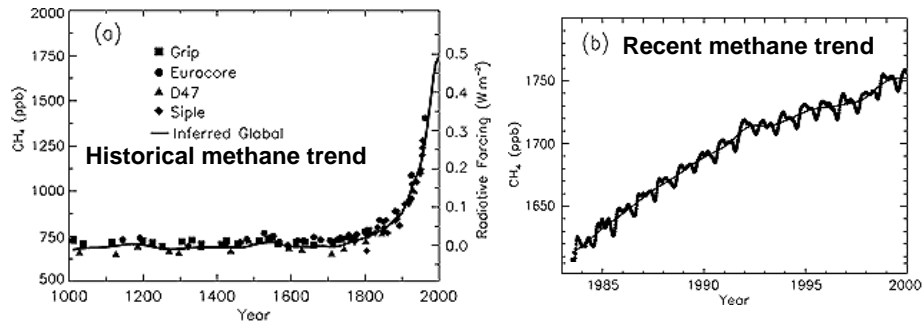


## Human influence on Methane Increase from 700 ppbv → 1745 ppbv



IPCC, 2001

## Biological formation of methane

- Anaerobic decomposition of organic material by methanogenic bacteria (flooded soils, wetlands, landfills, digestive tracts..)

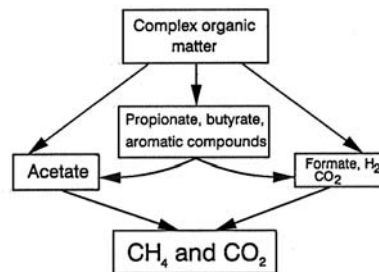
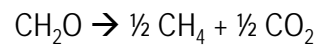


Fig. 1. Organic matter decomposition in methanogenic ecosystems

- Methane production is temperature dependent, with maximum growth 37°-45°C

## Present-day global sources of CH<sub>4</sub> (Tg CH<sub>4</sub>/yr)

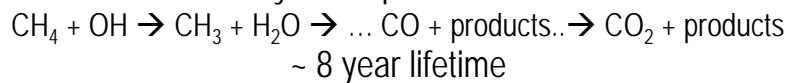
Natural Sources	200(±80)	Anthropogenic Sources	330 (±100)
Wetlands	145-230	Fossil fuels	100
Termites	20-30	Landfills & Waste	35-70
Ocean	5-15	Ruminants	70-90
Hydrates	5	Rice agriculture	30-80
Geological sources	5-15	Biomass burning	40-80
Wild animals	15		
Wildfires	2-5		

60% of present sources are anthropogenic

*IPCC, 2008, Chap 7*

## Methane lifetime

– Loss of methane by atmospheric oxidation:

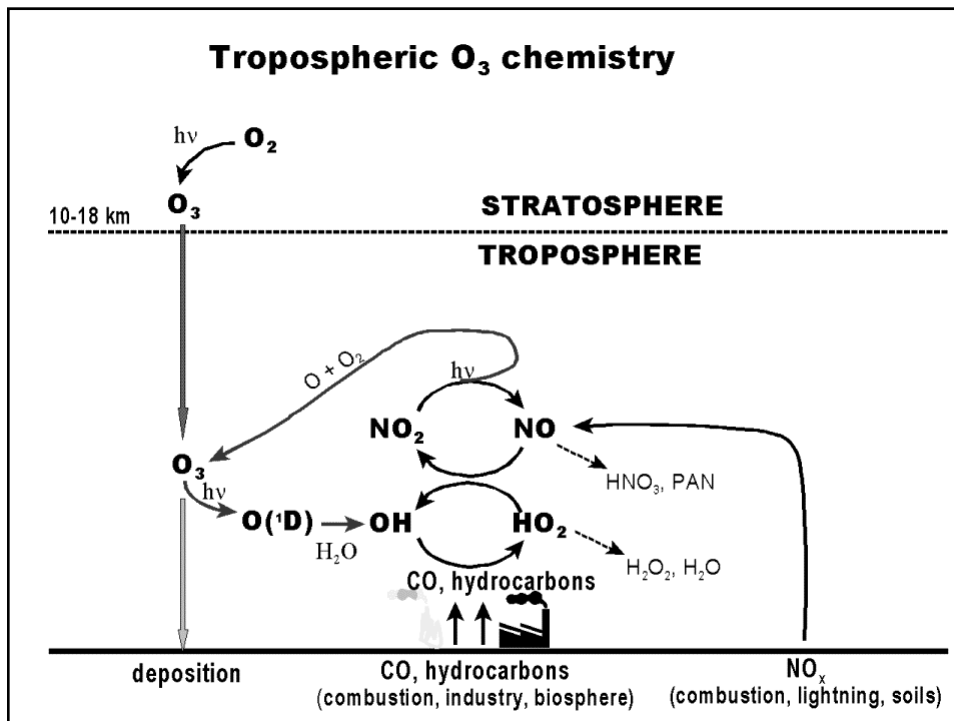


– The reaction CH<sub>4</sub> + OH represents ~30% of OH loss

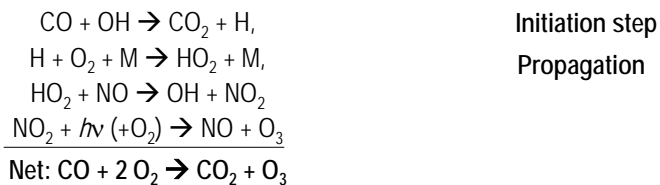
– Increase in CH<sub>4</sub> emissions → increase in CH<sub>4</sub> concentrations → decrease in OH levels → increase in the lifetime of CH<sub>4</sub> → further increases in CH<sub>4</sub> concentrations (positive feedback)

– Example: 1% increase in CH<sub>4</sub> results in a 0.32% decrease in OH → effective CH<sub>4</sub> lifetime ~ 12 years

# The OH titration problem

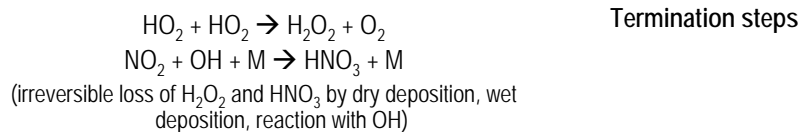


## CO Oxidation mechanism:



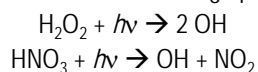
Initiation step

Propagation



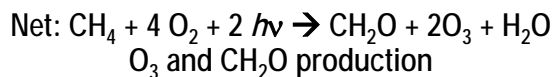
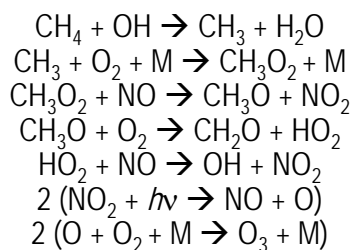
Termination steps

Reformation of radicals through photolysis:

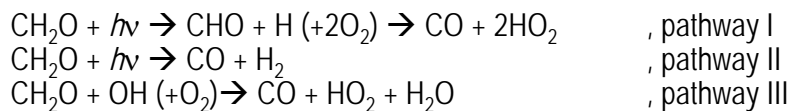


**HO<sub>x</sub> (= OH+HO<sub>2</sub>+H) and NO<sub>x</sub> (= NO+NO<sub>2</sub>) catalyze O<sub>3</sub> production  
In the troposphere**

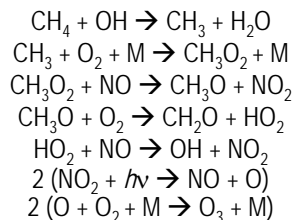
## Methane oxidation cycle (high NO<sub>x</sub>)



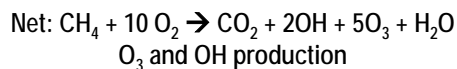
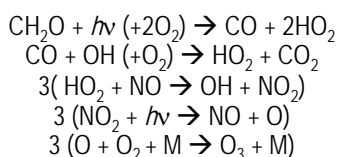
Formaldehyde (CH<sub>2</sub>O) itself can photolyze (2 branches), or react with OH:



## Methane oxidation cycle (high NO<sub>x</sub>) – cont.

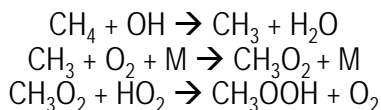


Pathway I:

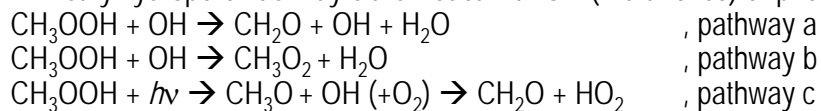


Pathway I is the most efficient at producing O<sub>3</sub> and OH

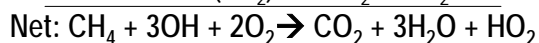
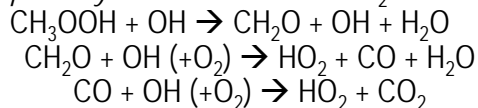
## Methane oxidation cycle (no NO<sub>x</sub>)



Methylhydroperoxide may either react with OH (2 branches) or photolyze:



Let's follow *pathway a* and assume that CH<sub>2</sub>O will react with OH:



No O<sub>3</sub> production and 2HO<sub>x</sub> molecules are lost

## Methane oxidation cycle - summary

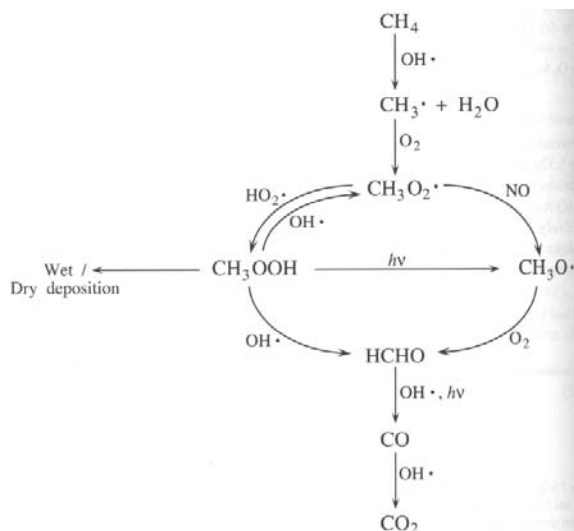
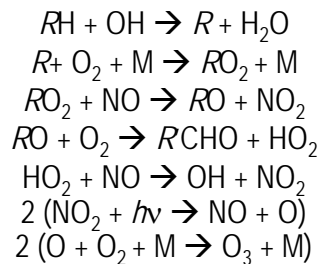


FIGURE 5.2 Atmospheric methane oxidation chain.

Seinfeld J. H. and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 1998

## Generalized hydrocarbon oxidation cycle

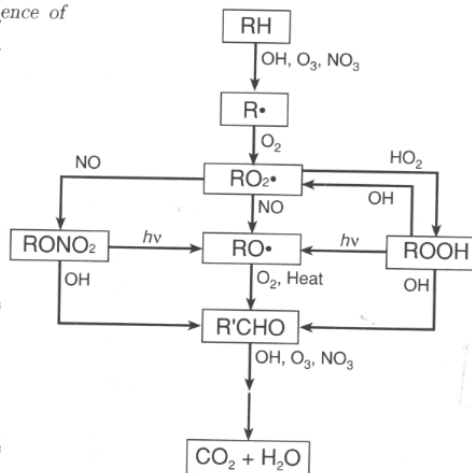


$RH$  = organic hydrocarbon, with  $R$  = organic group  
 $RO_2$  = organic peroxy radical,  $RO$  = alkoxy radical  
 $RCHO$  = aldehyde

## Non-methane hydrocarbon oxidation

Table 9.1  
Types of Organic Species Present in the Atmosphere

Type of Compound	General Chemical Formula	Examples
Alkanes	R-H	CH <sub>4</sub> , methane CH <sub>3</sub> CH <sub>3</sub> , ethane
Alkenes	R <sub>2</sub> C=CR <sub>2</sub>	CH <sub>2</sub> =CH <sub>2</sub> , ethene or ethylene CH <sub>3</sub> -CH=CH <sub>2</sub> , propene
Alkynes	RC≡CR	HC≡CH, acetylene
Aromatics	C <sub>6</sub> H <sub>6</sub> (cyclic)	C <sub>6</sub> H <sub>6</sub> , benzene C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ), toluene
Alcohols	R-OH	CH <sub>3</sub> OH, methanol CH <sub>3</sub> CH <sub>2</sub> OH, ethanol
Aldehydes	R-CHO	CH <sub>2</sub> O, formaldehyde CH <sub>3</sub> CHO, acetaldehyde
Ketones	RCOR	CH <sub>3</sub> C(O)CH <sub>3</sub> , acetone
Peroxides	R-OOH	CH <sub>3</sub> OOH, methylhydroperoxide
Organic acids	R-COOH	HC(O)OH, formic acid CH <sub>3</sub> C(O)OH, acetic acid
Organic nitrates	R-ONO <sub>2</sub>	CH <sub>3</sub> ONO <sub>2</sub> , methyl nitrate CH <sub>3</sub> CH <sub>2</sub> ONO <sub>2</sub> , ethyl nitrate
Alkyl peroxy nitrates	RO <sub>2</sub> NO <sub>2</sub>	CH <sub>3</sub> O <sub>2</sub> NO <sub>2</sub> , methyl peroxy nitrate
Acylperoxy nitrates	R-C(O)OONO <sub>2</sub>	CH <sub>3</sub> C(O)O <sub>2</sub> NO <sub>2</sub> , peroxyacetyl nitrate (PAN)
Alkyl radicals	R•	CH <sub>3</sub> •, methyl radical CH <sub>3</sub> CH <sub>2</sub> •, ethyl radical
Acyl radicals	RC•O	CH <sub>3</sub> C•=O, acetyl radical
Alkoxy radicals	RO•	CH <sub>3</sub> O•, methoxy radical
Peroxy radicals	ROO•	CH <sub>3</sub> O <sub>2</sub> •, methylperoxy radical CH <sub>2</sub> (OH)CH <sub>2</sub> O <sub>2</sub> •, 2-hydroxyethylperoxy radical
Biogenic compounds	C <sub>5</sub> H <sub>8</sub> C <sub>10</sub> H <sub>16</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )-CH=CH <sub>2</sub> , isoprene α-pinene, β-pinene
Multifunctional species		CH <sub>3</sub> C(O)CHO, methylglyoxal CH <sub>2</sub> (OH)CHO, glycolaldehyde



## Global emissions of volatile organic compounds (VOCs)

<b>ANTHROPOGENIC SOURCES</b>	<b>~100 TgC/yr</b>
Energy use and transfer	43 TgC/yr
Biomass burning	45 TgC/yr
Organic solvents	15 TgC/yr
<b>NATURAL SOURCES</b>	<b>~1170 TgC/yr</b>
<b>Emissions from vegetation</b>	
<i>isoprene</i> (C <sub>5</sub> H <sub>8</sub> )	500 TgC/yr
monoterpenes	125 TgC/yr
other VOC	520 TgC/yr
<b>Oceanic emissions</b>	6-36 TgC/yr

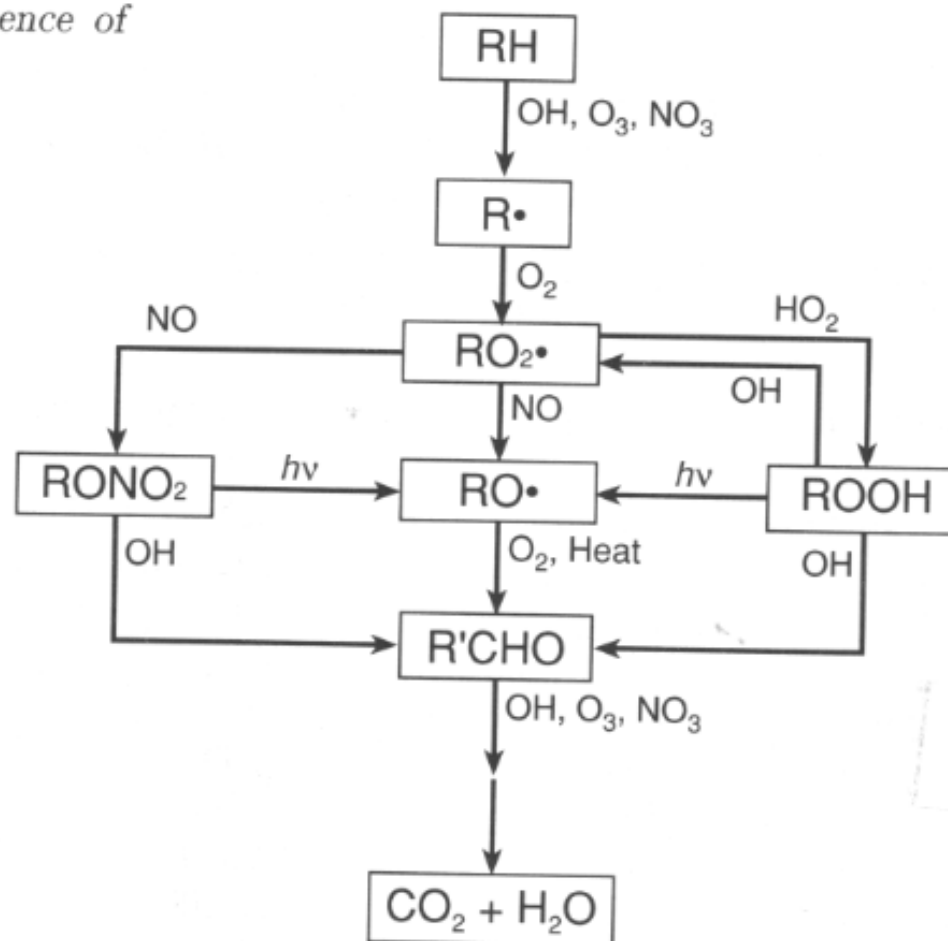
*Brasseur et al., 1998*

# Non-methane hydrocarbon oxidation

**Table 9.1**  
Types of Organic Species Present in the Atmosphere

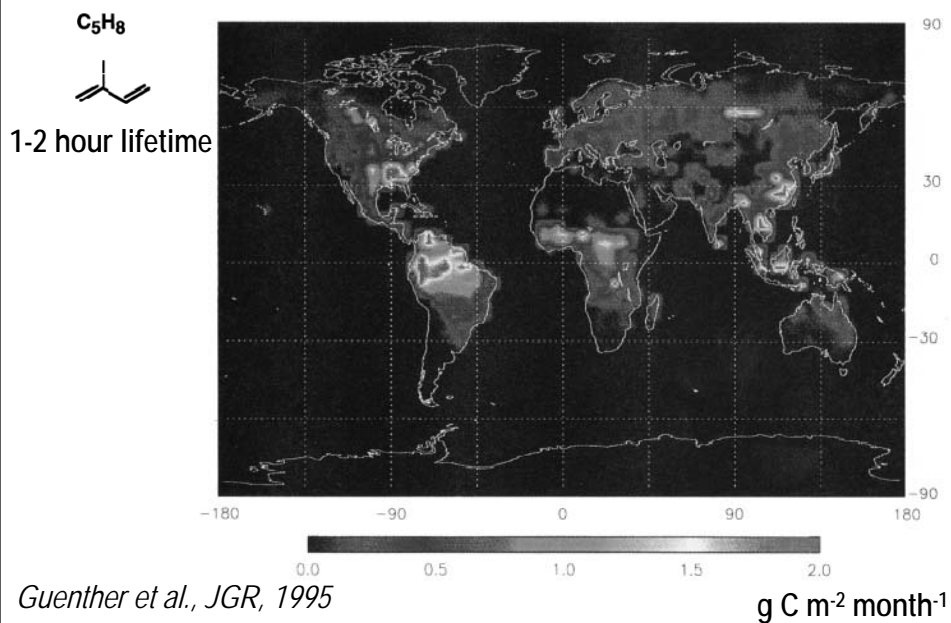
Type of Compound	General Chemical Formula	Examples
Alkanes	$R-H$	$CH_4$ , methane $CH_3CH_3$ , ethane
Alkenes	$R_2C=CR_2$	$CH_2=CH_2$ , ethene or ethylene $CH_3-CH=CH_2$ , propene
Alkynes	$RC\equiv CR$	$HC\equiv CH$ , acetylene
Aromatics	$C_6R_6$ (cyclic)	$C_6H_6$ , benzene $C_6H_5(CH_3)$ , toluene
Alcohols	$R-OH$	$CH_3OH$ , methanol $CH_3CH_2OH$ , ethanol
Aldehydes	$R-CHO$	$CH_2O$ , formaldehyde $CH_3CHO$ , acetaldehyde
Ketones	$RCOR$	$CH_3C(O)CH_3$ , acetone
Peroxides	$R-OOH$	$CH_3OOH$ , methylhydroperoxide
Organic acids	$R-COOH$	$HC(O)OH$ , formic acid $CH_3C(O)OH$ , acetic acid
Organic nitrates	$R-ONO_2$	$CH_3ONO_2$ , methyl nitrate $CH_3CH_2ONO_2$ , ethyl nitrate
Alkyl peroxy nitrates	$RO_2NO_2$	$CH_3O_2NO_2$ , methyl peroxy nitrate
Acylperoxy nitrates	$R-C(O)OONO_2$	$CH_3C(O)O_2NO_2$ , peroxyacetyl nitrate (PAN)
Alkyl radicals	$R\cdot$	$CH_3\cdot$ , methyl radical $CH_3CH_2\cdot$ , ethyl radical
Acyl radicals	$RC\cdot O$	$CH_3C\cdot=O$ , acetyl radical
Alkoxy radicals	$RO\cdot$	$CH_3O\cdot$ , methoxy radical
Peroxy radicals	$ROO\cdot$	$CH_3O_2\cdot$ , methylperoxy radical $CH_2(OH)CH_2O_2\cdot$ , 2-hydroxyethylperoxy radical
Biogenic compounds	$C_5H_8$ $C_{10}H_{16}$	$CH_2=C(CH_3)-CH=CH_2$ , isoprene $\alpha$ -pinene, $\beta$ -pinene
Multifunctional species		$CH_3C(O)CHO$ , methylglyoxal $CH_2(OH)CHO$ , glycolaldehyde

ence of

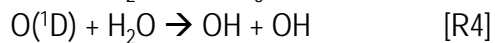
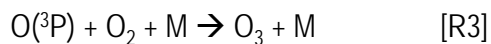
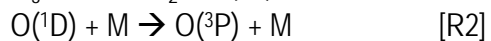
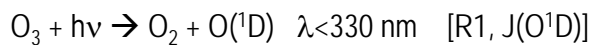
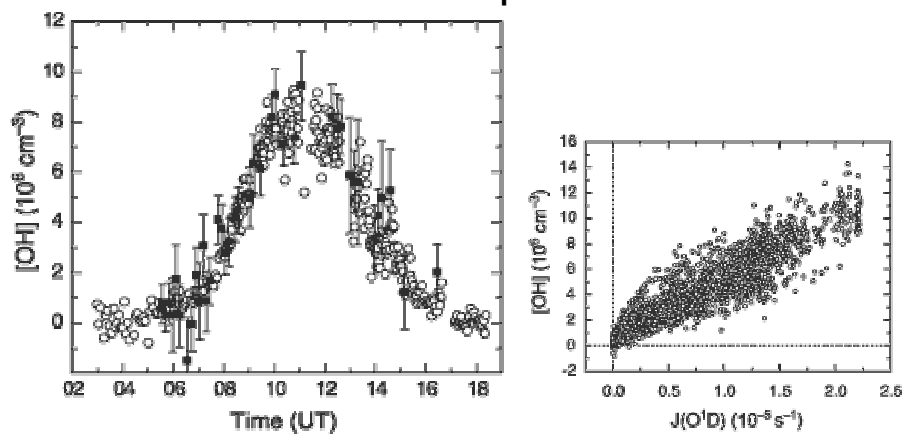




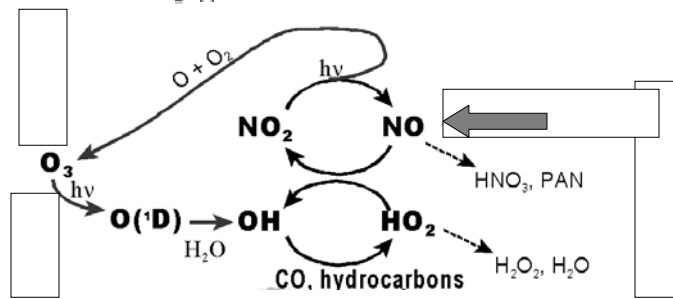
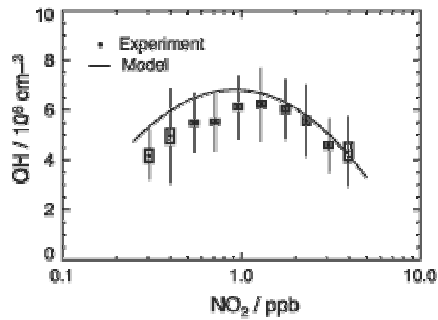
## Global distribution of isoprene emissions: July



## Observed diurnal dependence of OH



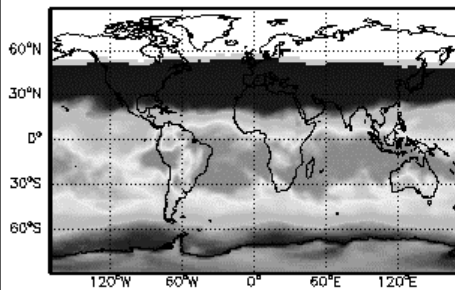
### Observed dependence of OH on NO<sub>2</sub>



### Model calculated OH for January and July: 5 km altitude

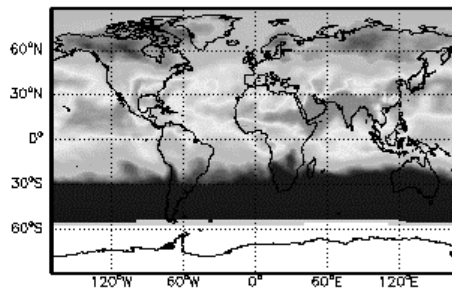
#### January (5 km)

OH January at 500 hPa (5 km) (1997(v4.11\_2x2.5))



#### July (5 km)

OH July at 500 hPa (5 km) (1997(v4.11\_2x2.5))

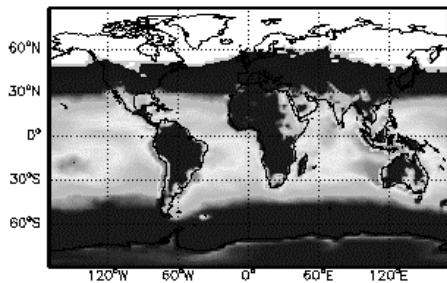


0.00 0.83 1.67 2.50 1E6 cm<sup>-3</sup>

## Model calculated OH for January and July: surface

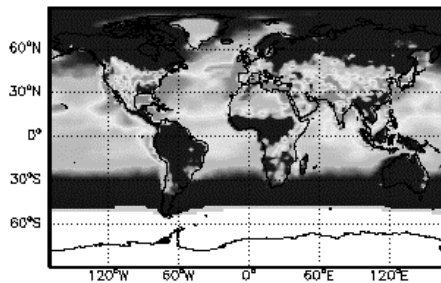
### January (surface)

OH January at Surface (1997(v4.11\_2x2.5))



### July (surface)

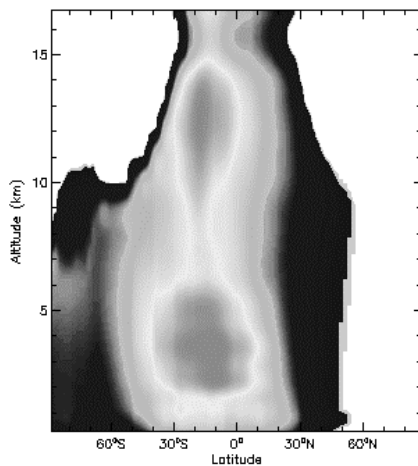
OH July at Surface (1997(v4.11\_2x2.5))



0.00 0.83 1.67 2.50  $1\text{E}6 \text{ cm}^{-3}$

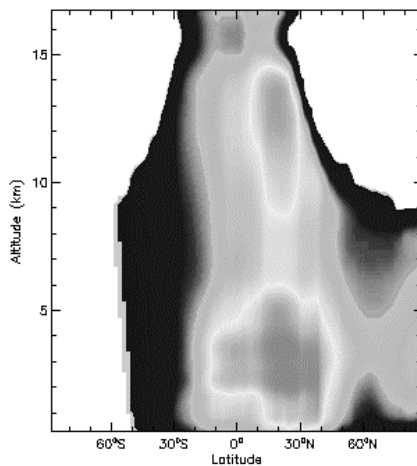
## Model calculated OH for January and July: zonal average

Zonal average – OH January (1997(v4.11\_2x2.5))



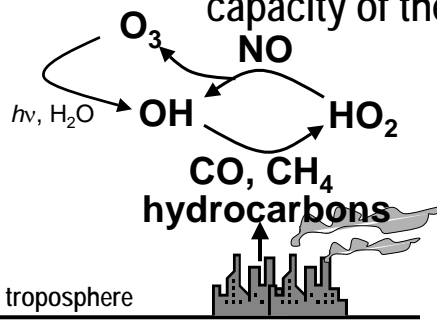
0.00 0.83 1.67 2.50  $1\text{E}6 \text{ cm}^{-3}$

Zonal average – OH July (1997(v4.11\_2x2.5))



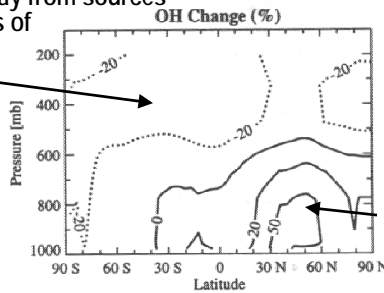
0.00 0.83 1.67 2.50  $1\text{E}6 \text{ cm}^{-3}$

# Have human activities changed the oxidizing capacity of the atmosphere?



→ Since pre-industrial times CO has increased by factors of 3-4; CH<sub>4</sub> increased by ~150%; O<sub>3</sub> increased by 50-100%; NO increased by factors of 2-8 .... What has happened to OH?

Decrease in OH away from sources driven by increases of CO (~months)



→ Little change in OH globally (buffering)

Increase in OH near sources driven by increases of NO<sub>x</sub> (~days)

Wang & Jacob, 1999