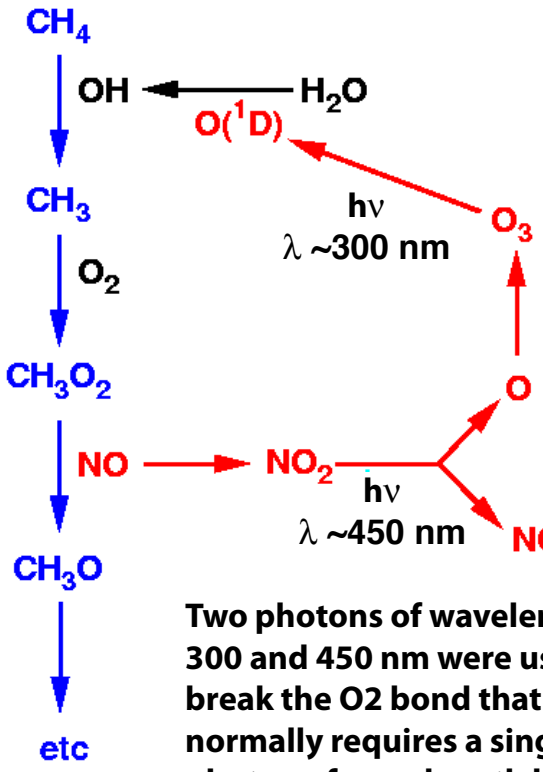
Atmospheric Chemistry

Lecture 16

Summarizing Methane Oxidation

- Produces $CO_2 + 2H_2O$ with a minor channel that produces H_2 instead of the second H_2O
- Produces formaldehyde, CH_2O and carbon monoxide, CO as part of the degradation chain
- Can oxidize NO to NO_2 leading to O atom production and hence ozone production
- Can produce HO_x radicals or destroy them depending on conditions

How does methane oxidation lead to ozone formation?



Two photons of wavelength 300 and 450 nm were used to break the O2 bond that normally requires a single photon of wavelength less than 242 nm

$CH_4 + OH \rightarrow CH_3 + H_2O$ (x2)

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ (x2)

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$ (x2)

$NO_2 + h\nu \rightarrow NO + O$ (x2)

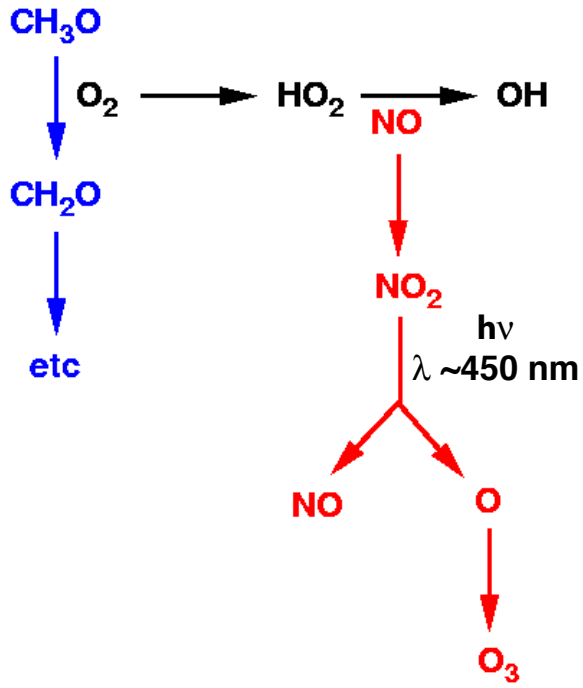
$O + O_2 + M \rightarrow O_3 + M$ (x2)

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

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

$$2CH_4 + 2O_2 + 2h\nu\ (\lambda < 427nm) + h\nu\ (\lambda < 308nm) \rightarrow O_3 + 2H_2O + 2CH_3O$$

Production of a second ozone molecule in a hydrocarbon oxidation chain



$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

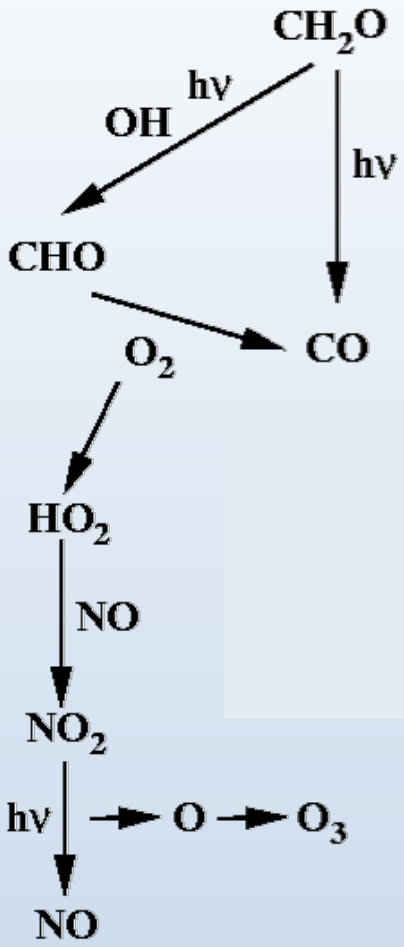
$$HO_2 + NO \rightarrow OH + NO_2$$

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

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

$$CH_3O + 2O_2 + h\nu(\lambda < 427nm) \rightarrow CH_2O + OH + O_3$$

One more O_3 formation



$CH_2O + OH \rightarrow CHO + H_2O$

$CHO + O_2 \rightarrow CO + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

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

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

$CH_2O + 2O_2 + h\nu\ (\lambda < 427nm) \rightarrow CO + H_2O + O_3$

Looking at the entire oxidation chain (one of the branches)

$CH_4 + OH + 2O_2 + NO \rightarrow CH_2O + HO_2 + NO_2 + H_2O$

$CH_2O + 2O_2 + 2OH \rightarrow CO_2 + H_2O + 2HO_2$

$CH_4 + 4O_2 + 3OH + NO \rightarrow CO_2 + 2H_2O + 3HO_2 + NO_2$

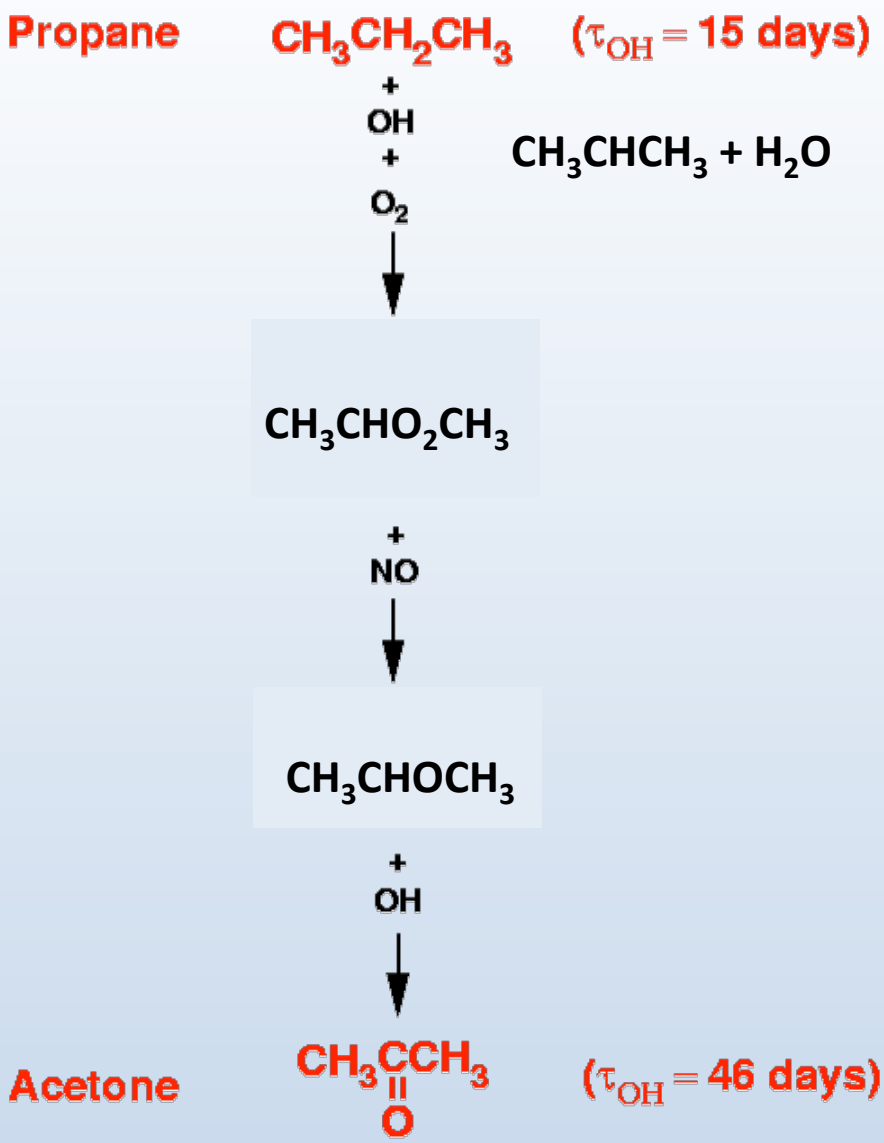
3x: $HO_2 + NO \rightarrow OH + NO_2$

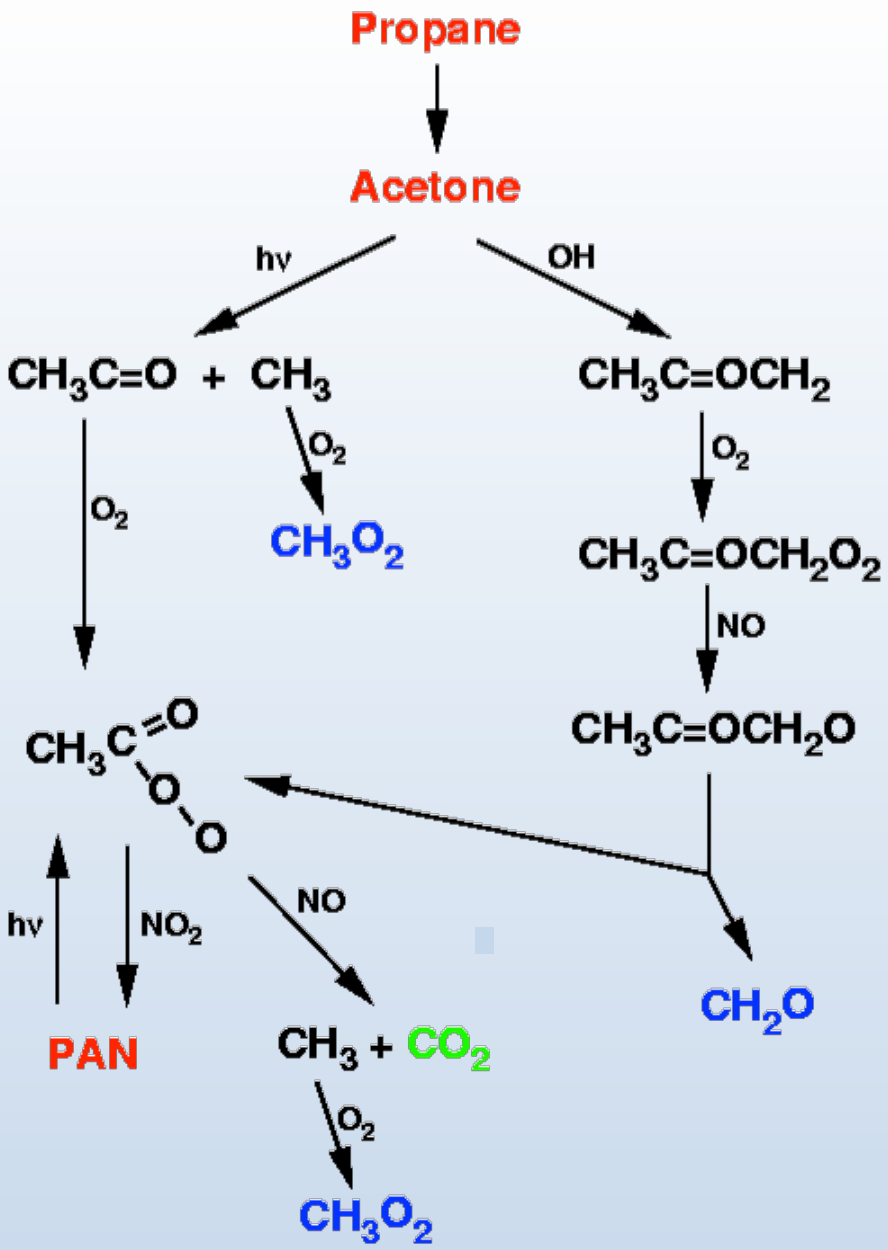
$CH_4 + 4O_2 + 4NO \rightarrow CO_2 + 2H_2O + 4NO_2$

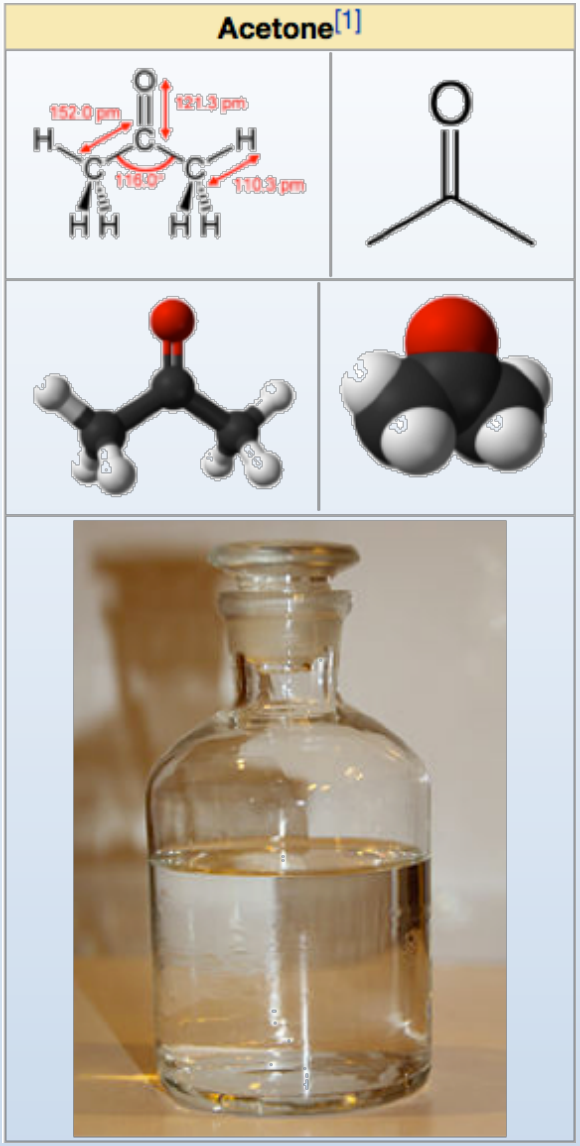
break into 2 compound reactions

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$4NO + 2O_2 \rightarrow 4NO_2$


Propane
$CH_3CH_2CH_3$
(τ_{OH} = 15 days)
+
OH
+
O_2
$CH_3CHCH_3 + H_2O$
$CH_3CHO_2CH_3$
+
NO
CH_3CHOCH_3
+
OH
CH_3CCH_3
O
Acetone
(τ_{OH} = 46 days)

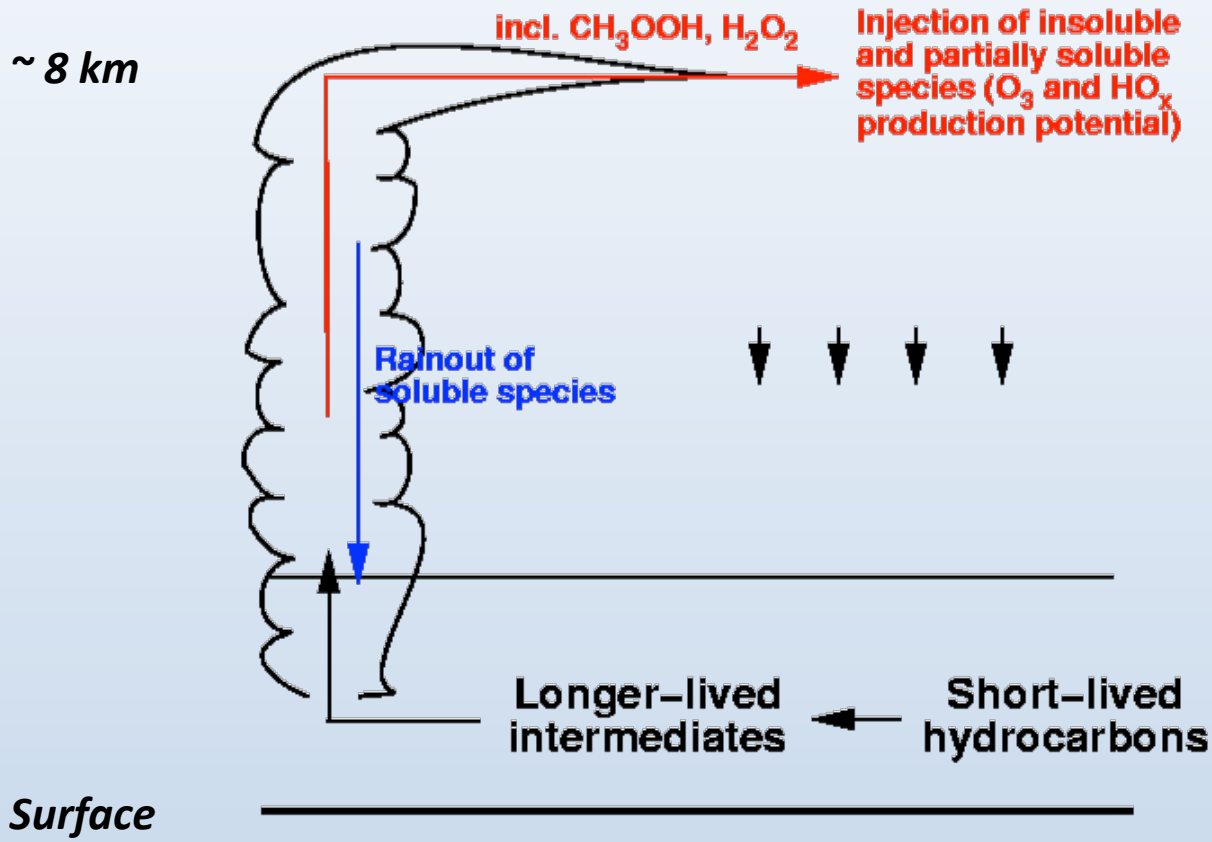

Propane
Acetone
hν
OH
$CH_3C{=}O$ + CH_3
$CH_3C{=}OCH_2$
O_2
CH_3O_2
$CH_3C{=}OCH_2O_2$
NO
$CH_3C{=}OCH_2O$
$CH_3C(=O)OO$
hν
NO_2
NO
PAN
CH_3 + CO_2
CH_2O
O_2
CH_3O_2

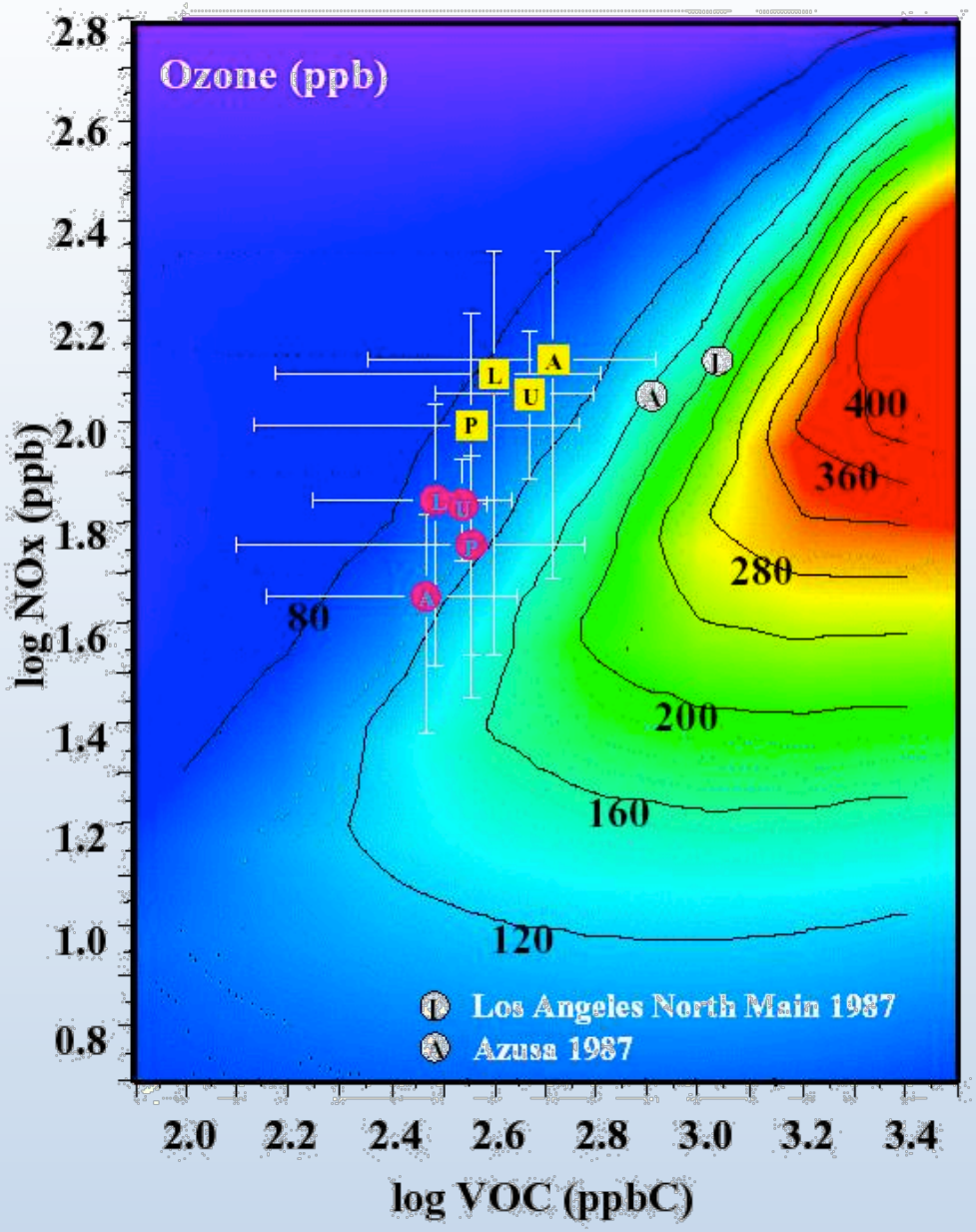

Acetone[1]
152.0 pm
121.3 pm
110.3 pm

- Methane, CH_4 : Methyl peroxy, CH_3O_2
- Methyl hydrogen peroxide, CH_3OOH
- Formaldehyde H_2CO
- Carbon Monoxide, CO

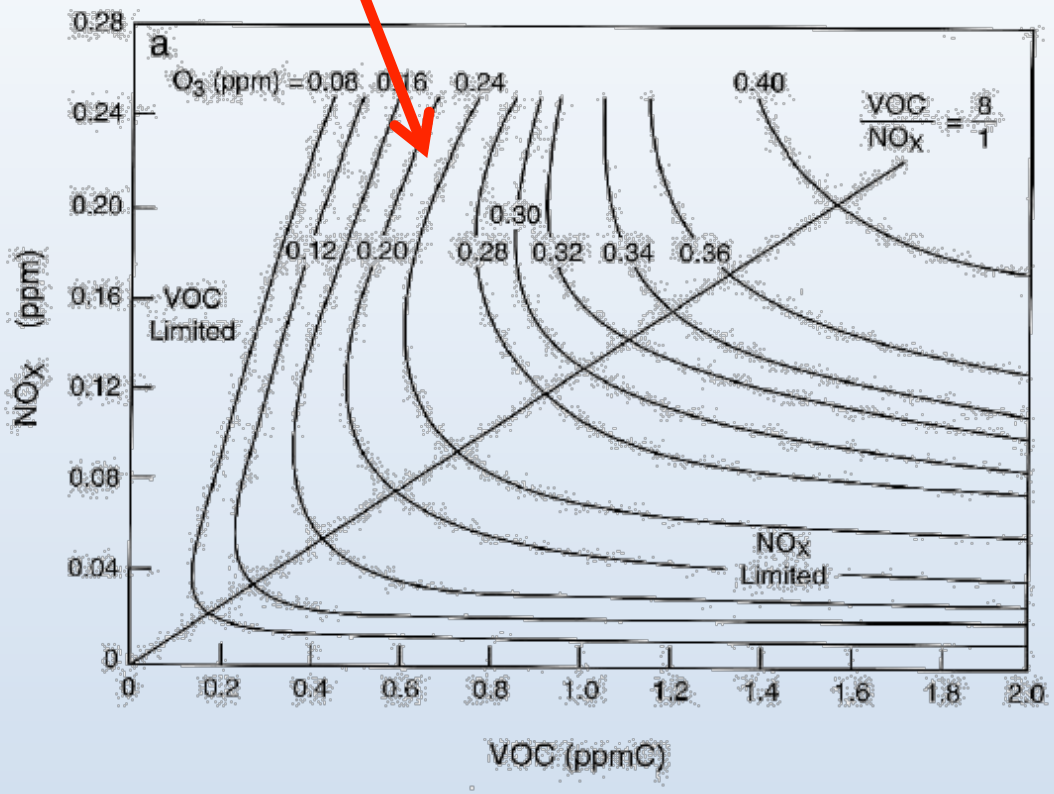
- Propane, C_3H_8
- Propene, C_3H_6
- Acetone, $CH_3C{=}OCH_3$
- Acetaldehyde, CH_3CHO
- PAN, $CH_3C{=}OOONO_2$

Short-lived hydrocarbons can contribute to global ozone production through intermediates

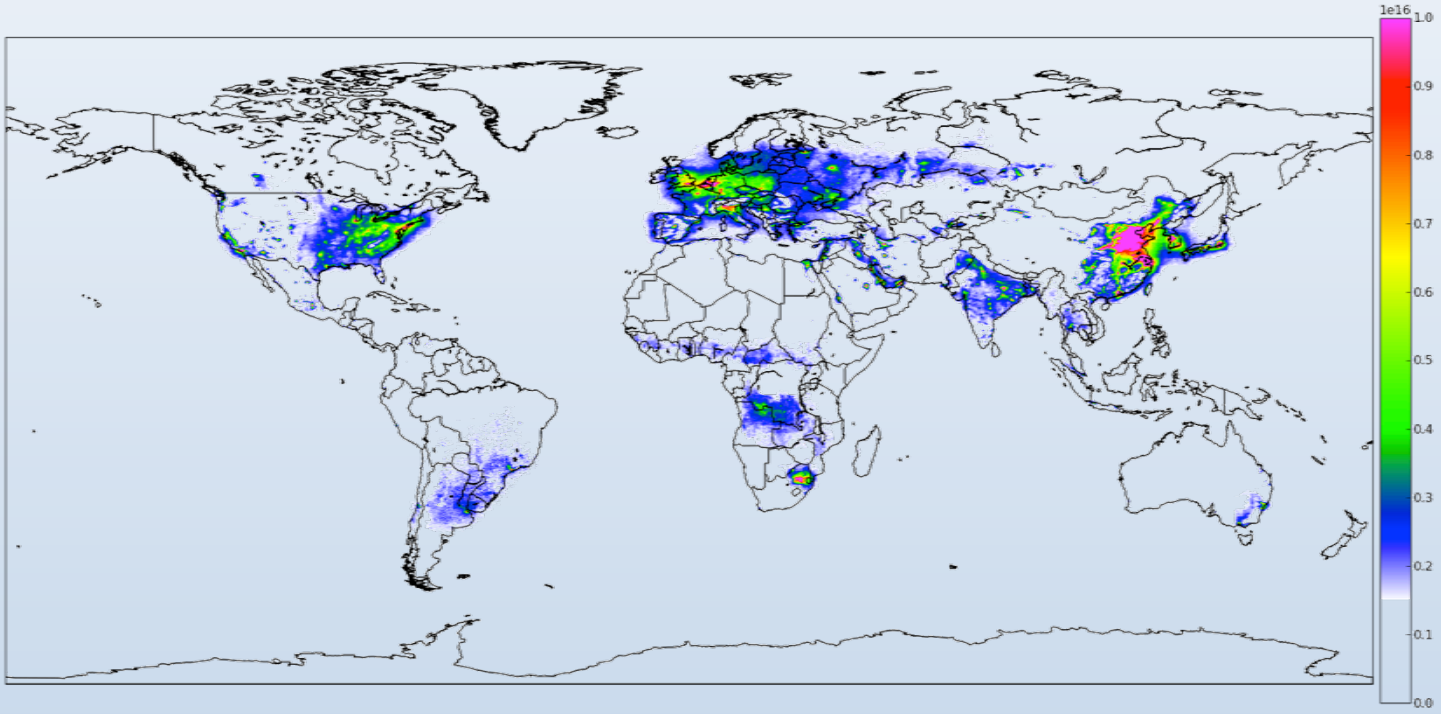



Ozone (ppb)
log NOx (ppb)
log VOC (ppbC)
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
400
360
280
200
160
120
80
L
A
U
P
Los Angeles North Main 1987
Azusa 1987

High NO_x → nitrate formation

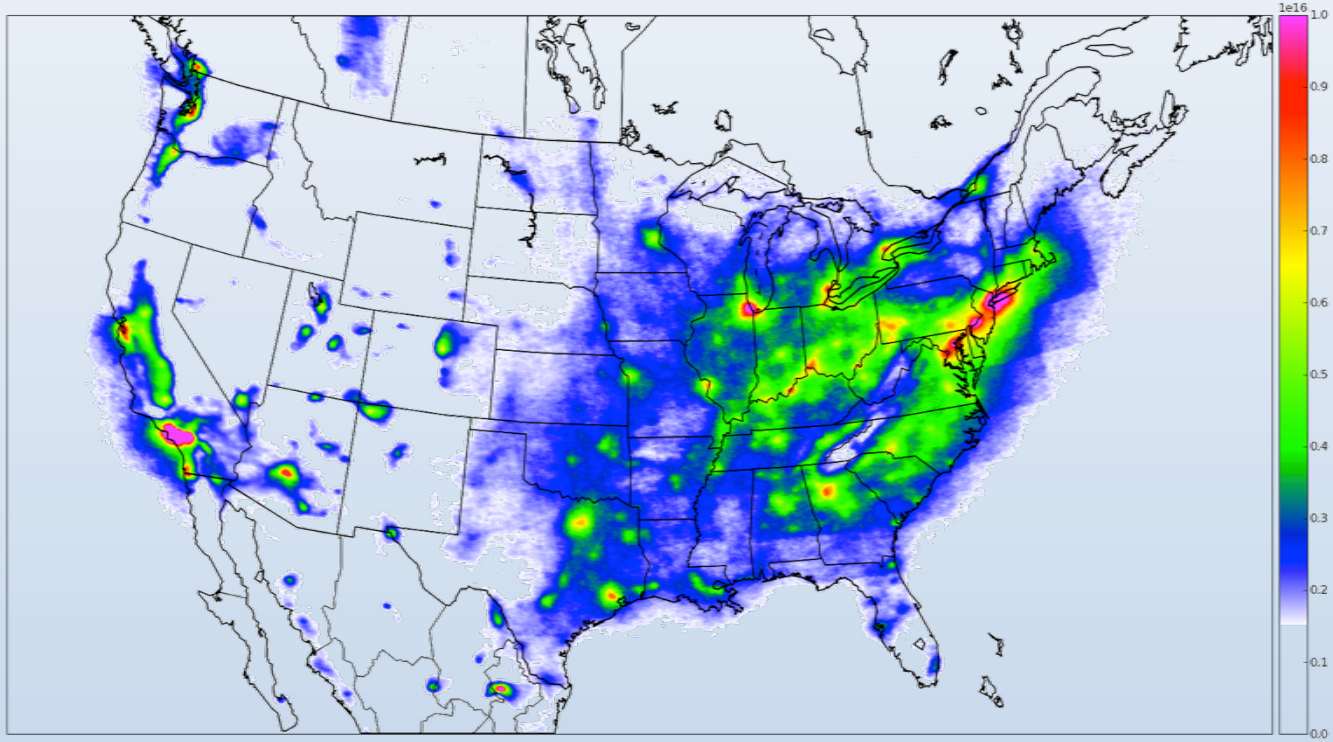


Measurements of NO_2 column amount from OMI instrument on Aura satellite



Phoenix Brown cloud

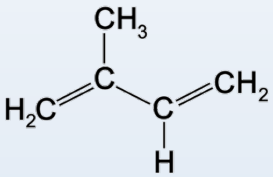
Aura OMI NO_2 column measurements over the continental US



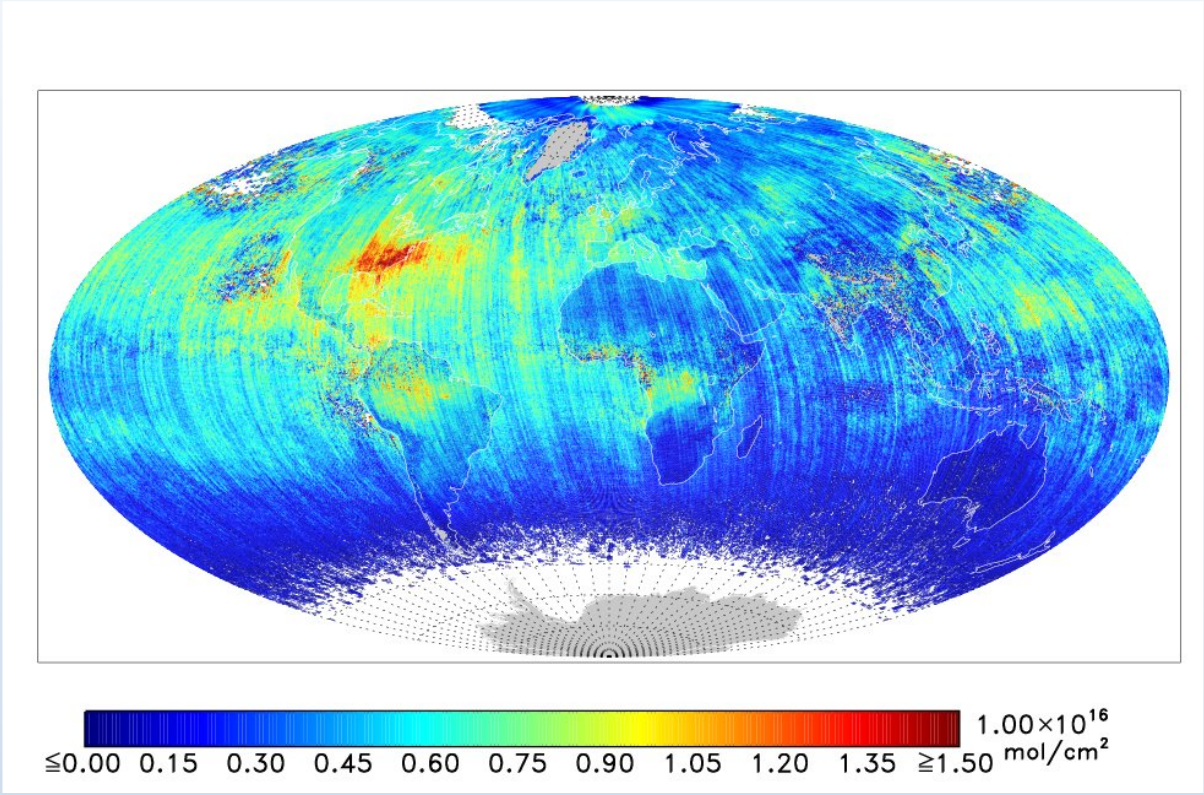
Formaldehyde can be measured from satellite as a surrogate for VOCs

Monthly average OMI HCHO vertical columns for July 2005

http://www.knmi.nl/omi/research/product/HCHO/introduction.html



isoprene (C_5H_8)



Formaldehyde