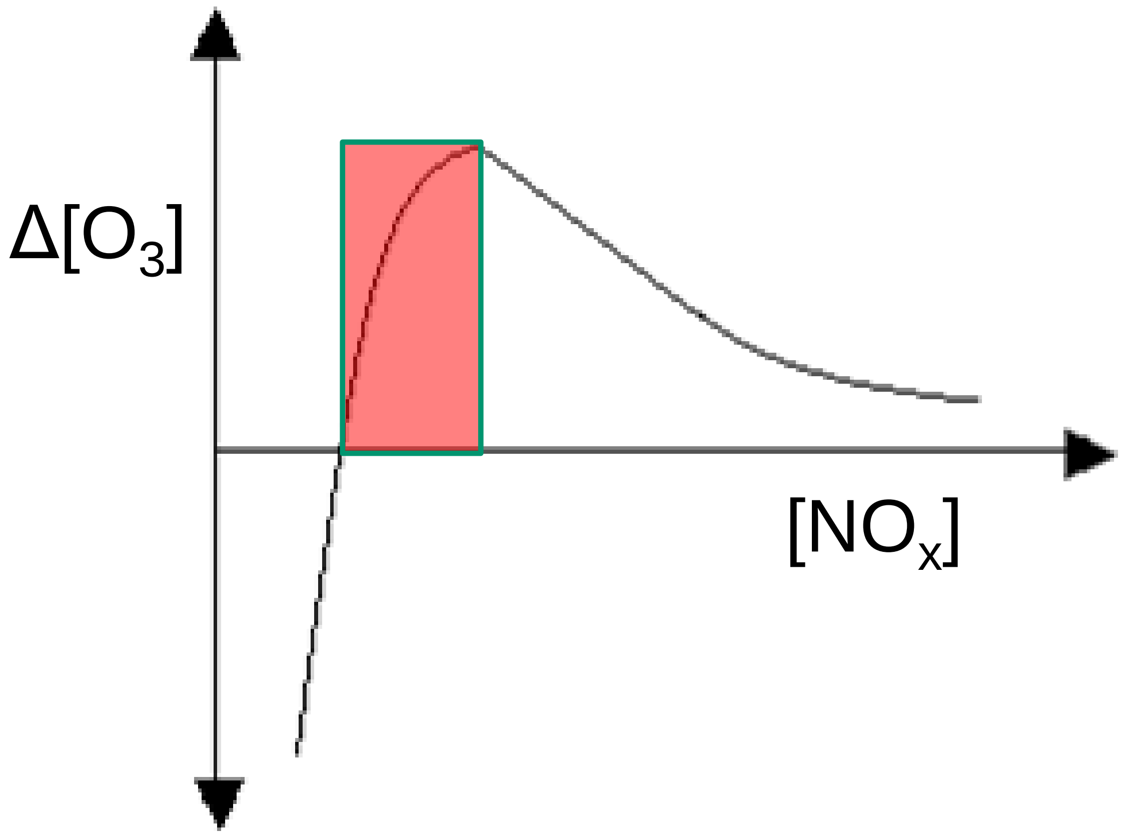
$HO_2 + O_3 \rightarrow OH + 2O_2$

Net: $CO + O_3 \rightarrow CO_2 + O_2$



Ozone Chemistry- higher NO_x environment



Examples: Outflow from pollution centres and biomass burning regions

Ozone Chemistry- higher NO_x environment

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

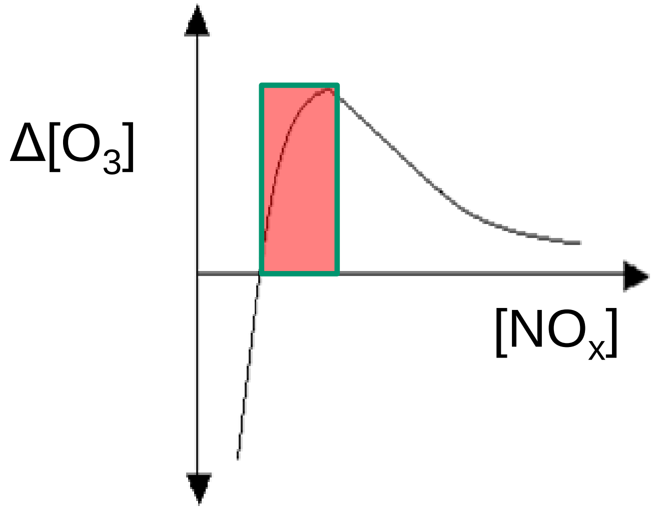
$HO_2 + O_3 \rightarrow OH + 2O_2$

NO competes with O_3 for HO_2

$NO + HO_2 \rightarrow NO_2 + OH$

$NO_2 + hv \rightarrow NO + O(^3P)$

$O(^3P) + O_2 + M \rightarrow O_3 + M$



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Ozone Chemistry- higher NO_x environment

$CO + OH \rightarrow CO_2 + H$

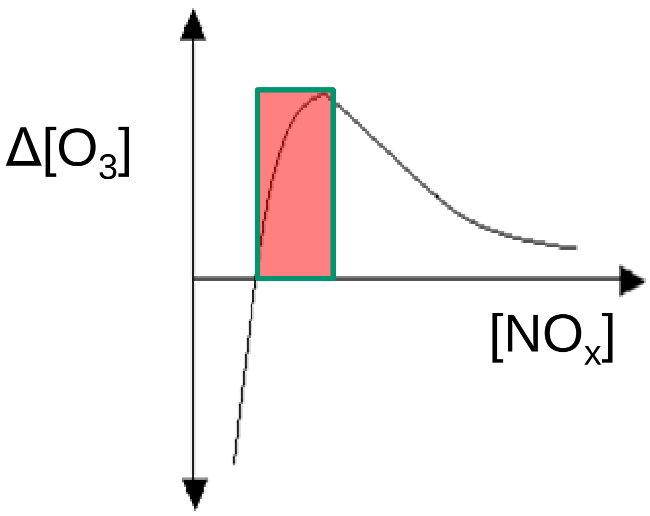
$H + O_2 + M \rightarrow HO_2 + M$

$NO + HO_2 \rightarrow NO_2 + OH$

$NO_2 + h\nu \rightarrow NO + O(^3P)$

$O(^3P) + O_2 + M \rightarrow O_3 + M$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3$



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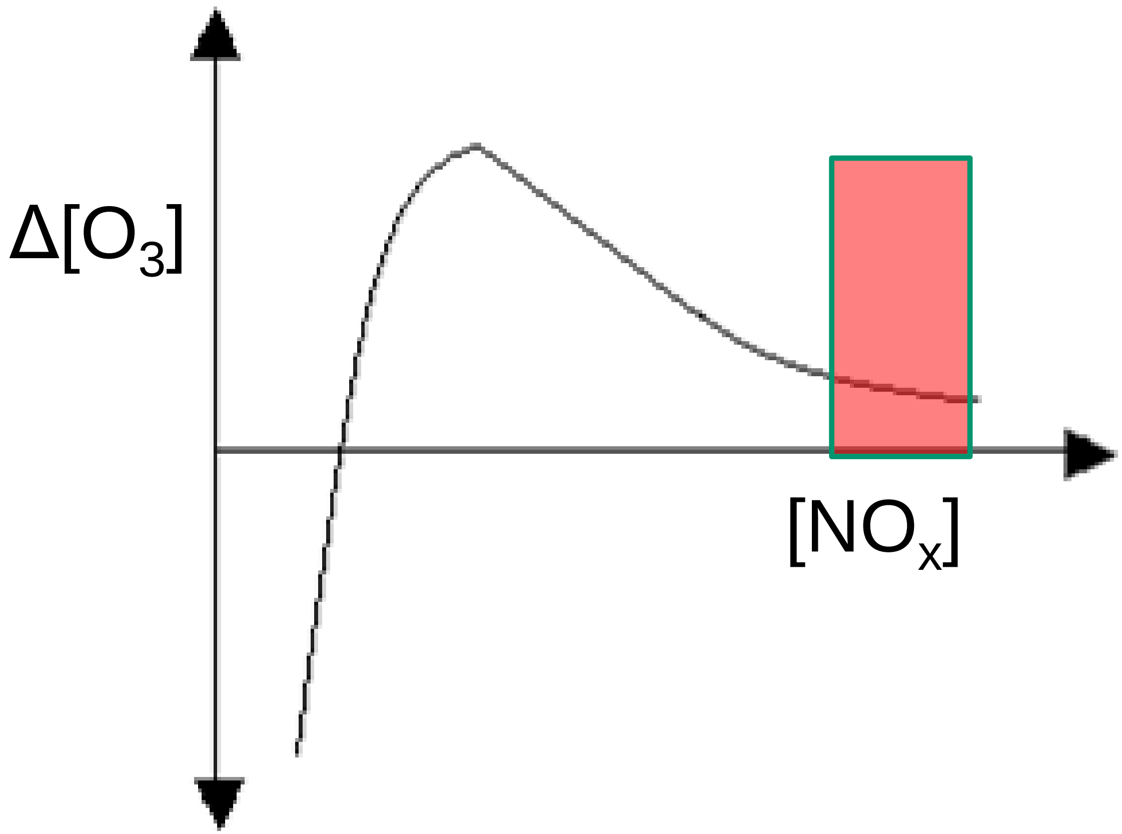
Ozone Chemistry- very high NO_x environment



Examples: Urban environments, airports

Ozone Chemistry- very high NO_x environment

This cycle should just accelerate?

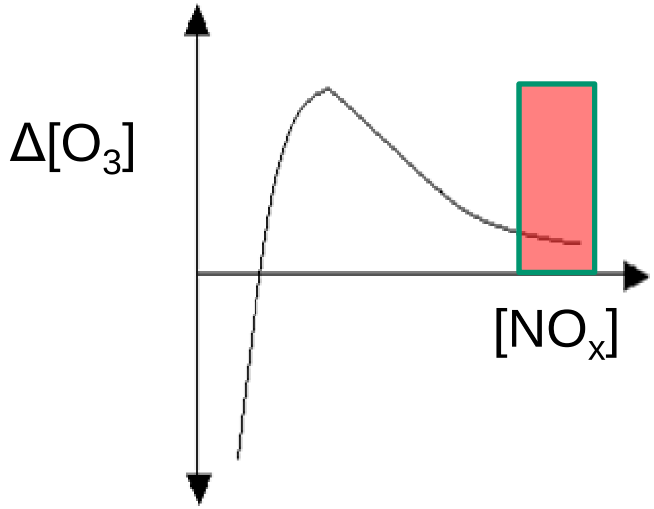
$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$NO + HO_2 \rightarrow NO_2 + OH$

$NO_2 + h\nu \rightarrow NO + O(^3P)$

$O(^3P) + O_2 + M \rightarrow O_3 + M$



But now NO_2 is so high that it reacts with OH

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Ozone Chemistry- higher NO_x environment

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

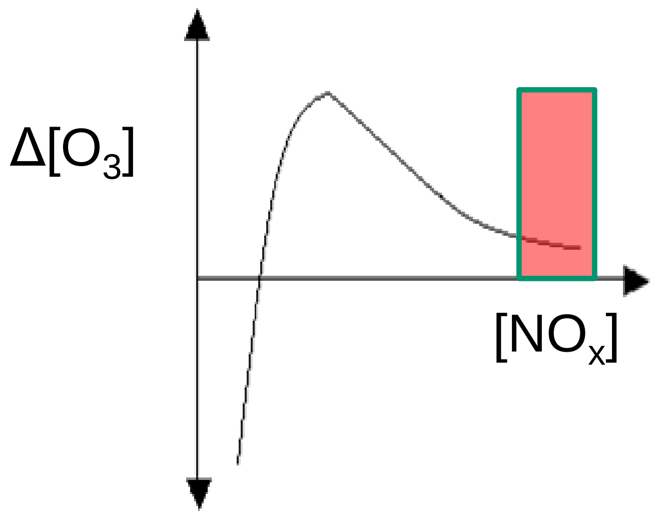
$NO + HO_2 \rightarrow NO_2 + OH$

$NO_2 + h\nu \rightarrow NO + O(^3P)$

$O(^3P) + O_2 + M \rightarrow O_3 + M$

But $OH + NO_2 \rightarrow HNO_3$

Net: Low ozone production



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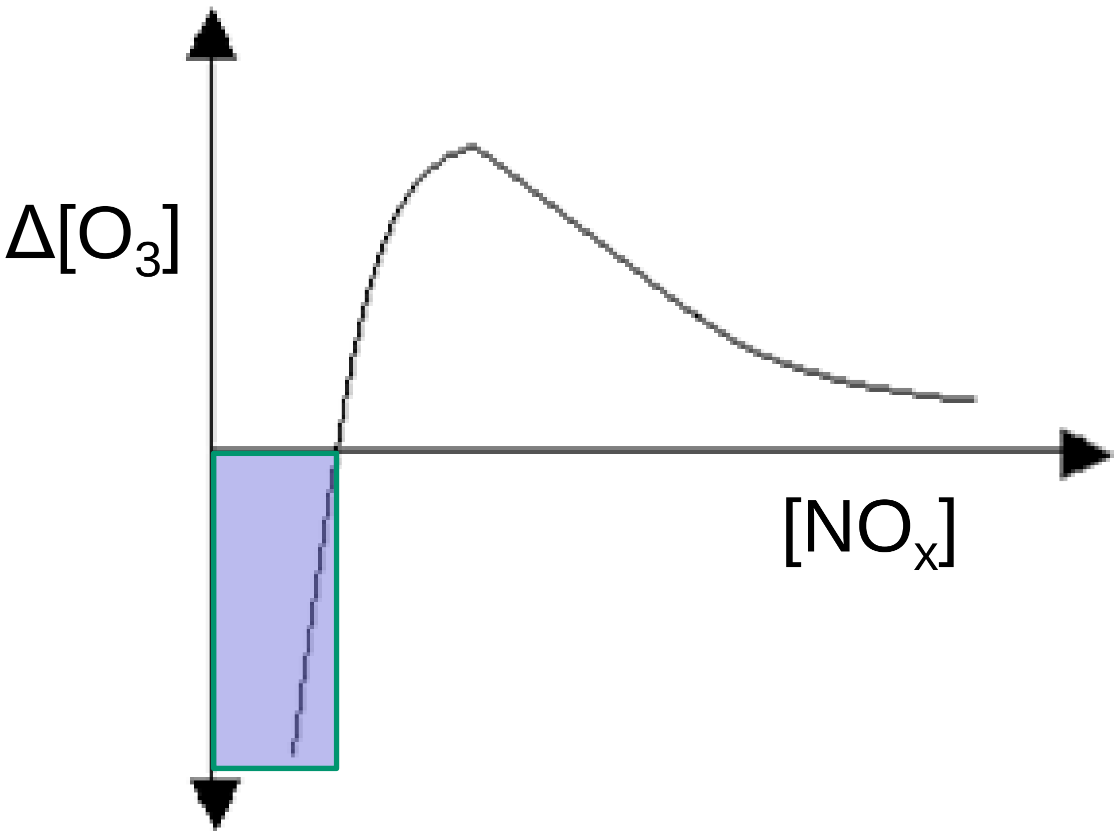
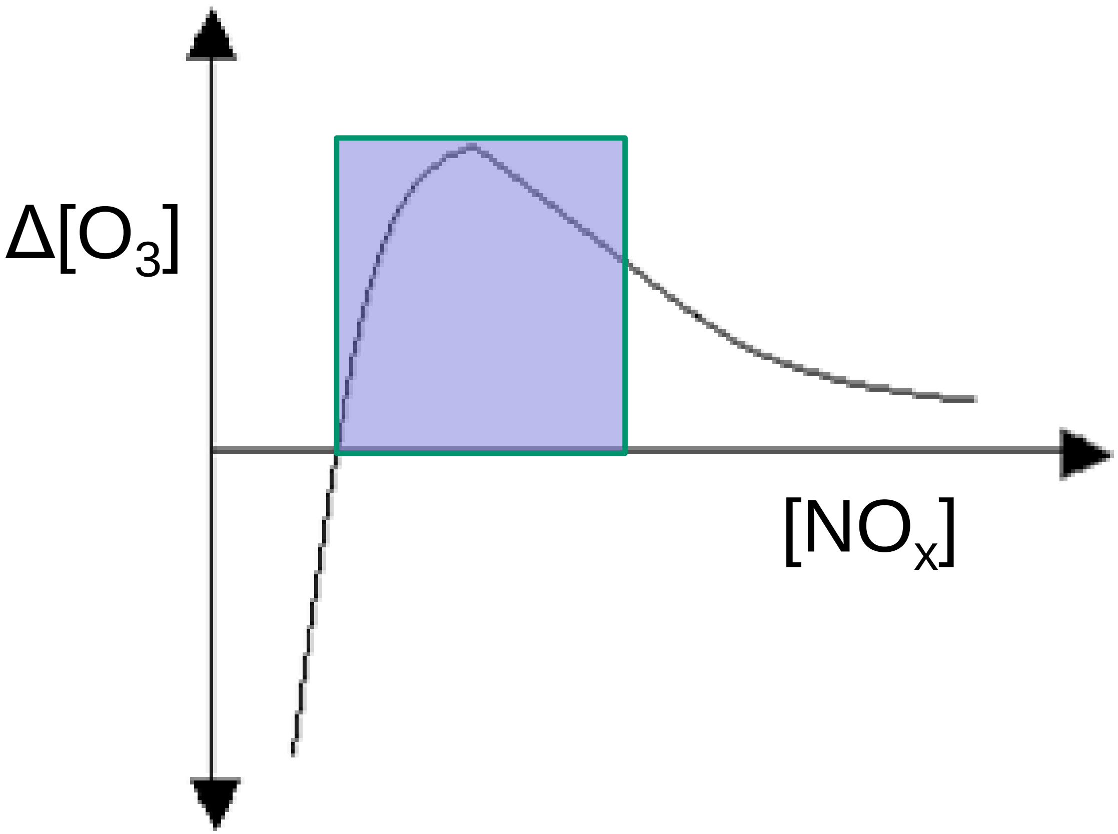
Aircraft sample this whole curve



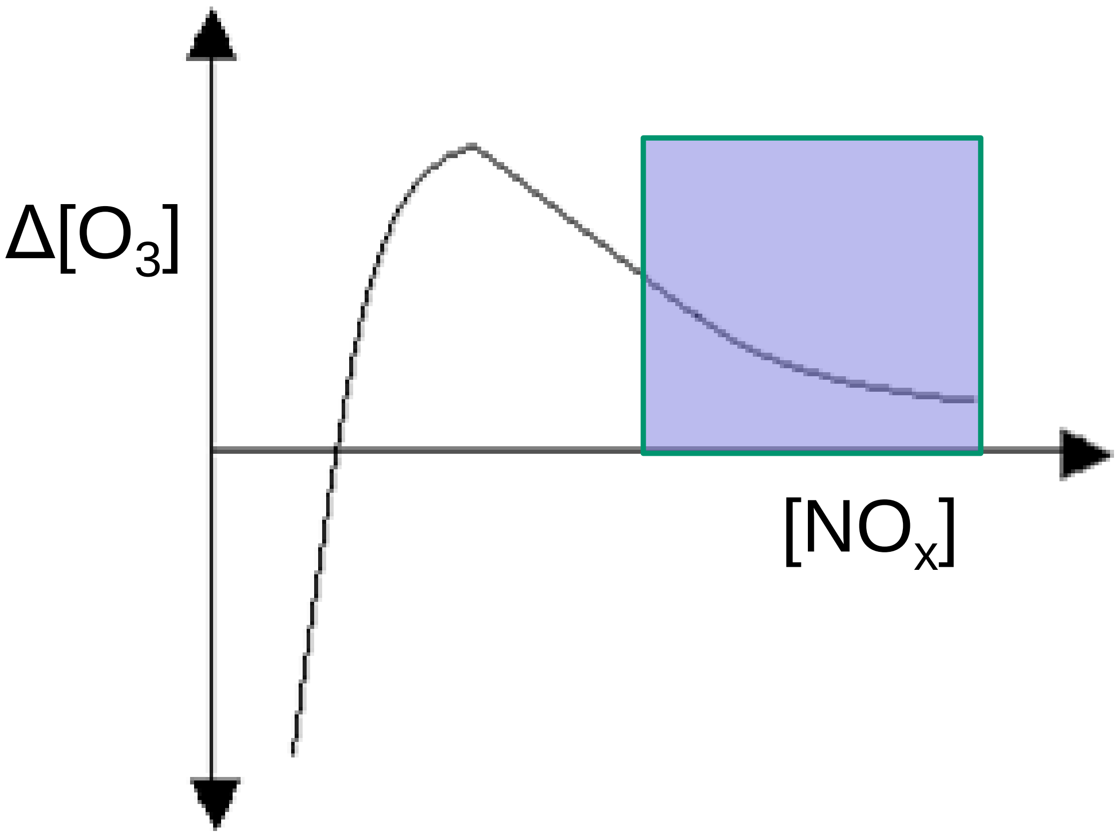
Cruise

Aircraft sample this whole curve



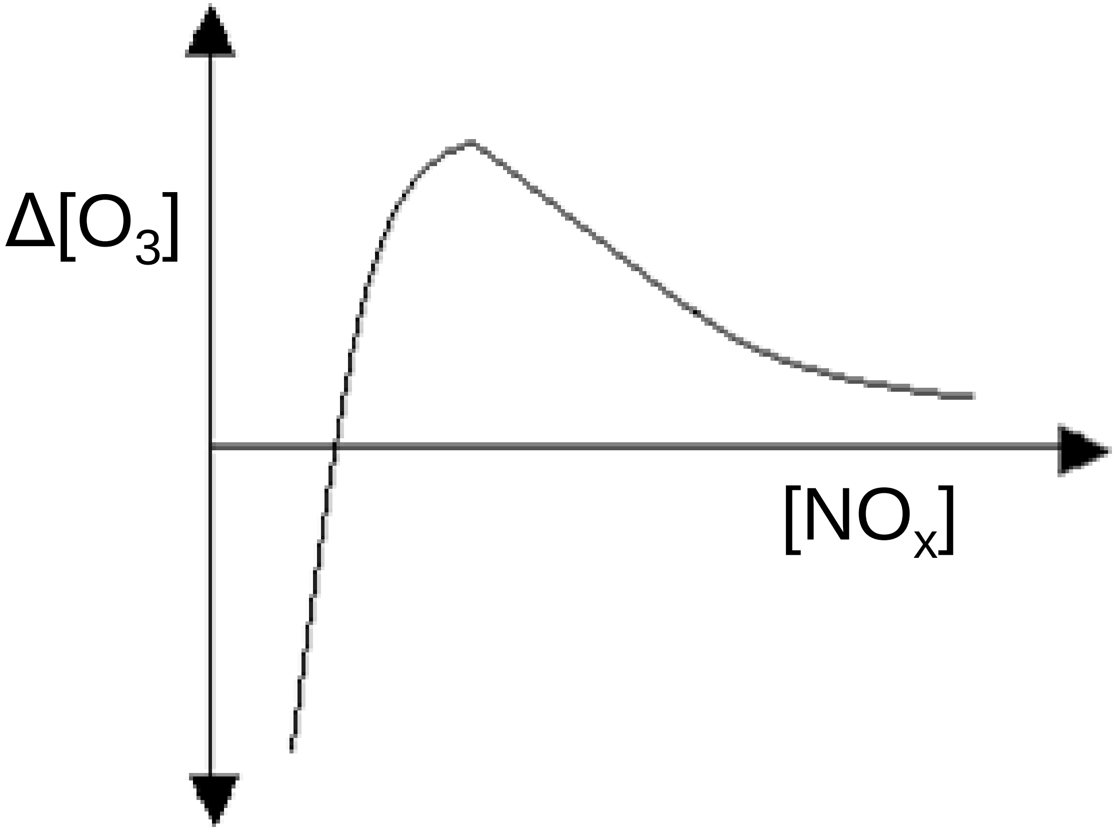
Climb and descent

Aircraft sample this whole curve



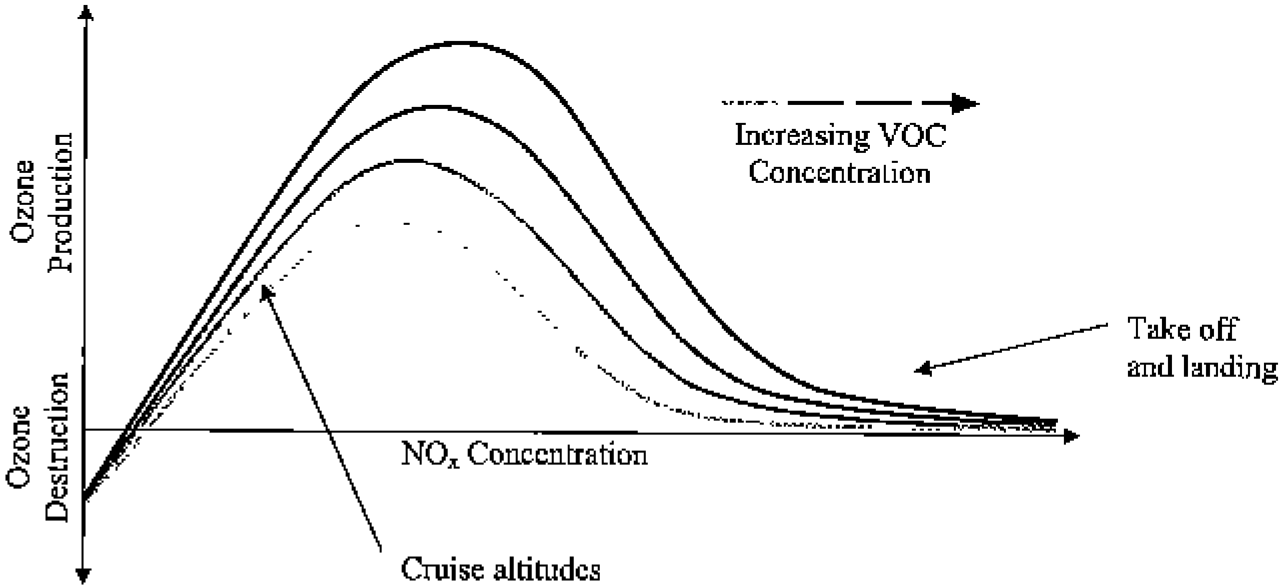
Taxi, take-off and landing

Role of VOCs

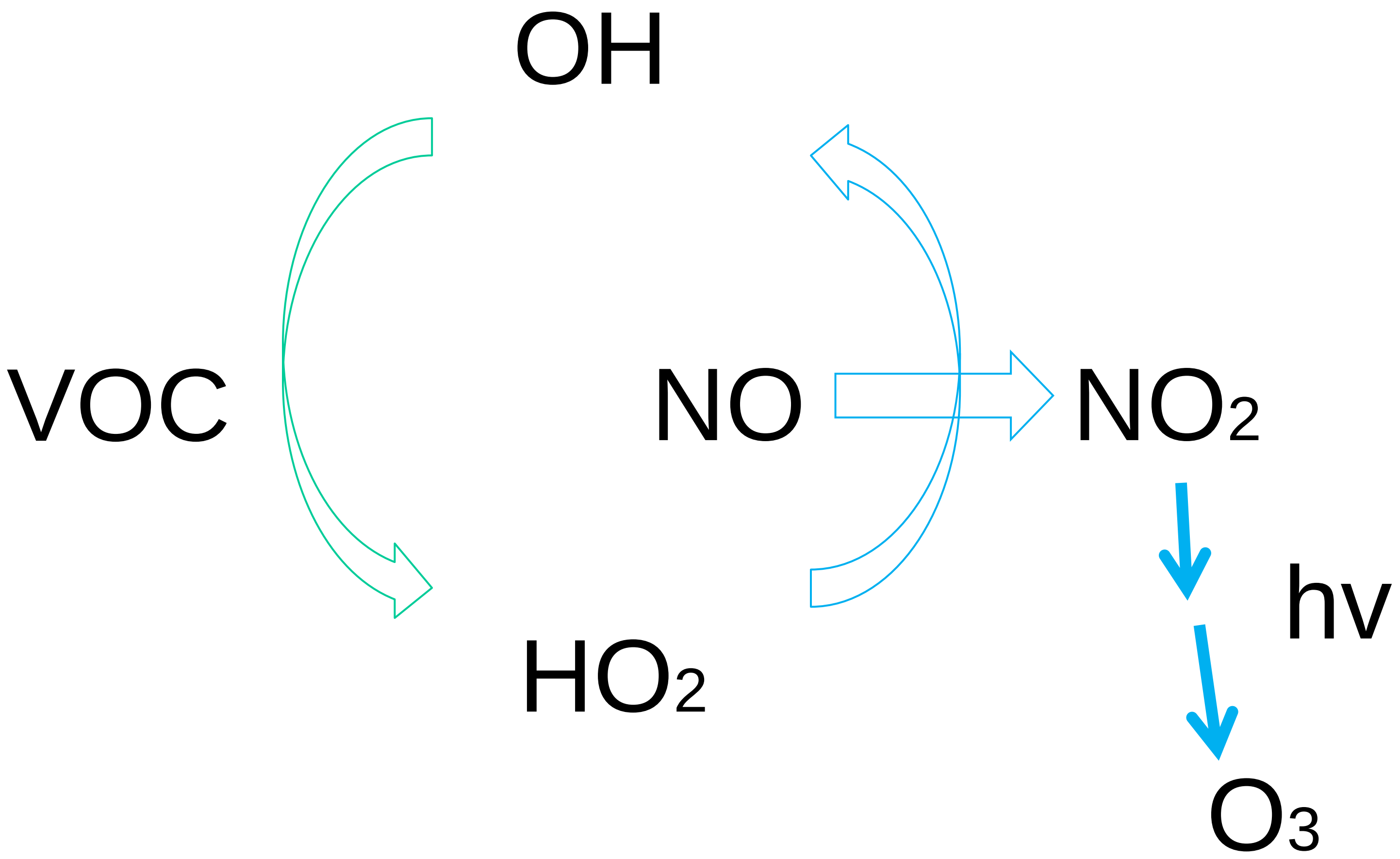


The curve drawn is for one VOC level

Non-linearity of O_3 production



The effect of NOx and VOC concentrations on the net rate of O_3 production.



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Climate

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Granny's model of climate 1

Earth Sun

Temperature of the Earth ~ 10^o C

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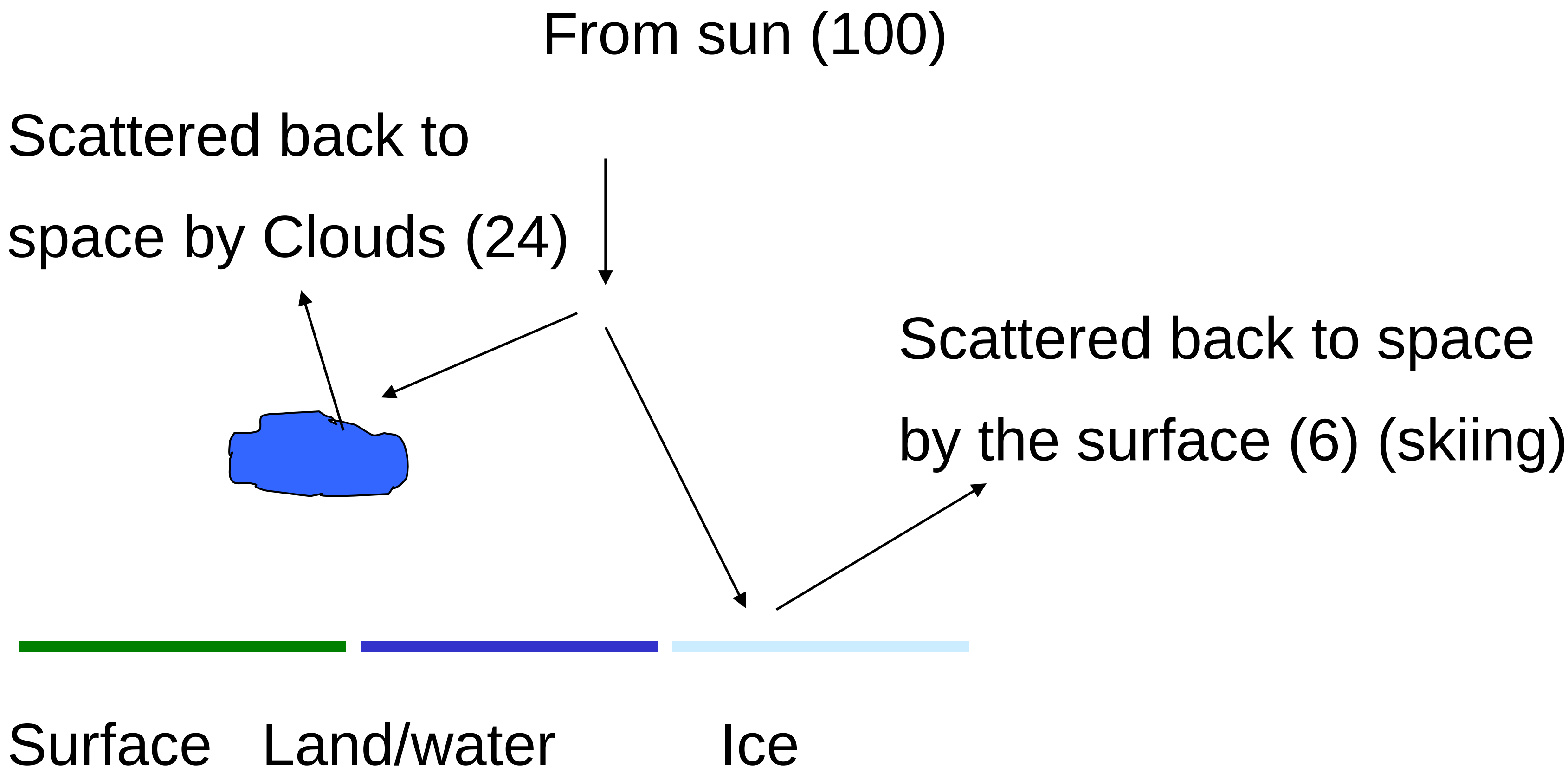
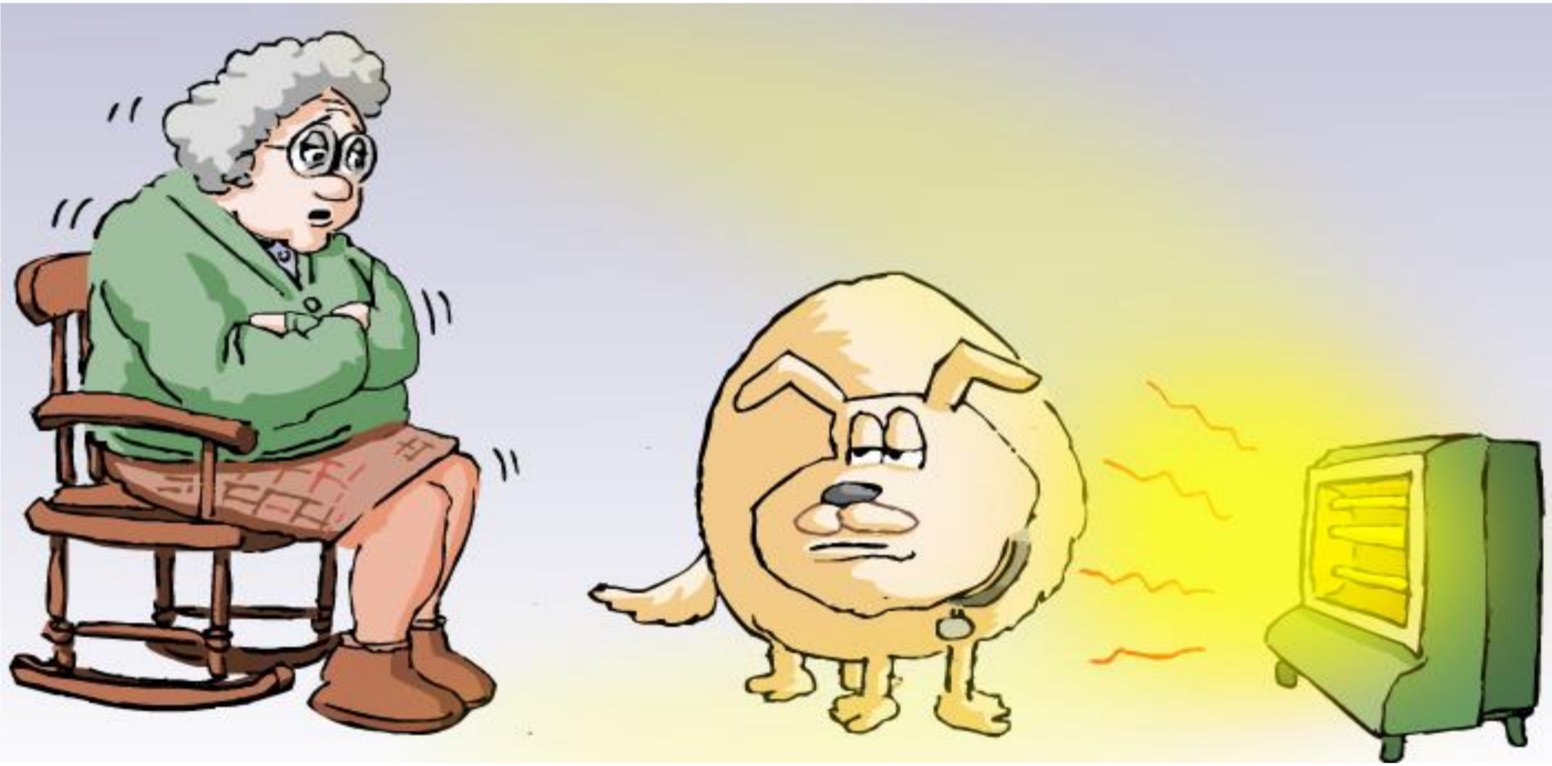
Big problemo: clouds and ice



30% of incoming solar radiation reflected back out to space without being absorbed (Earth's albedo A = 0.3)

Granny's model of climate 2



Earth Sun

With clouds and ice

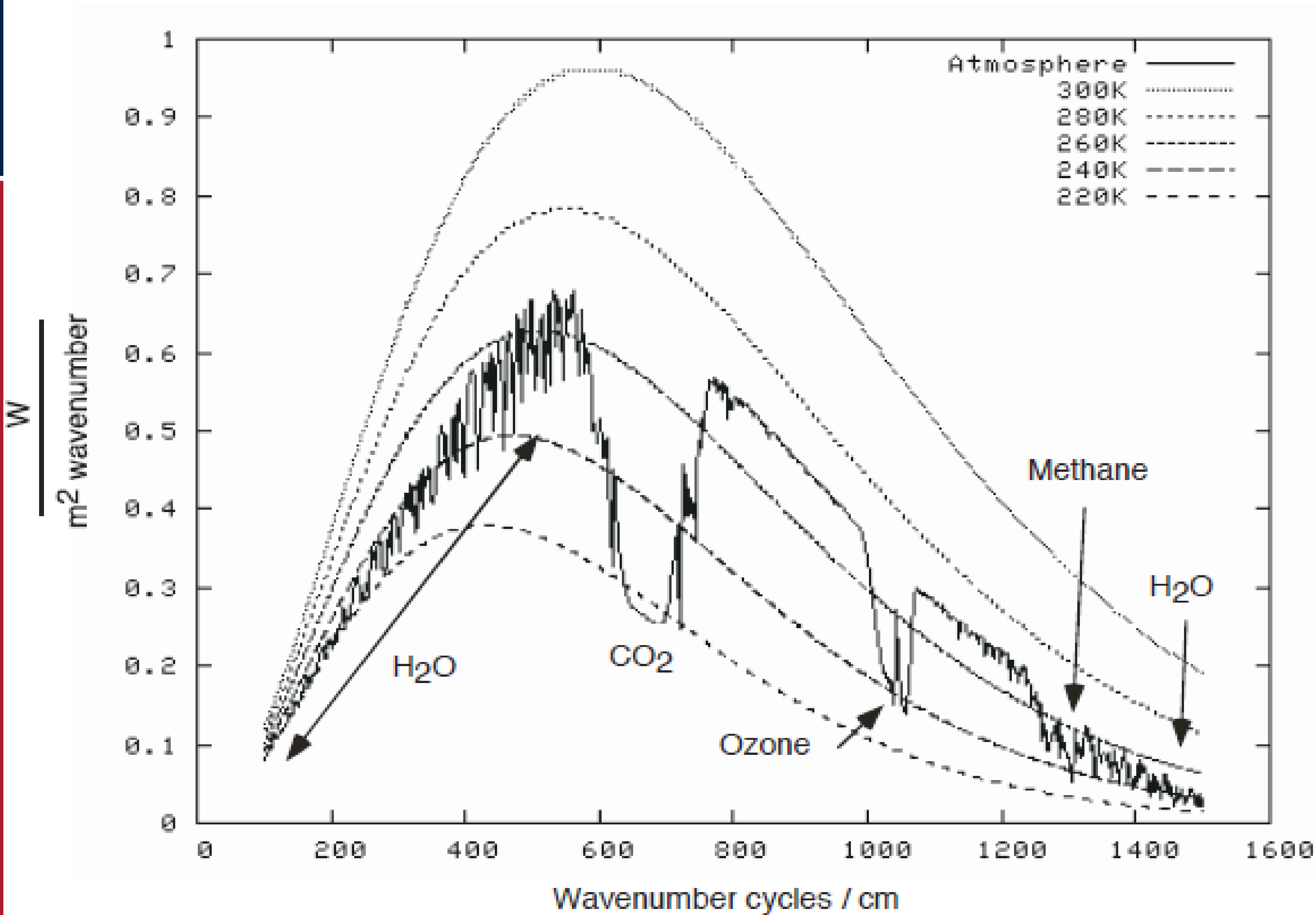
Temperature of the Earth ~ - 18º C

Granny is now very cold

What can she do to warm herself up?

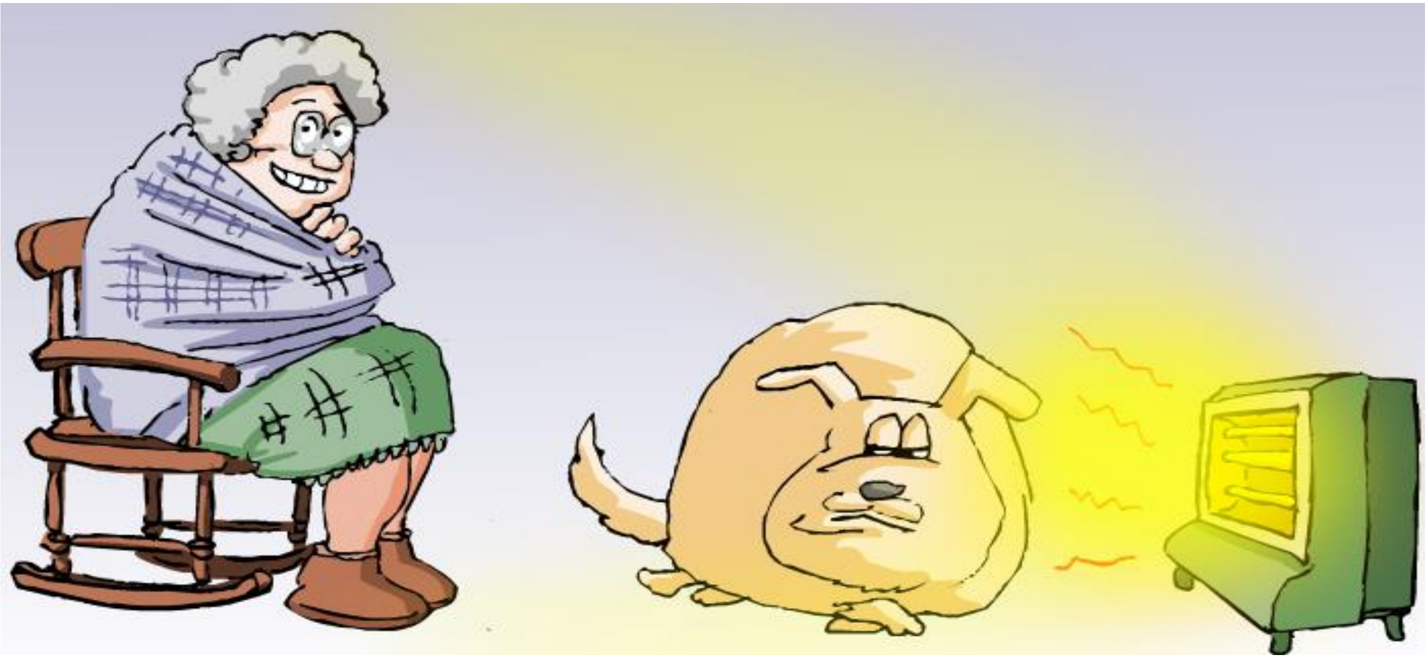
Move closer?

Get a blanket?



Atmosphere
300K
280K
260K
240K
220K
Methane
H2O
CO2
Ozone
H2O
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
200
400
600
800
1000
1200
1400
1600
W / m2 wavenumber
Wavenumber cycles / cm

Granny's model of climate 3 with blankets



Earth Sun

with clouds and ice and greenhouse gases

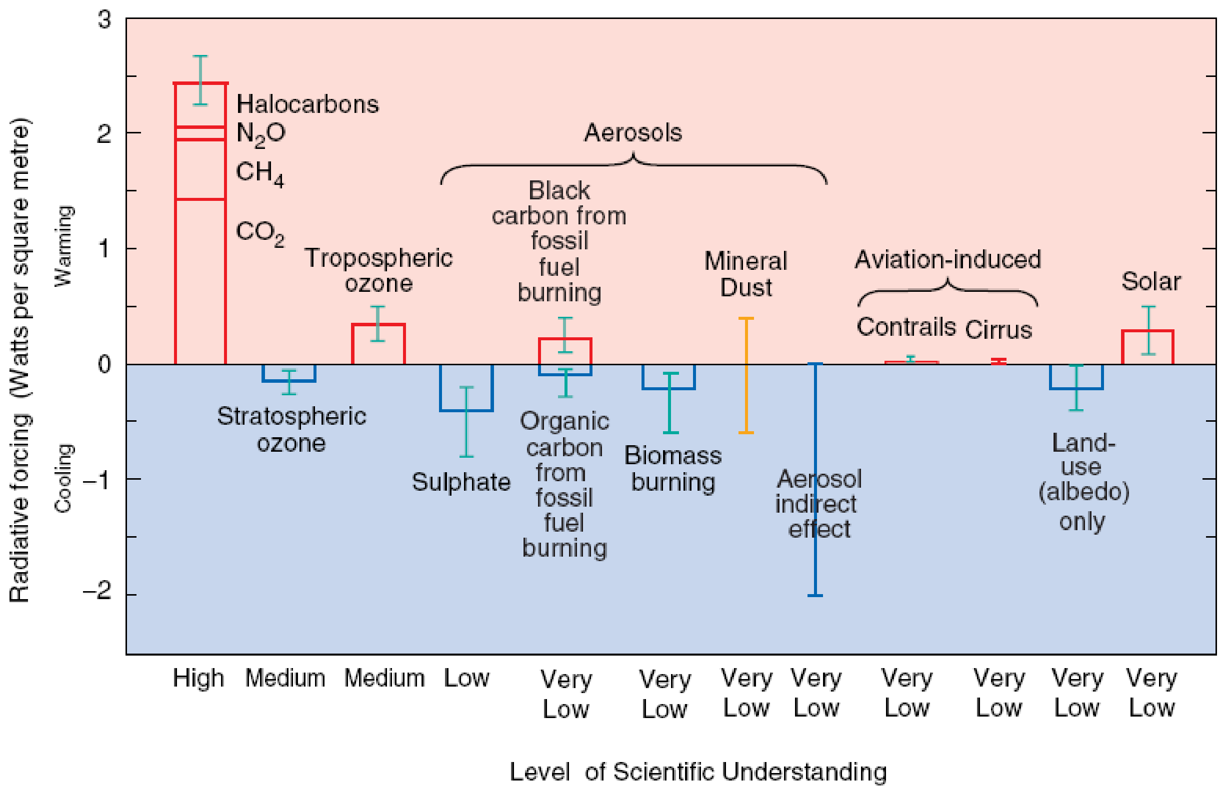
Temperature of the Earth ~ 16º C

Thanks to Mike Stuart 2008

www.disphoria.co.uk

For the granny cartoons

Factors affecting climate system



Establishing a link between global warming and man-made greenhouse gas pollution

The global mean radiative forcing of the climate system for the year 2000, relative to 1750 (IPCC, 2001).

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What was the point of the last (15) mins?

1. Increase aerosol or clouds (Troposphere) reflect back more incoming solar radiation (Good) – Harvard team suggesting bioengineering of the stratosphere (not really)
2. Destroy tropospheric (surface) ozone in the background atmosphere (Good) increasing it is bad for climate and health (Bad)

So, what about aircraft?

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Direct (CO_2) vs. indirect (NOx) impact

About 2/6 CO_2

- Well mixed
- 100 years +
- Adds to global burden
- Behaviour in atmosphere simple
- Impact depends on concentration
- Not on location

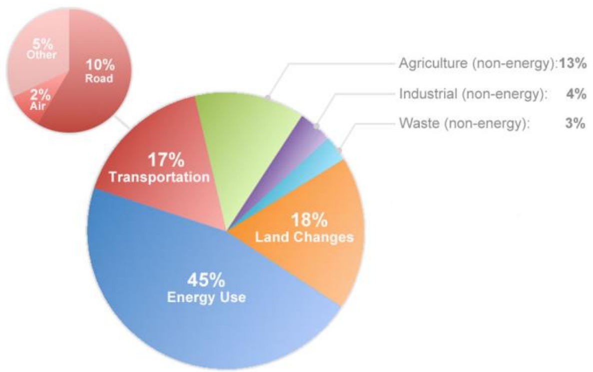


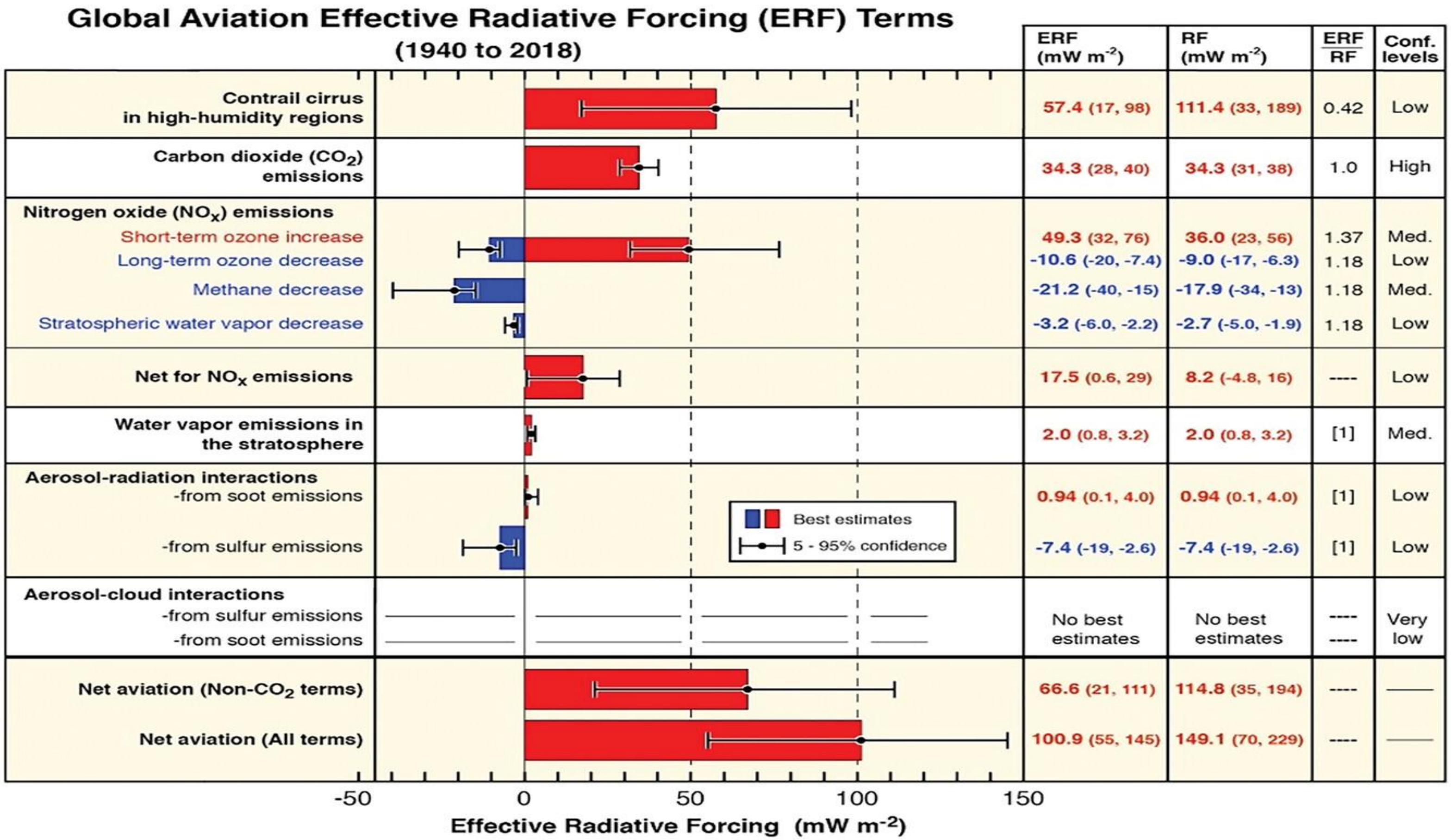
Fig. 1. Total global CO_2 emissions by sector, [WRI, 2005 World Greenhouse Gas Emissions, adapted from http://tcktcktck.org/2011/09/transportation-2/1095.

About 1/6 NOx

- Leads to tropospheric ozone O_3 production
- UV light + NOx + HC
- Stratospheric O_3 good
- Tropospheric O_3 GHG
- Key oxidant (e.g. CH_4)
- Component of smog (air quality)
- In – situ production small
- NOx at 9 – 11 km = more O_3

About 3/6 Contrails

Warming (all day) and cooling (daytime)



Effective radiative forcing contributions from global aviation emissions (Lee et al, 2021)

Models

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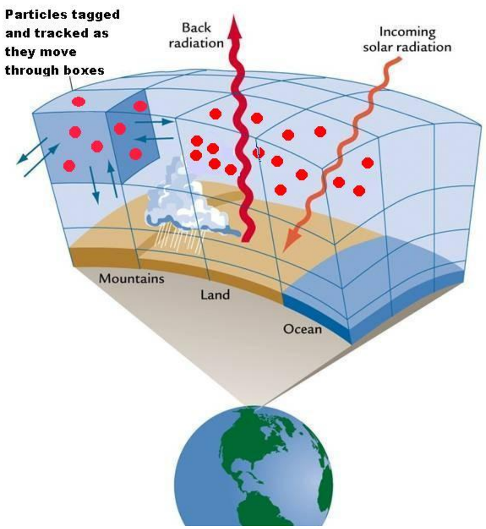
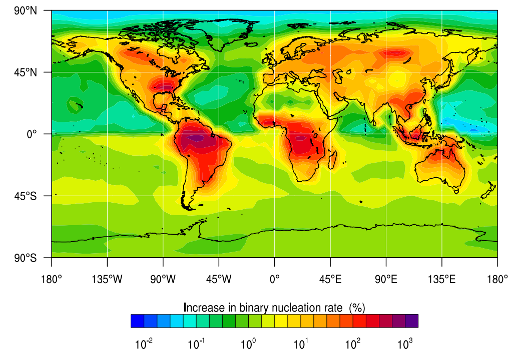
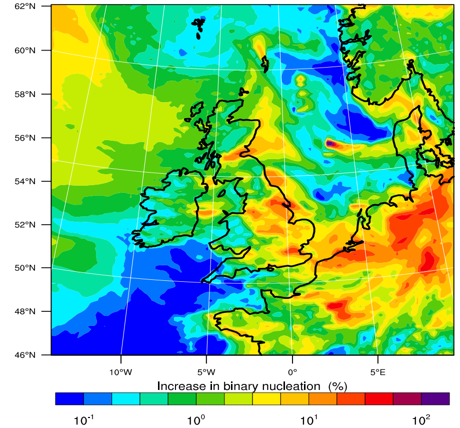
Models





STOCHEM-CRI 5 degrees by 5 degrees
Detailed Chemistry, surface and non-surface emissions, several aircraft impact studies



WRF-chem-CRI 15 km by 15 km
Detailed Chemistry, surface and non-surface Emissions.

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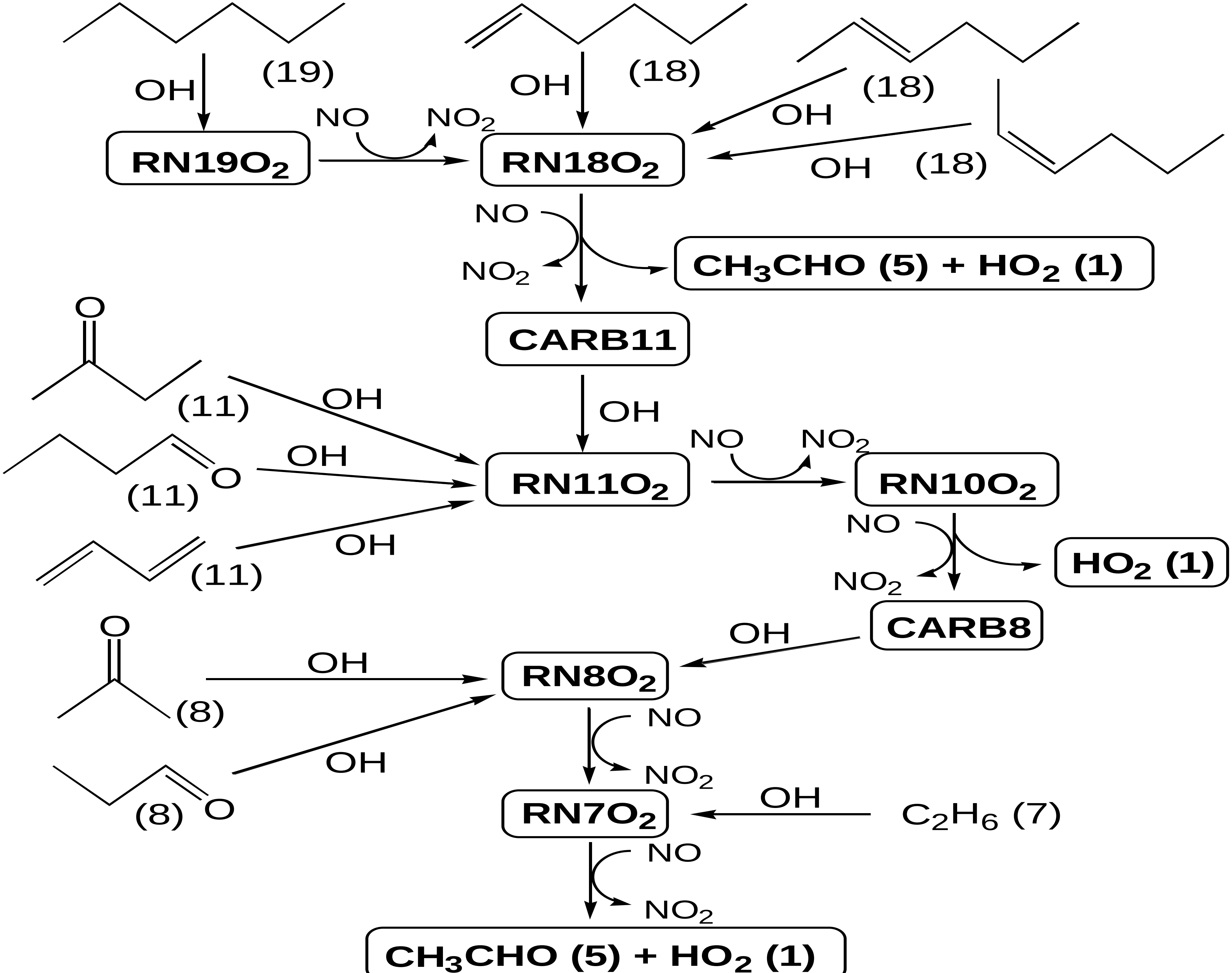

(19)
OH
NO
NO2
RN19O2
(18)
OH
RN18O2
(18)
OH
OH
(18)
NO
NO2
CH3CHO (5) + HO2 (1)
CARB11
O
(11)
OH
OH
RN11O2
NO
NO2
RN10O2
(11)
O
OH
(11)
OH
NO
NO2
HO2 (1)
CARB8
O
OH
OH
RN8O2
(8)
NO
NO2
OH
(8)
O
RN7O2
OH
C2H6 (7)
NO
NO2
CH3CHO (5) + HO2 (1)

Aircraft case studies using STOCHEM-CRI

Dr. Donata Wasiuk

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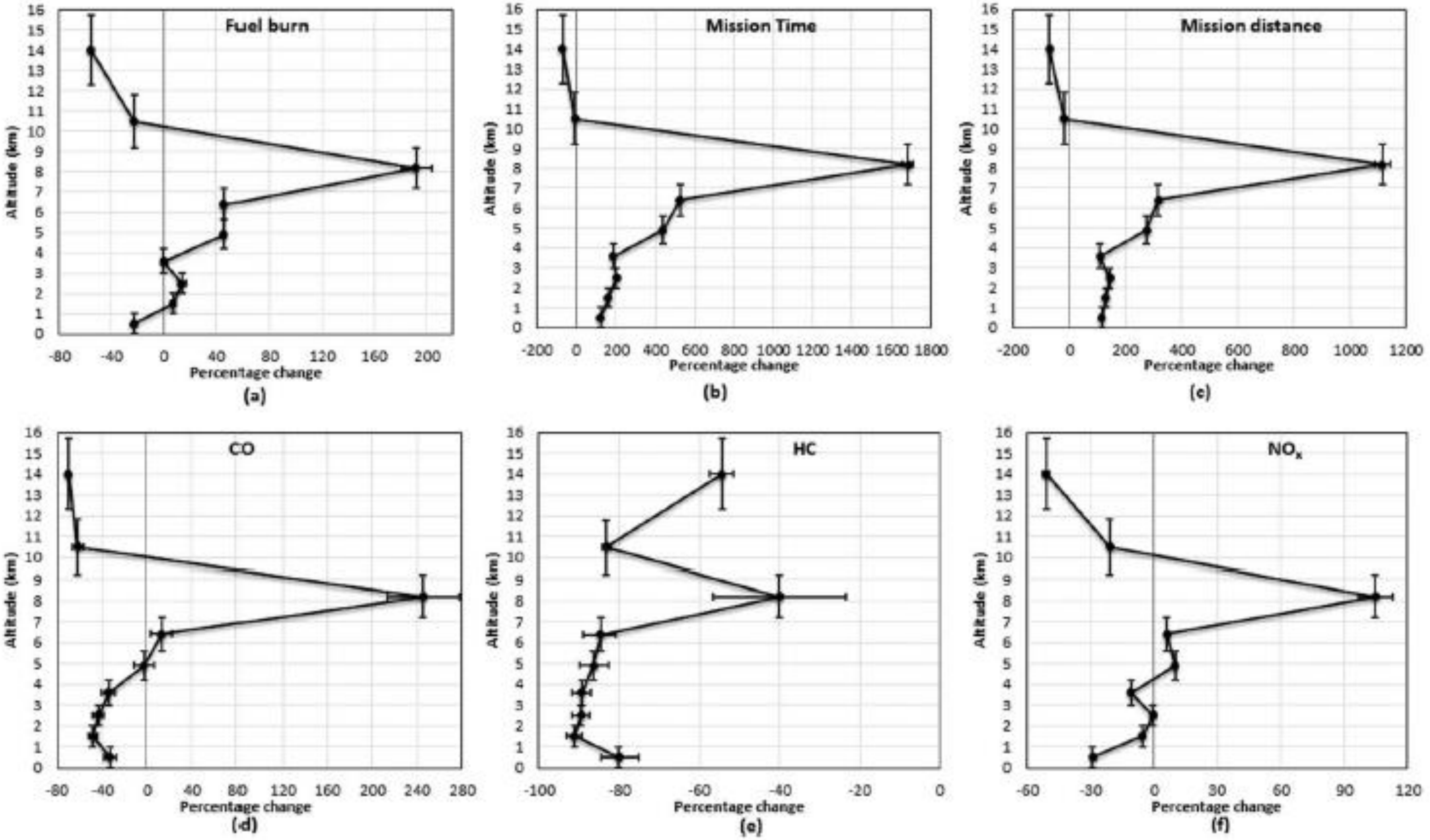
Emission inventory estimates

Year	Fuel burn (Tg)	CO2 (Tg)	H2O (Tg)	VOC (Tg)	NOx (Tg))	SOx (Tg)
2005	147.6	464.7	181.5	0.28	3.4	0.12
2006	188.2	594.3	232.8	0.10	2.7	0.22
2006	152.2	479.3	187.2	0.24	3.5	0.13
2007	160.9	506.8	198.0	0.23	3.7	0.14
2008	229.0	725.0	282.0	0.09	3.2	0.18
2008	163.0	513.4	200.5	0.21	3.8	0.14
2010	240.0	n/a	n/a	0.3	3.02	n/a
2010	163.9	516.0	201.5	0.17	3.9	0.14

Wilkerson et al., ACP 2006; Cheze et al., Energy Policy, 2011; Yan et al., ACP, 2014

Turbo to prop Wasiuk *et al*., J.G.R. **121**, 8730 (2016)



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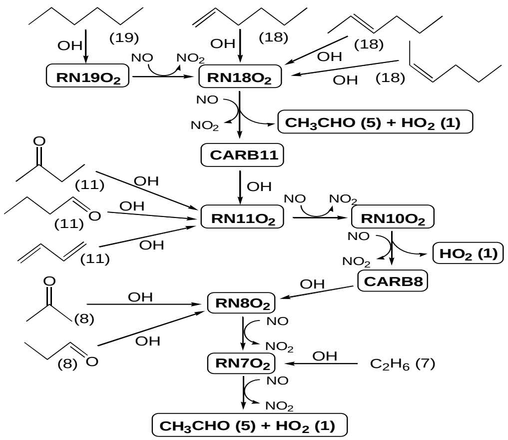

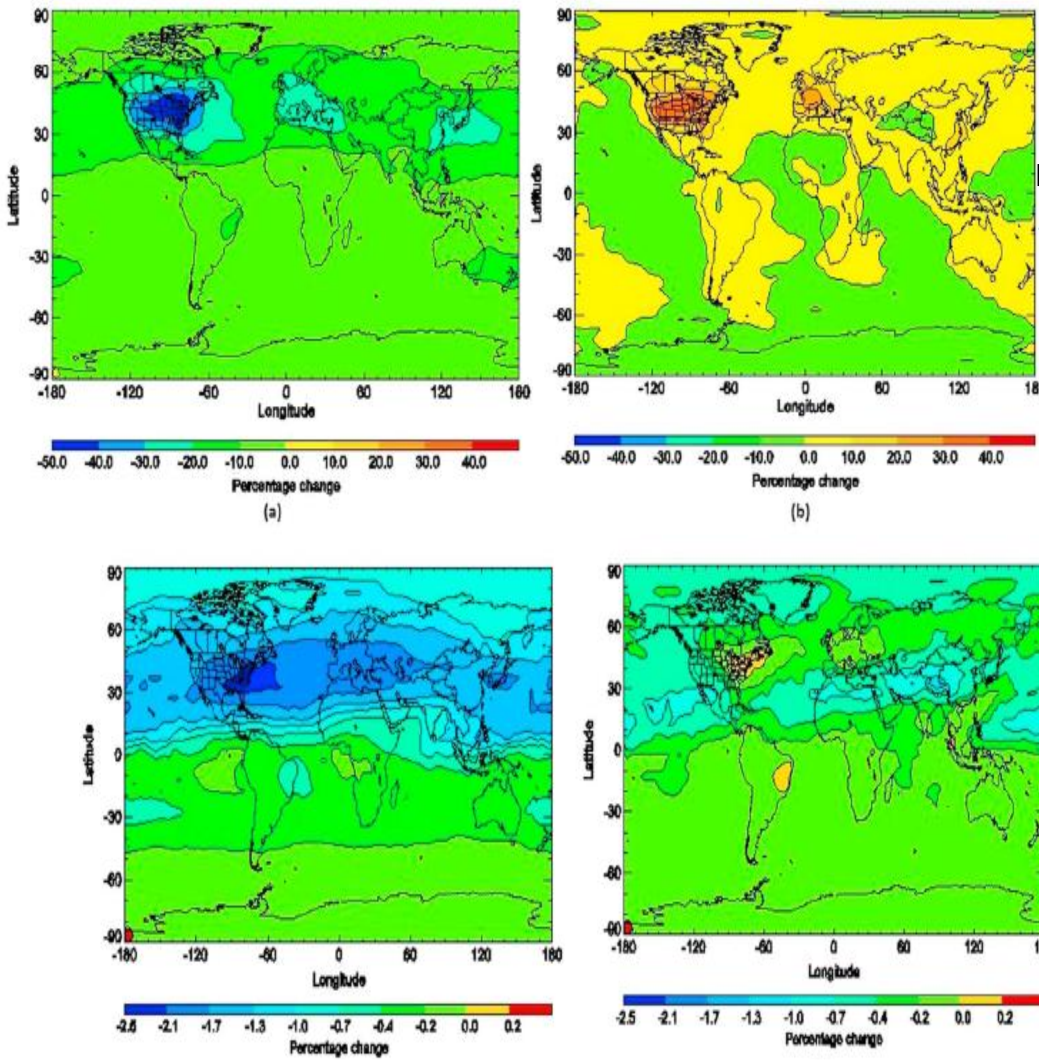

NOx 12-16 km and 7-9 km

Ozone 12-16 km & 7-9 km

Turbo-fan / turbo-prop

Switching turbo-fan to turbo-prop aircraft, where feasible. Overall reduction in NOx and Ozone production.

Wasiuk et al., 2016. J. Geophys. Res. DOI 10.1002/2016JD025051

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Switching, where possible, to a turbo-prop aircraft, instead of a turbo-fan, will reduce ozone formation (climate cooling) and NOx emissions.

Can a change in fuel type offset **CO_2** emissions and possibly **O_3** production

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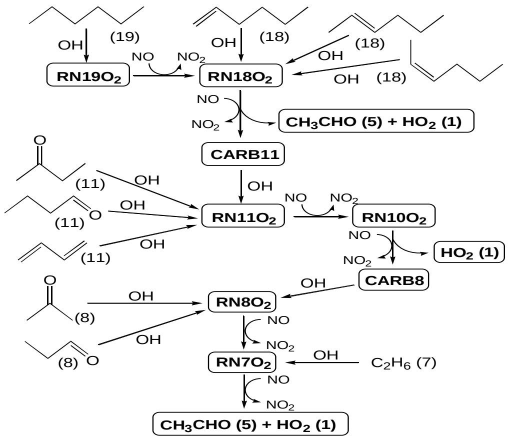

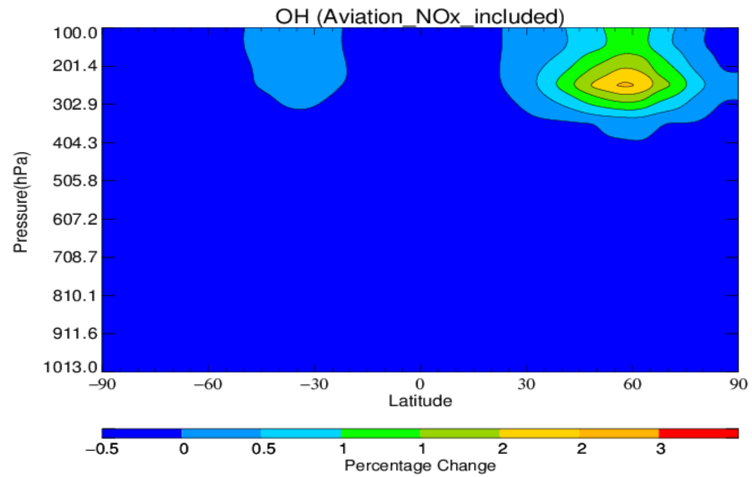

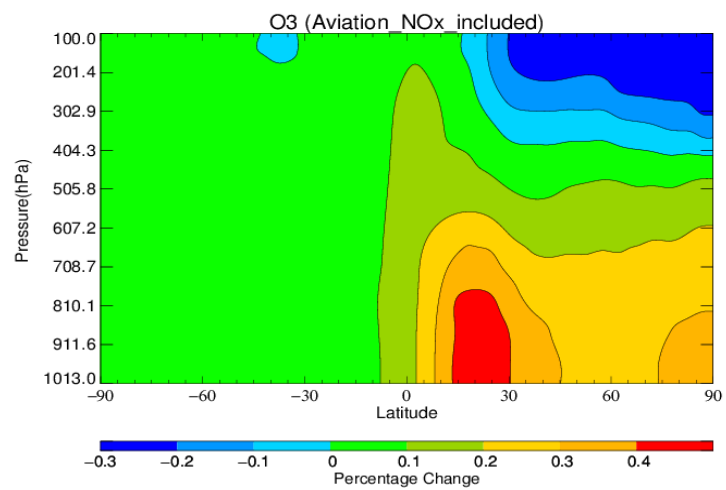

Biofuels and alternative fuels

Switching to 10% biofuel. Rise in OH in the upper Troposphere and reduction in ozone.

Hydrogen. Khan et al. 2022, Atmosphere DOI 10.3390/atmos13101660

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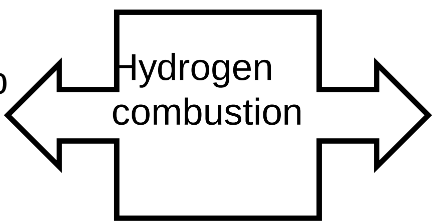
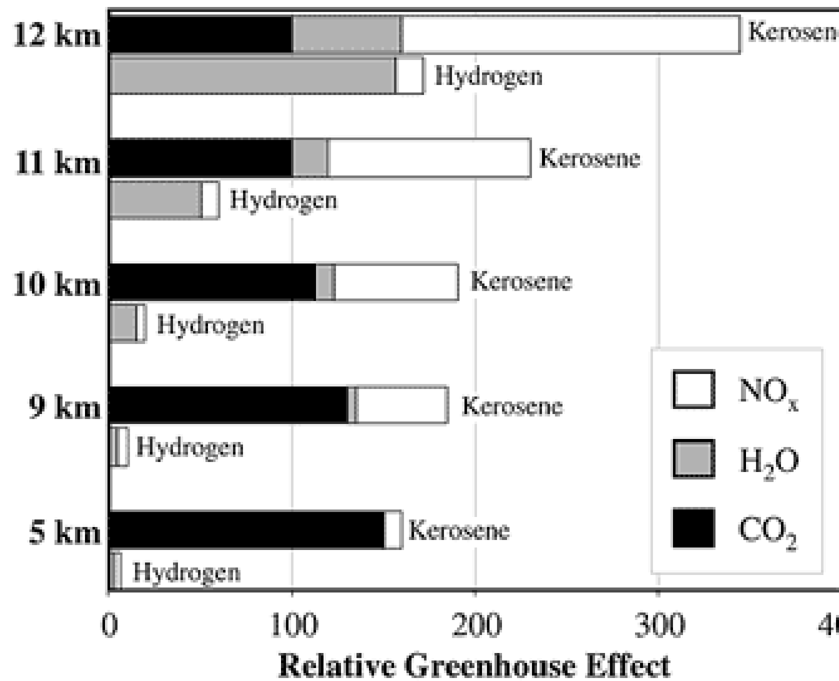
Impact of using Hydrogen fuel in Aviation

80-90% less NOx



2.6 times more water vapour



Comparison of relative net greenhouse effects fo
hydrogen and Kerosene (IPCC)

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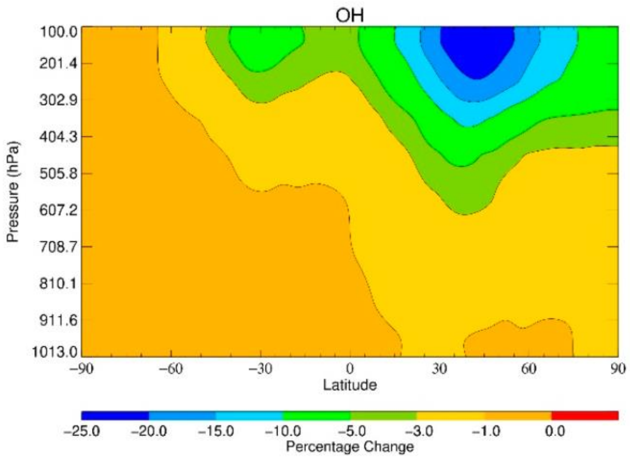
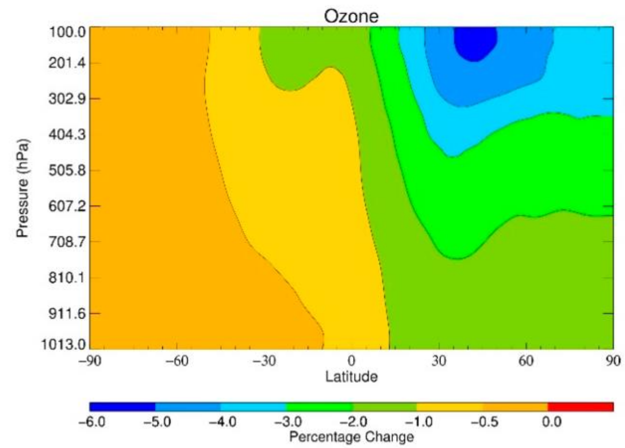
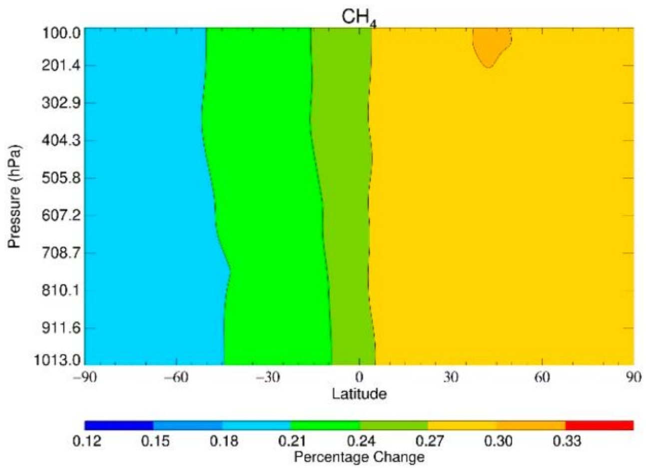
Impact of reduced NO_x emissions from hydrogen aircraft on climate





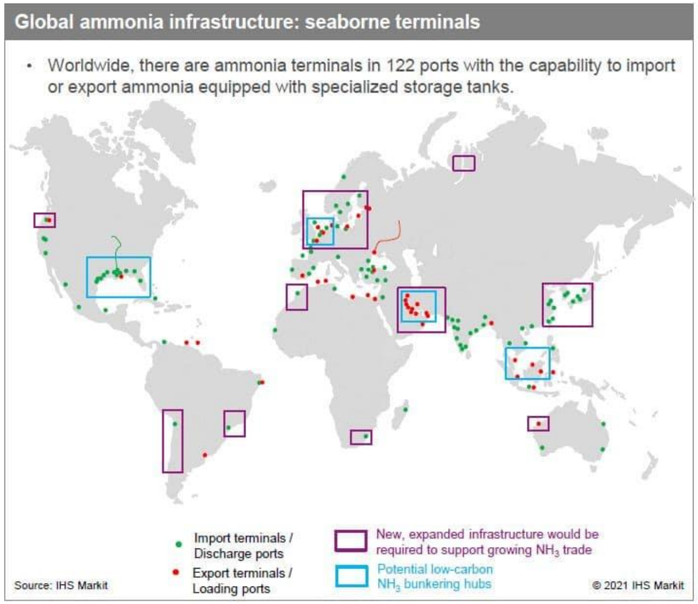


Overall radiative forcing change considering ozone decrease and methane increase is -0.016 Wm^{-2}

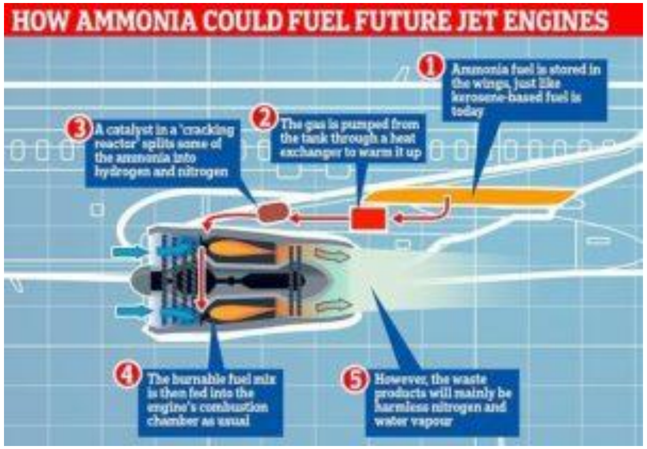
Khan et al., 2022, Atmosphere, 13, https://doi.org/10.3390/atmos1310166

Is ammonia better than hydrogen?

⇒ Ammonia fuel is easy to transport and store
⇒ Ammonia can produce more energy than hydrogen
⇒ Infrastructure for ammonia is already established.



Environmental impacts:
=> Near-elimination of NO_x in engine exhaust
=> Can greatly reduce formation of contrails



Leakage of NH_3 will greatly impact on air quality and climate by increasing particulate matters and nitrous oxide (N_2O).

Switching, to a biofuel could be beneficial. The fuel is generated from new carbon and so carbon dioxide is captured and released on combustion. The problem is that the availability of biofuel for aircraft is small and cannot service the whole fleet.

Hydrogen combustion produces water and NOx emissions but no carbon dioxide, but problems with generation, storage and the required new aircraft design mean that this is not a solution today.

Formation flying?

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Other ways to mitigate climate impacts from aviation emissions

- **Climate-optimal routing –** optimising flight routes to avoid climate sensitive regions of the atmosphere.
  - Potential to reduce aviation climate impact by **10-20%** for only a **1-2%** additional fuel consumption.

- **Formation flight** – aligning flight tracks to overlap aircraft plumes
  - Aerodynamic benefits – **5-8%** reduction in fuel burn and CO_2.
  - Emissions saturation benefits (non-CO_2) – reduced ozone production efficiency **(~5%)** and diminishing contrail effect **(~15%)** for follower aircraft.

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Ozone Chemistry- higher NO_x environment

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

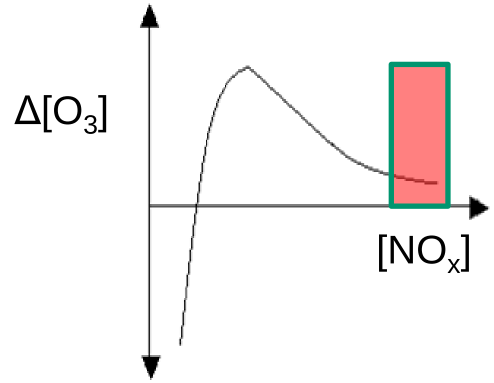
$NO + HO_2 \rightarrow NO_2 + OH$

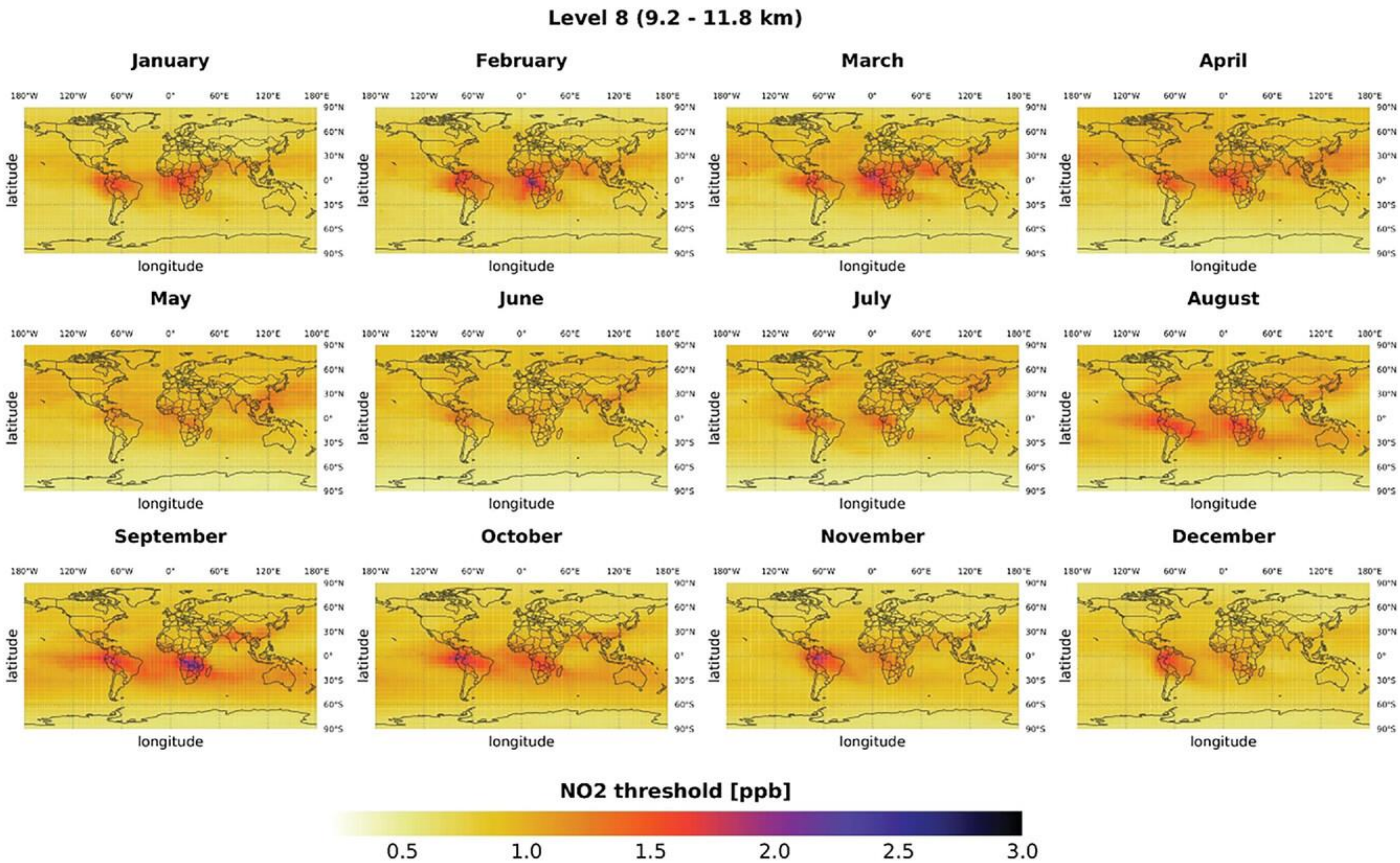
$NO_2 + h\nu \rightarrow NO + O(^3P)$

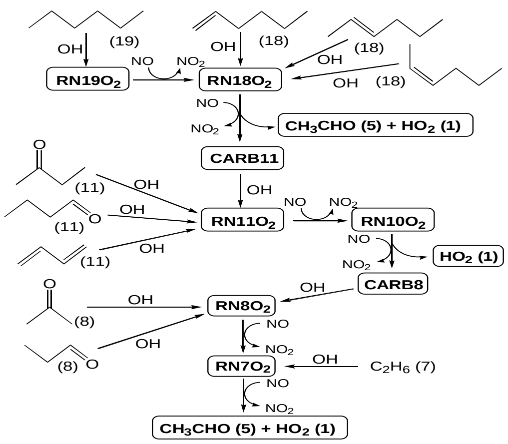
$O(^3P) + O_2 + M \rightarrow O_3 + M$

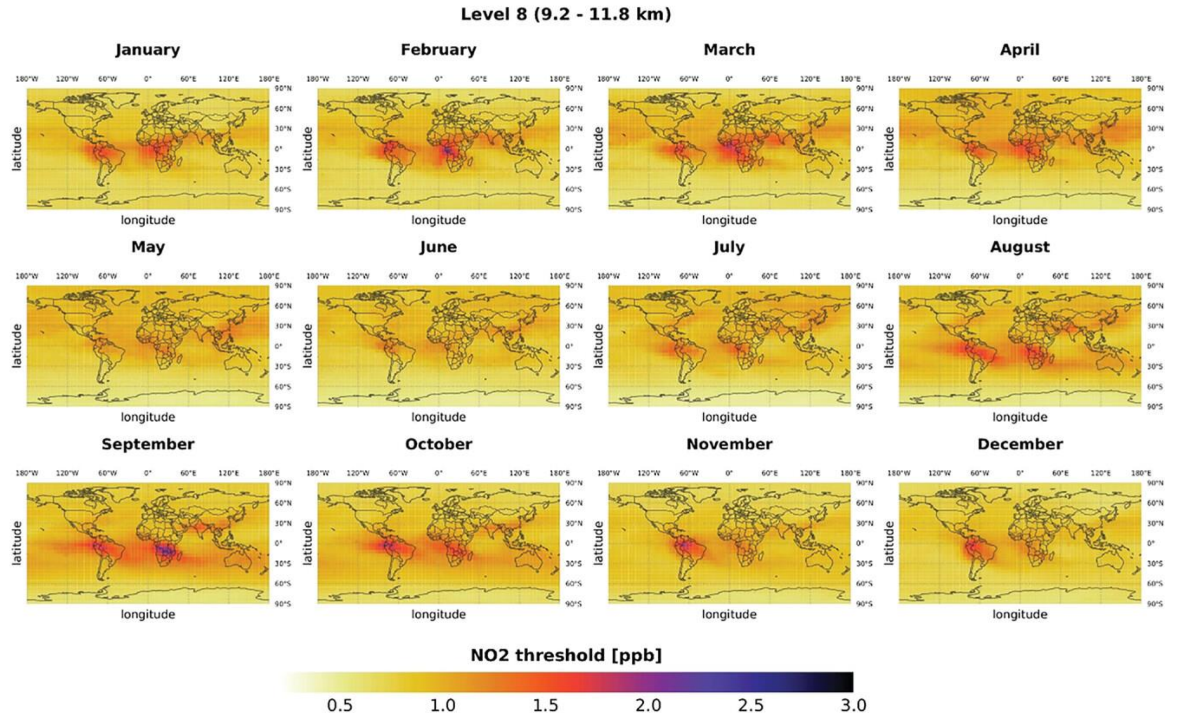
But $OH + NO_2 \rightarrow HNO_3$

Net: Low ozone production




Level 8 (9.2 - 11.8 km)
January
February
March
April
May
June
July
August
September
October
November
December
latitude
longitude
180°W
120°W
60°W
0°
60°E
120°E
180°E
90°N
60°N
30°N
0°
30°S
60°S
90°S
NO2 threshold [ppb]
0.5
1.0
1.5
2.0
2.5
3.0





NOx saturation in upper Troposphere

Formation flight – aligning flight tracks to overlap aircraft plumes

Aerodynamic benefits – **5-8%** reduction in fuel burn and CO_2.

Emissions saturation benefits (non-CO_2) – reduced ozone production efficiency **(~5%)** and diminishing contrail effect **(~15%)** for follower aircraft.

Khan et al. 2023, Int. J. Chem. Kinet. https://doi.org/10.1002/kin.21644

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A kinetic model feasibility study for climate benefit through formation flying of aircraft

At high NO_x,

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

$H + O_2 + M \rightarrow HO_2 + M$ (2)

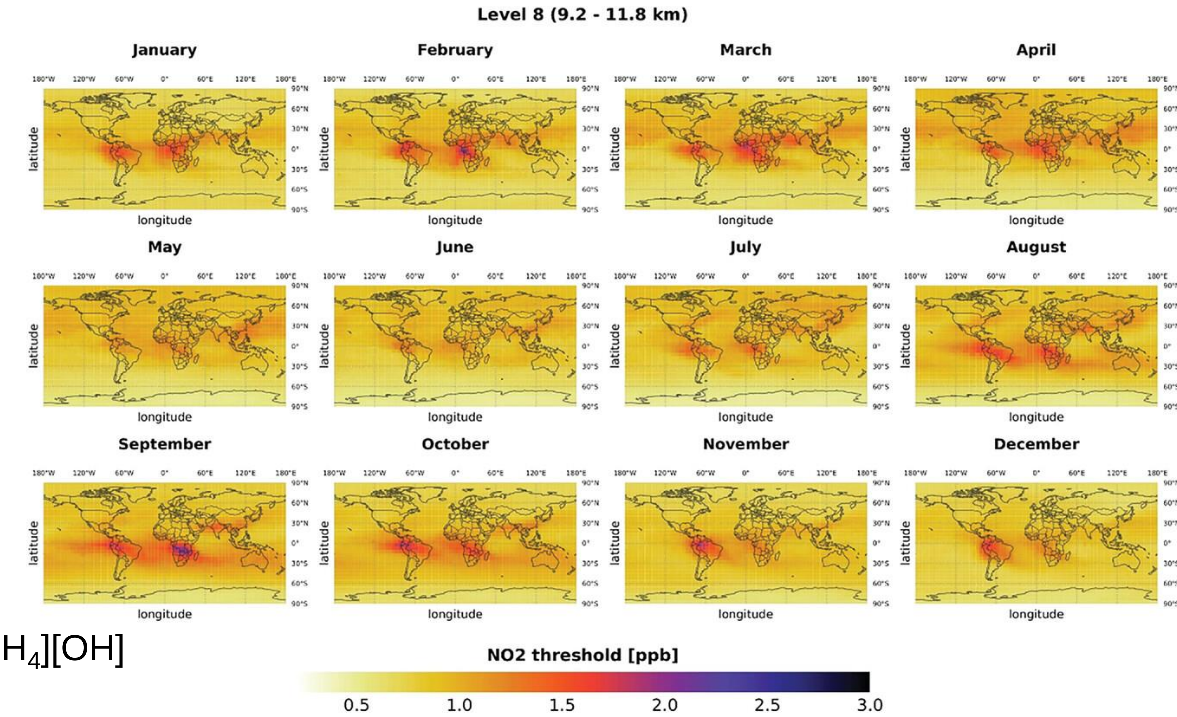
$NO + HO_2 \rightarrow NO_2 + OH$ (3)

$NO_2 + h\nu \rightarrow NO + O(^3P)$ (4)

$O(^3P) + O_2 + M \rightarrow O_3 + M$ (5)

$OH + NO_2 + M \rightarrow HNO_3 + M$ (6)

$OH + CH_4 \rightarrow Products$ (7)



$k_6[NO_2]_{equiv}[OH][M] = k_1[OH][CO] + k_7[CH_4][OH]$

$[NO_2]_{equiv} = (k_1[CO] + k_7[CH_4])/k_6[M]$

Khan et al. 2023, Int. J. Chem. Kinet. https://doi.org/10.1002/kin.21644

A kinetic model feasibility study for climate benefit through formation flying of aircraft

At high NO_x,

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

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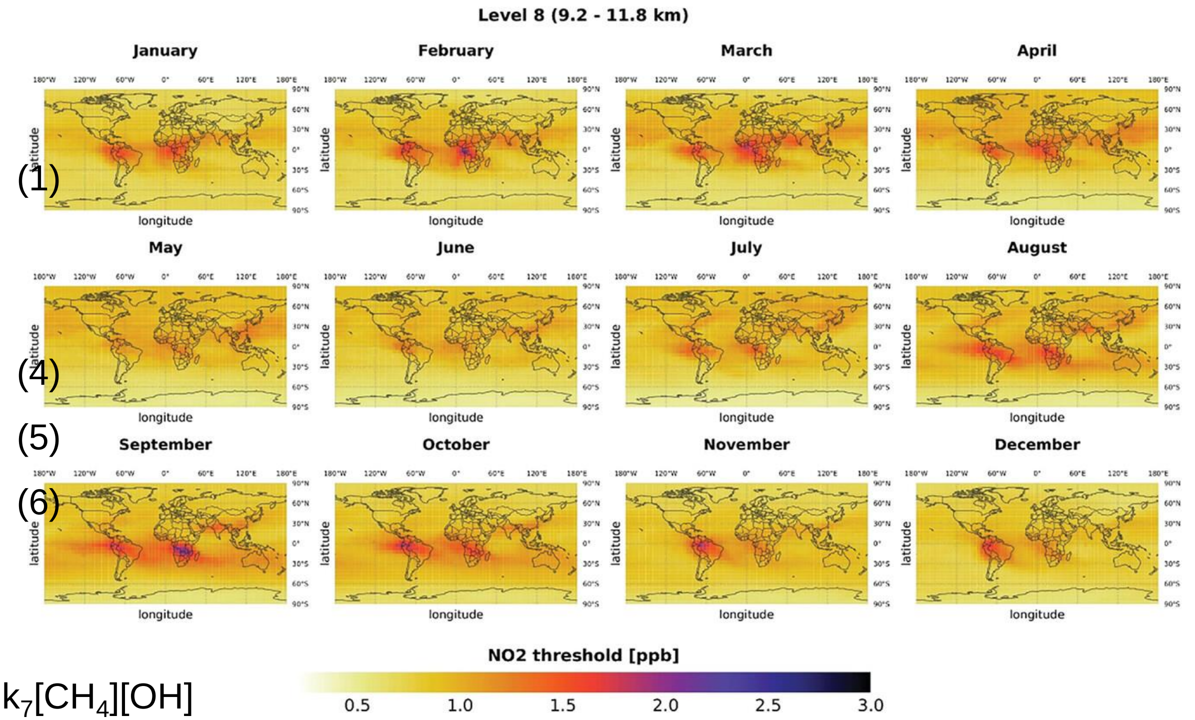
$OH + CH_4 \rightarrow \text{Products}$ (7)



$$k_6[NO_2]_{equiv}[OH][M] = k_1[OH][CO] + k_7[CH_4][OH]$$

$$[NO_2]_{equiv} = k_1[CO] + k_7[CH_4]/k_6[M]$$

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Contrails?

Contrails

- About 3% of flights generate warming contrails, these can be avoided by re-routing and /or once made, other contrail forming flights can fly through the contrail as no further formation can occur (water limited)
- Deliberately generate more cooling contrails ?
- All dependent on mission planning

Summary

1. Aircraft sample a very wide range of Ozone/NOx ratios
2. Switching from Turbo to Prop planes would have a non-negligible impact on both NOx and Ozone
3. The emissions inventory hasn’t changed much from 2005-2011 but the geographical distribution has changed; non-negligible differences between different studies
4. (Bio/new) fuels are worth considering, there could be some pleasant surprises …
5. Worth remembering this is one of only two non surface emission sources of chemicals

Summary

- Biofuel / SAFs may reduce climate impact but some may be more effective than others for certain missions (e.g. North Atlantic Corridor), and certain parts of the slight.
- Re-routing for some missions may be highly effective in reducing climate impacts
- Formation flying could also be very effective but not everywhere and probably cruise (upper troposphere) only

Summary

- Contrail (3/6) could be largely eliminated and indeed cooling contrails could be promoted
- Re-routing for some missions may be highly effective in reducing climate impacts
- Formation flying could also be very effective but not everywhere and probably cruise (upper troposphere) only, but for mid-latitude flights where much ozone is generated halving (1/6) is possible.
- Not much can be done to reduce carbon dioxide warming through combustion in the near future (apart from carbon capture)

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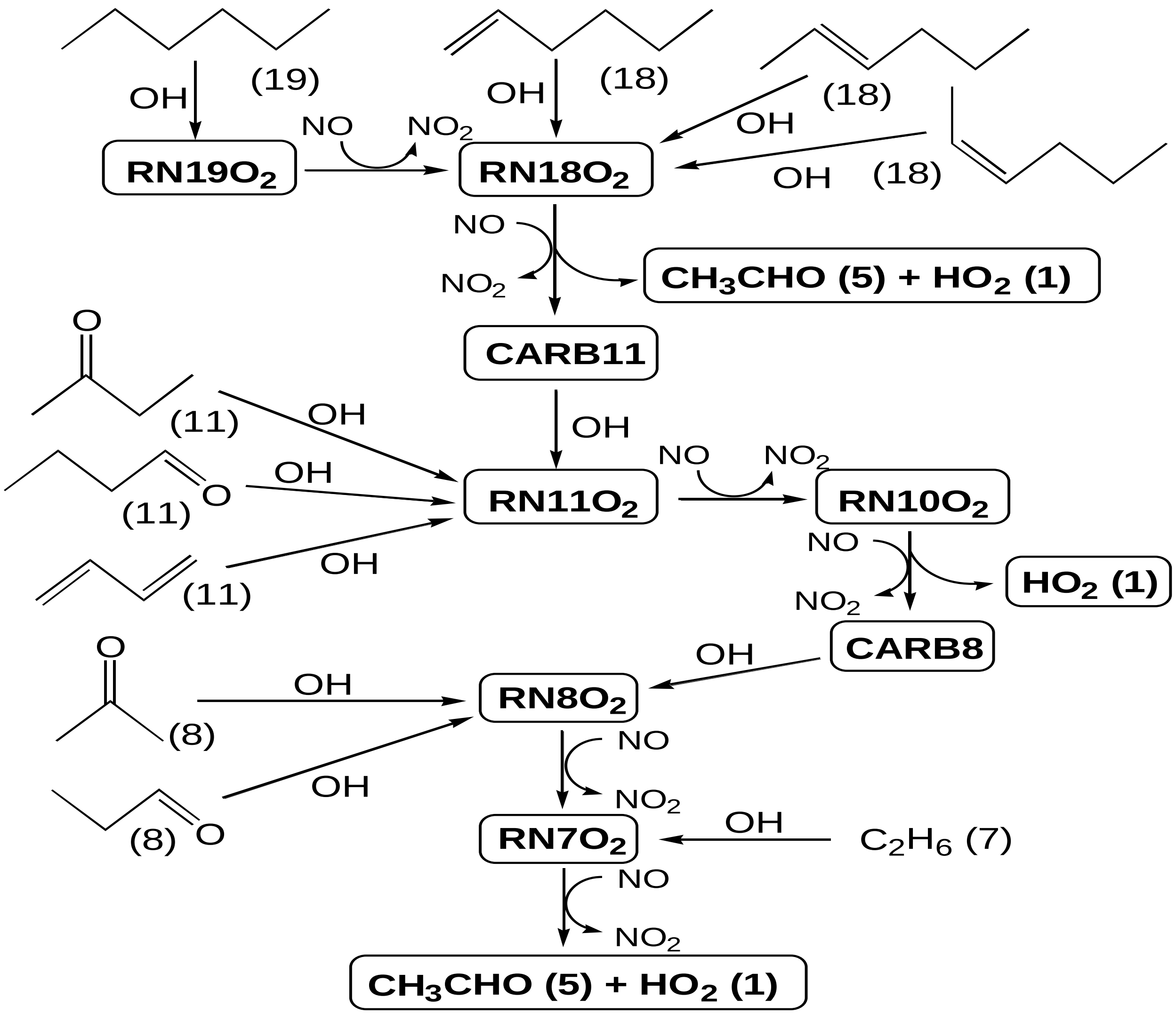

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Direct (CO_2) vs. indirect (NOx) impact

CO_2

- Well mixed
- 100 years +
- Adds to global burden
- Behaviour in atmosphere simple
- Impact depends on concentration
- Not on location

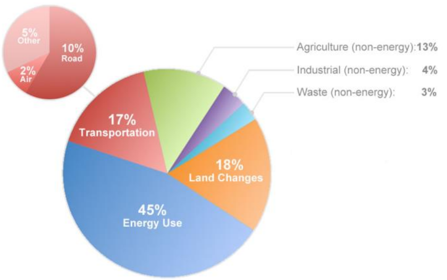

Fig. 1. Total global CO_2 emissions by sector, [WRI, 2005 World Greenhouse Gas Emissions, adapted from http://tcktcktck.org/2011/09/transportation-2/1095.

NOx

- Leads to tropospheric ozone O_3 production
- UV light + NOx + HC
- Stratospheric O_3 good
- Tropospheric O_3 GHG
- Key oxidant (e.g. CH_4)
- Component of smog (air quality)
- In – situ production small
- NOx at 9 – 11 km = more O_3

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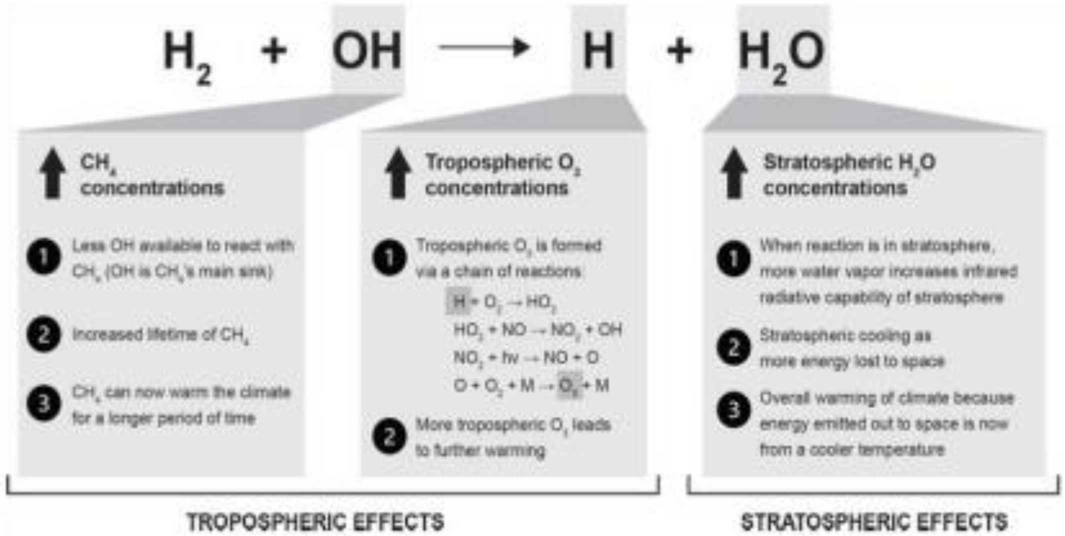
Possible impacts of hydrogen leakage during production, storage and transportation



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Conclusions

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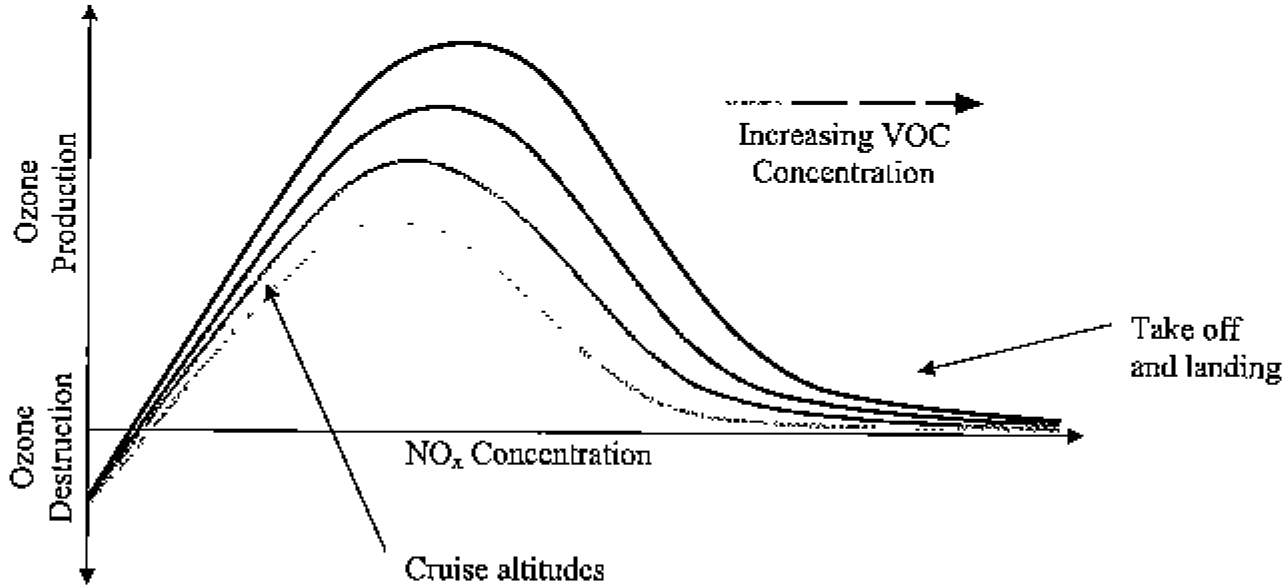
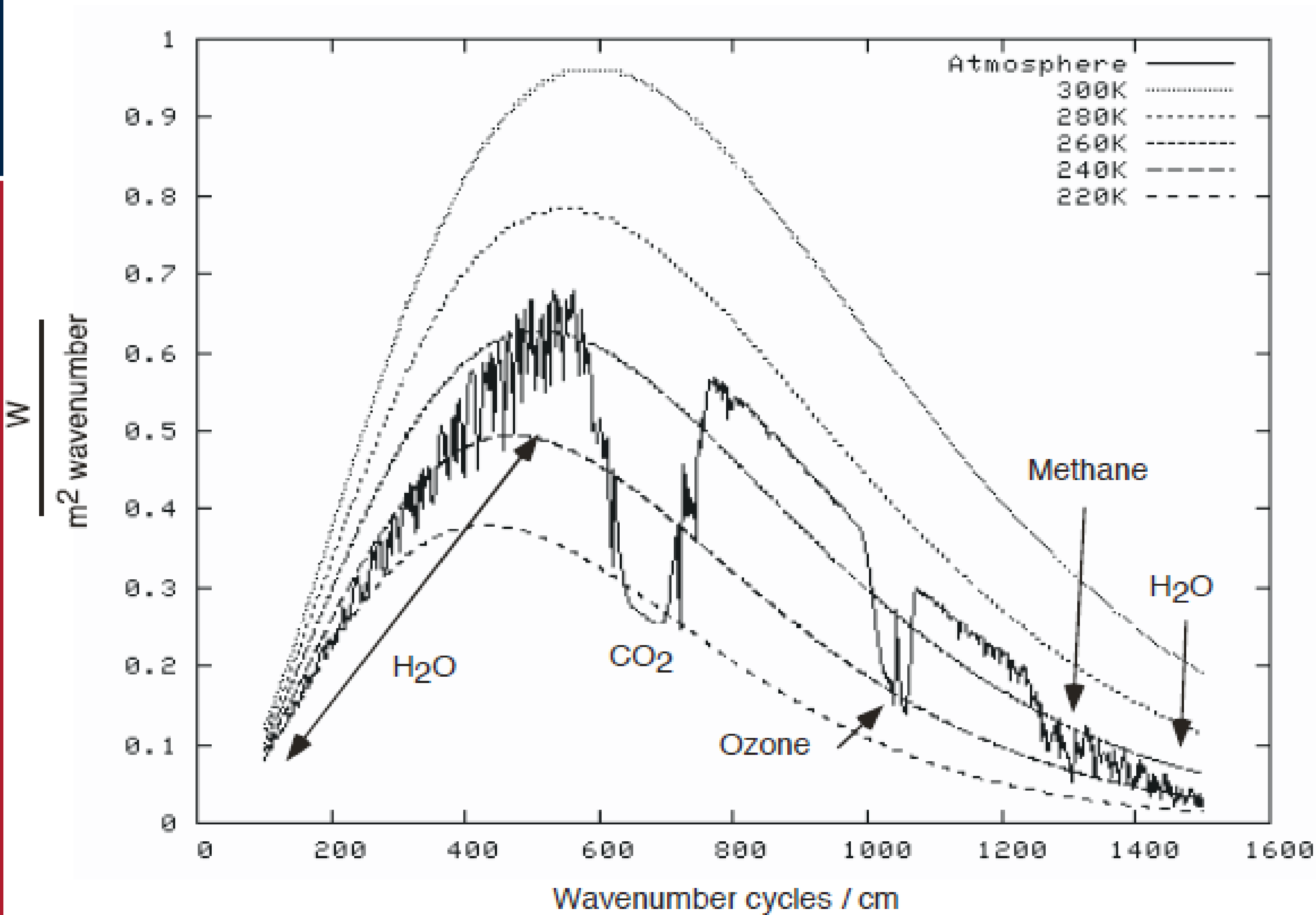
Non-linearity of O_3 production



The effect of NOx and VOC concentrations on the net rate of O_3 production.



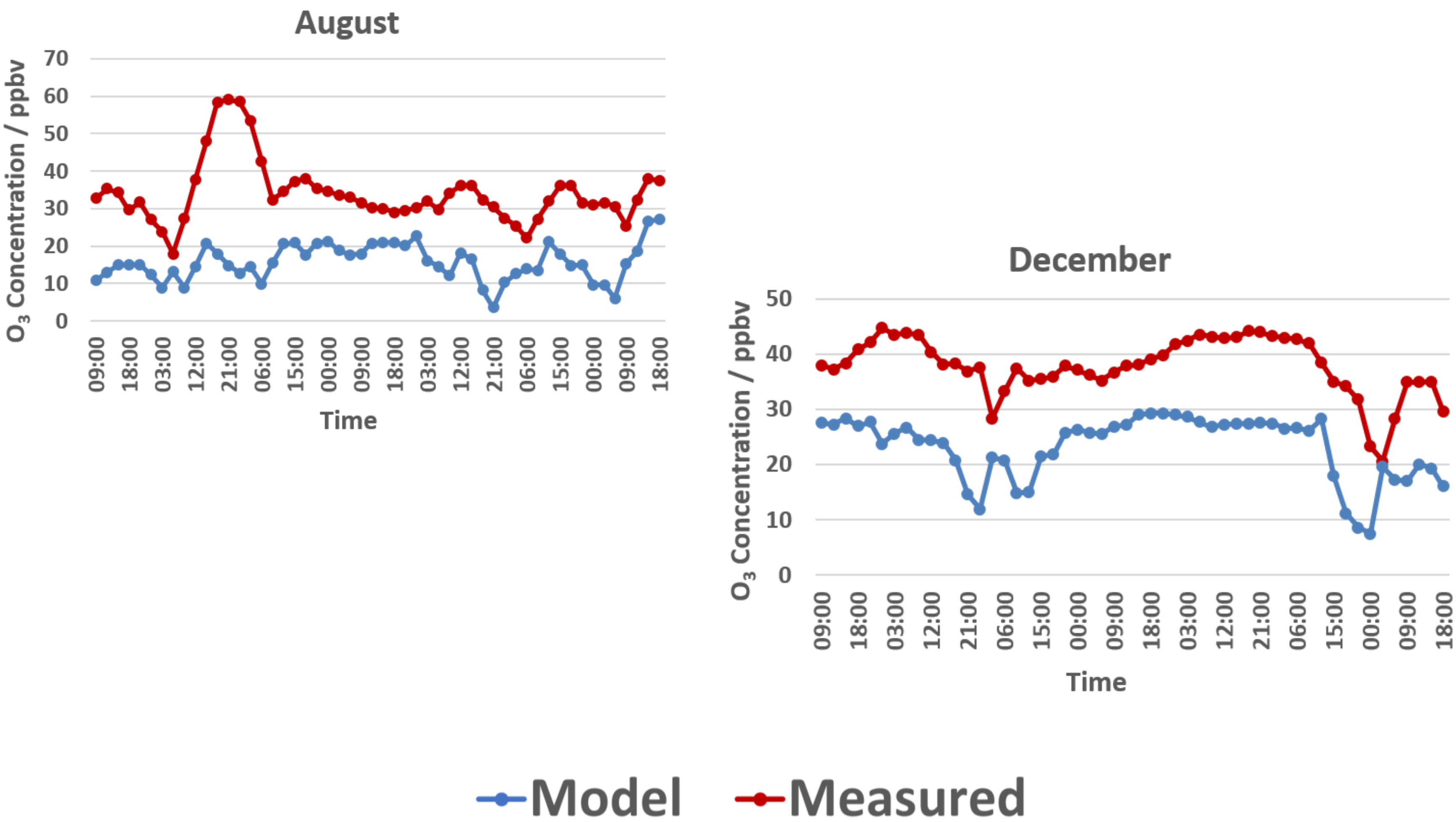
Atmosphere
300K
280K
260K
240K
220K
H2O
CO2
Ozone
Methane
H2O
W / m2 wavenumber
Wavenumber cycles / cm
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
200
400
600
800
1000
1200
1400
1600

Thoughts

1. Taxi, landing, take off (NOx and VOC control important)
2. Impact of Asian fleet will be larger on atmosphere than Europe and N. America, faster photochemistry, can different fuels make a difference in these different environments?
3. Ozone is a GHG and in terms of short time horizons (say 10-30 years) controlling this will be just as important as CO_2
4. (Bio/new) fuels are worth considering

Thanks to

Aston Hill (Rural Background) – O_3



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