INTRODUCTION TO ATMOSPHERIC CHEMISTRY

PART II Photochemistry

09/09/2019 I ROBERT WEGENER

All data, graphics, tables, if not differently cited of copied from: B. J. Finlayson Pitts and J. N. Pitts, Jr.; "Chemistry of the Upper and Lower Atmosphere"; Academic Press, San Diego, 2000,
or from: J. H. Seinfeld and S. N Pandis; "Atmospheric Chemistry and Physics", John Wileys & Sons, 1998.
Or from: IPCC Reports

Part III Photochemistry

- Reaction with radicals
- OH radical chemistry
- Oxidation of CO and methane
- The photostationary equlibrium
- The role of Nox in Ozone Production

Tropospheric Chemistry (gas phase)

Sources

biological = ***biogenic***

industrial = ***anthropogenic***

Table 3: Composition of the Atmosphere

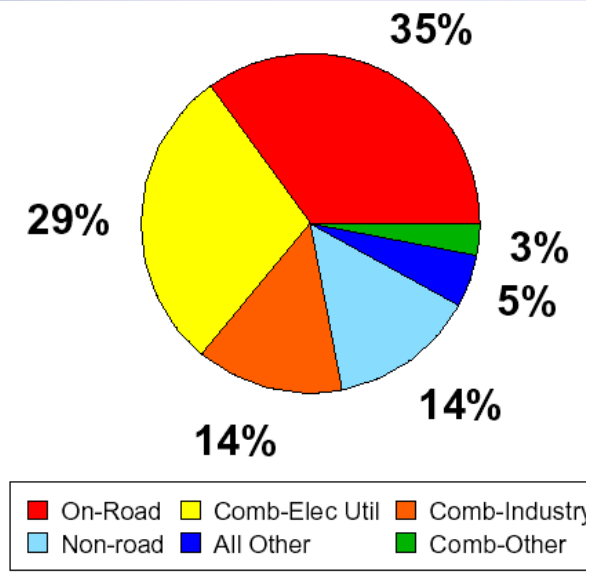
species	relative abundance (parts per billion by volume)	source	comment
N_2	7.81×10^8	biologic	long lived
O_2	2.01×10^8	biologic	long lived
H_2O	$10^6 - 10^7$	physical	long lived
Ar	9.34×10^6	radiogenic	permanent
CO_2	3.5×10^5	biologic, industrial	variable, increasing
Ne	1.8×10^4	interior	permanent
He	5.2×10^3	radiogenic	escaping
CH_4	1.6×10^3	biologic	variable, increasing
Kr	1.0×10^3	interior	permanent
H_2	5.0×10^2	biologic, photochemical	variable
N_2O	3.0×10^2	biologic, industrial	increasing
CO	1.0×10^2	photochemical, industrial	variable, increasing
SO_2	$<10^2$	industrial, photochemical	variable
O_3	$<10^2$	photochemical	variable
Xe	9×10^1	interior	permanent
NO, NO_2, NO_x	variable	industrial, biologic	—*
CH_3Cl	6.0×10^{-1}	biologic	short lived
CCl_2F_2	2.9×10^{-1}	industrial	increasing
[illegible]	[illegible]	[illegible]	[illegible]
CCl_4	1.2×10^{-1}	industrial	increasing
CH_3CCl_3	9.8×10^{-2}	industrial	increasing
[illegible]	[illegible]	[illegible]	[illegible]
CH_3Br	1.0×10^{-2}	biologic, industrial	possibly increasing

*Relatively short lived, with an average lifetime of roughly one month.

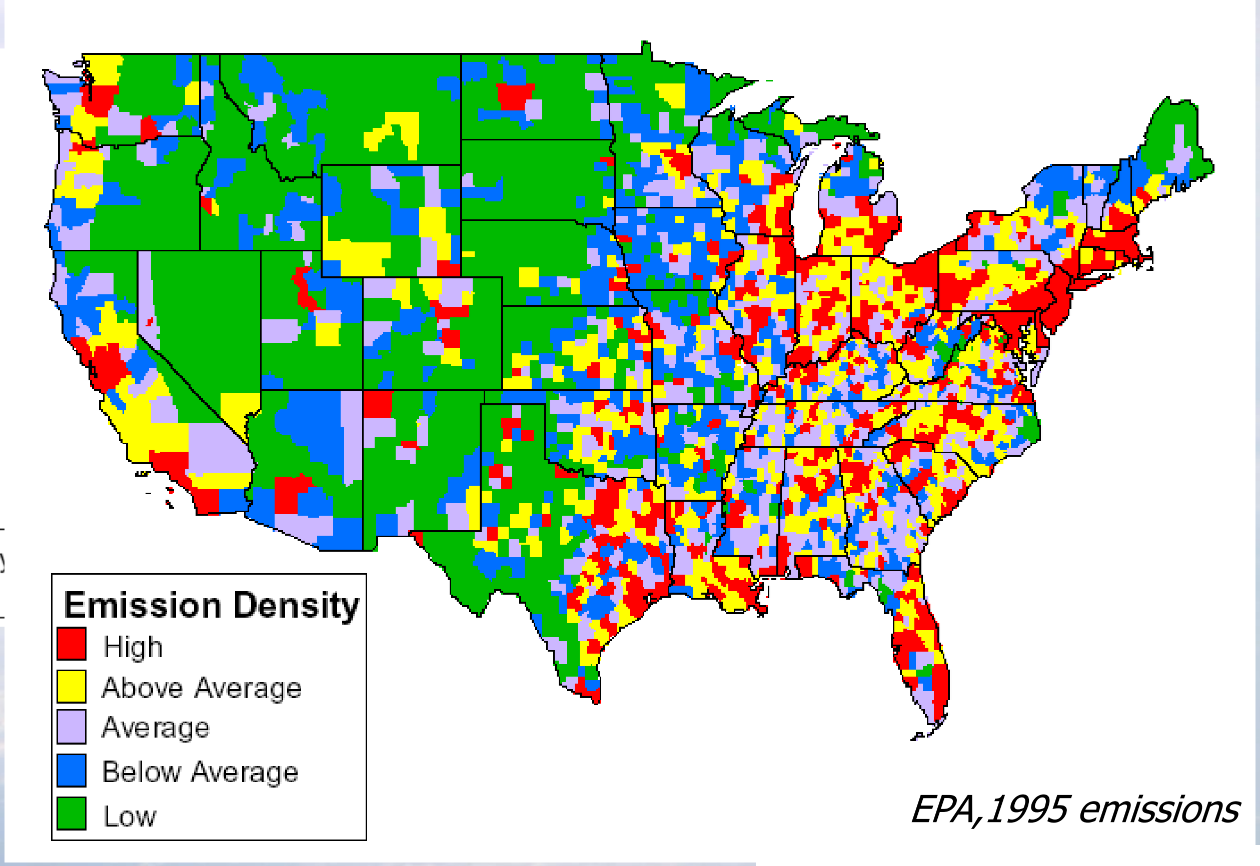
no emission

TROPOSPHERIC CHEMISTRY

NO_x



VOC's



EPA,1995 emissions

Tropospheric Chemistry

→

No chemical reaction
CH_4 lifetime $\rightarrow \infty$

The reaction with O_2 is <u>kinetically hindered</u> at low temperatures
(0 - 100km altitude: 205K - 310K)

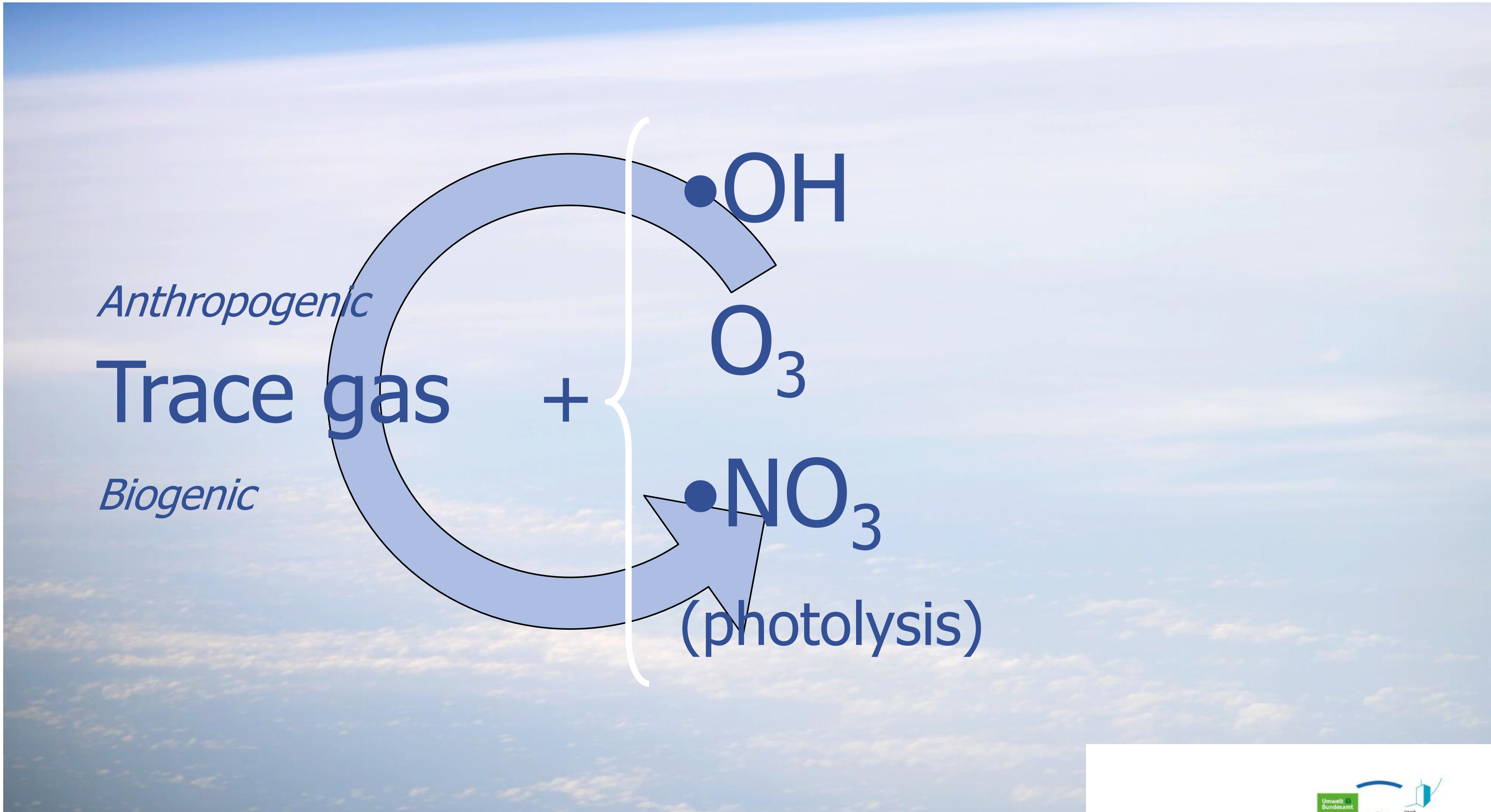
Atmsopheric Chemistry

$$CO + OH \longrightarrow CO_2 + H$$

1971: lifetime of CO in the troposphere shorter than expexted

$$NO_x + VOC + h\nu + O_2 \longrightarrow O_3$$

Atmsopheric Chemistry



Atmsopheric Chemistry

Table 2 Global turnover of the major tropospheric trace gases and attribution to the major oxidants

Trace gas	*Global lifetime*	*Global loss rate (Tmol per year)*	*Removal (%)*			
			OH[a]	*O_3*[b]	*NO_3*[c]	*Other*
CO	1.5 months	100	85	–	–	15 (Soil uptake)
H_2	2 years	38	25	–	–	75 (Soil uptake)
CH_4	8 years	36	90	–	–	10 (Soil uptake; stratos.)
Isoprene	Hours[d]	8	80	7	13	–
SO_2	Days[d]	5	30	–	–	70 (Hetero. in clouds)
NO_x	0.3–5 days[d]	3	50	40	–	10 (Soil uptake)
Terpenes	Hours[d]	1	20	25	55	–
C_2H_6	2 months	0.7	80	–	–	20 (Cl reaction)[e]
N_2O	120 years	0.6	–	–	–	100 (Stratosphere)
$(CH_3)_2S$	Days[d]	0.5	70[f]	–	30[f]	–

[a]Using a mean global OH concentration of 1×10^6 cm^{-3}.
[b]Using a mean global O_3 concentration of 30 ppbv.
[c]Using a mean global NO_3 concentration of 1 pptv.
[d]Order of magnitude or range of local lifetimes. These are too short and variable to make a global lifetime meaningful.
[e]Upper limit using a mean global Cl concentration of 1×10^3 cm^{-3}.
[f]3D model; Isaksen, private communication. Due to a strong anticorrelation induced by the oceanic emission of $(CH_3)_2S$ and continental emission of NO_2 removal by NO_3 is less than that calculated from the global means (footnote a), (footnote c) which would assign 85% of the $(CH_3)_2S$ loss to NO_3.
Adapted and expanded from Ehhalt, D.H., 1999a. Chapter 2: Gas phase chemistry of the troposphere. In: Zellner, R. (Guest ed.), Baumgärtel, H., Grünbein, W., Hensel, F. (eds.), Global Aspects of Atmospheric Chemistry, Topics in Physical Chemistry, vol. 6. Steinkopff, Darmstadt, pp. 21–109.

Sources of OH

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad \lambda \leq 340\ \text{nm}$$

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2$$
$$O(^1D) + O_2 \rightarrow O(^3P) + O_2$$
$$O(^1D) + H_2O \rightarrow \boxed{OH + OH}$$

Most O1D are quenched

Conz: 10^7 cm^{-3}

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$
$$(M = N_2,\ O_2)$$

O(3P) is too reactive

Conz: O1D 1000 cm^{-3}

~ 0.2 OH per O_3 photolyzed

Reactions of OH

$$CO + OH \rightarrow CO_2 + H$$

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

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

With NO > 0.1ppb

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

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

$$CO + 2O_2 + h\upsilon \rightarrow CO_2 + O_3$$

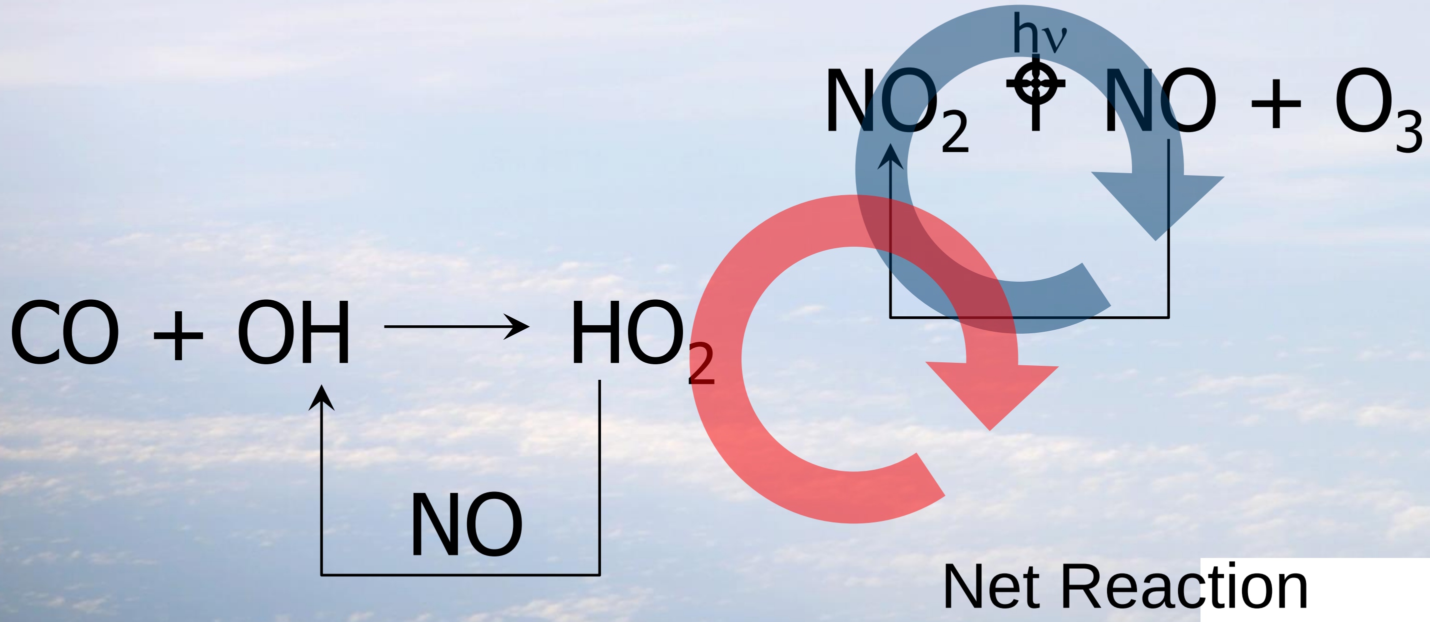
$$CO + OH + O_2 \rightarrow HO_2 + CO_2$$

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

Net Reaction

Reactions of OH

$$CO + 2O_2 + h\upsilon \rightarrow CO_2 + O_3$$



Reactions of OH in Remote regions

NO > 0.1ppb

$$CO + OH \rightarrow CO_2 + H$$

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

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

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

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

NO < 0.1ppb

$$CO + OH \rightarrow CO_2 + H$$

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

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$CO + 2O_2 + h\upsilon \rightarrow CO_2 + O_3$$

Ozone Production

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

Ozone Loss

Losses of OH

$$OH + HO_2 \rightarrow H_2O + O_2$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Clean Air

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

Polluted Air

Other Sources of OH

OH: - photolysis of ozone: $O_3 + h\nu \rightarrow O(^1D) + O_2$

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

- photolyis of HONO: $HONO + h\nu \rightarrow OH + NO$
- photolyis of HCHO: $HCHO + h\nu + NO_x \rightarrow\rightarrow OH$
- alkene ozonolysis: $R\text{-}C{=}C\text{-}R + O_3 \rightarrow\rightarrow OH$

Degradation of Methane

$CH_4 + OH$	$\rightarrow$	$CH_3 + H_2O$	(Alkyl)
$CH_3 + O_2 + M$	$\rightarrow$	$CH_3O_2 + M$	(Alkylperoxy)
In the presence of NO_x:			
$CH_3O_2 + NO$	$\rightarrow$	$CH_3O + NO_2$	(Alkoxy)
$CH_3O + O_2$	$\rightarrow$	$HCHO + HO_2$	(Aldehyd)
$HCHO + h\nu$	$\rightarrow$	$H + HCO$	
$HCO + O_2$	$\rightarrow$	$HO_2 + CO$	
$CO + OH + M$	$\rightarrow$	$CO_2 + H + M$	
$2H + 2\ O_2 + M$	$\rightarrow$	$2HO_2 + M$	
$4HO_2 + 4NO$	$\rightarrow$	$4OH + 4NO_2$	
$5NO_2 + 5O_2 + h\nu$	$\rightarrow$	$5NO + 5O_3$	

$$CH_4 + 10\ O_2 + h\nu \xrightarrow{+NO_x} CO_2 + 5\ O_3 + H_2O + 2\ OH \quad \text{(net)}$$

„combustion of the fuel“

„formation of oxidants“

Degradation of organic trace gases

- Typical scenario:
  - OH as oxidizing species
  - NO / NO_2 conversion by HO_2

- Oxidation chains driven by sunlight = "Photooxidation" cycles

- The "fuel" concentration in a slow cycle ***controls*** $[O_3]_{ss}$

Degradation of organic trace gases

Lifetime and reaction rates vary!

TABLE 6.8 Estimated Tropospheric Lifetimes of Organic Comp

	Lifetime against reaction with			
	OH^a	$O_3{}^b$	$NO_3{}^c$	$h\nu$
n-Butane	5.7 days	—	1.7 months	
Propene	6.6 h	1.6 days	5.9 h	
Benzene	12 days	—	—	
Toluene	2.4 days	—	1.1 month	
m-Xylene	7.4 h	—	10 days	
Formaldehyde	1.5 days	—	4 days	4 h
Acetaldeyde	11 h	—	20 h	5 days
Acetone	66 days	—	—	38 days
Isoprene	1.7 h	1.3 days	0.8 h	
α-Pinene	3.4 h	4.6 h	6 min	
β-Pinene	2.3 h	1.1 days	15 min	
Camphene	3.5 h	18 days	1.8 h	
2-Carene	2.3 h	1.7 h	1.8 min	
3-Carene	2.1 h	10 h	3.3 min	
d-Limonene	1.1 h	1.9 h	2.7 min	
Terpinolene	49 min	17 min	0.4 min	

[a] 12-h daytime OH concentration of 1.5×10^6 molecules cm^{-3} (0.06 ppt).
[b] 24-h average O_3 concentration of 7×10^{11} molecules cm^{-3} (30 ppb).
[c] 12-h average NO_3 concentration of 4.8×10^8 molecules cm^{-3} (20 ppt).

NO_2, O_3 and NO_2

$NO_2 + h\nu$	$\rightarrow$	$NO + O(^3P)$	$j_{5.1}$
$O(^3P) + O_2 + M$	$\rightarrow$	$O_3 + M$	$k_{5.2}$
$O_3 + NO$	$\rightarrow$	$NO_2 + O_2$	$k_{5.3}$

$$NO_2 \overset{h\nu}{\leftrightarrow} NO + O_3$$

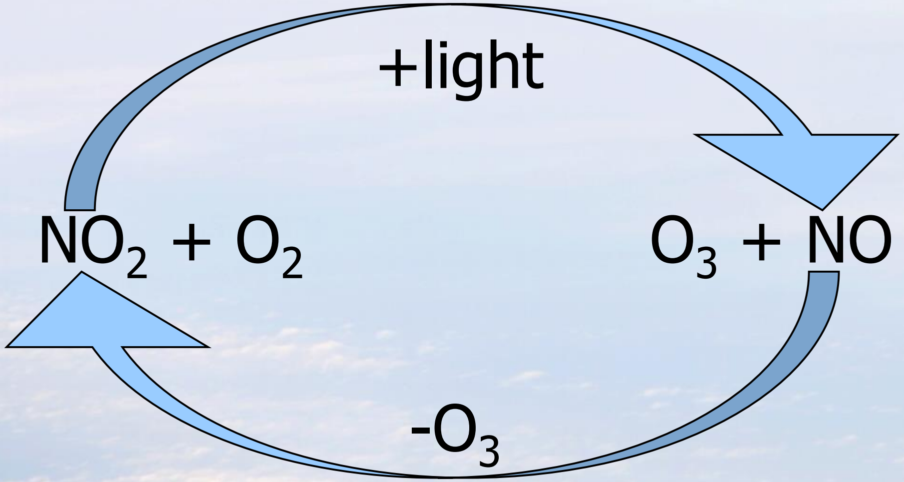
$$[O_3]_{PSS} = \frac{j_{5.1} \cdot [NO_2]}{k_{5.3} \cdot [NO]}$$

Photo stationary state relation

NO_2, O_3 and NO_2

Impact of NO_2 on the formation of ozone

- *Without VOCs: Leighthon equillibrium*



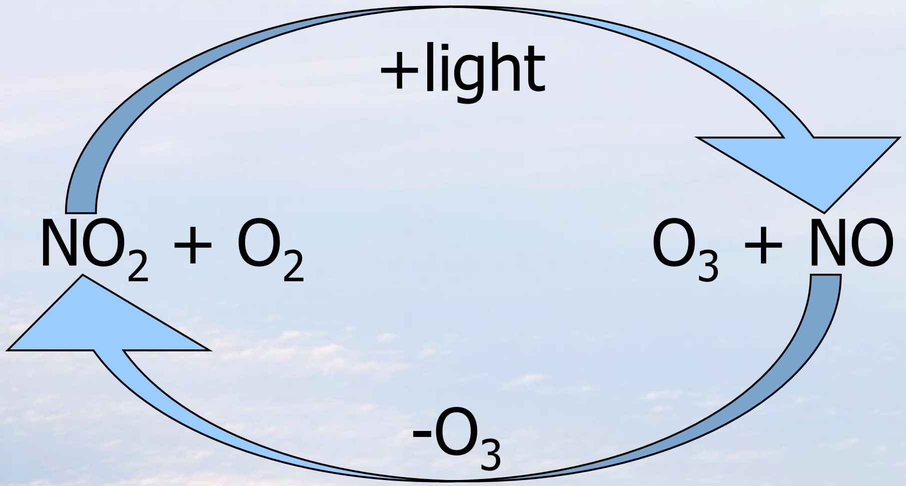
→ ***Establishment of a photostationary state***

→ ***No net formation of Ozone***

NO_2, O_3 and NO_2

Impact of NO_2 on the formation of ozone

- *Without VOCs: Leighthon equillibrium*



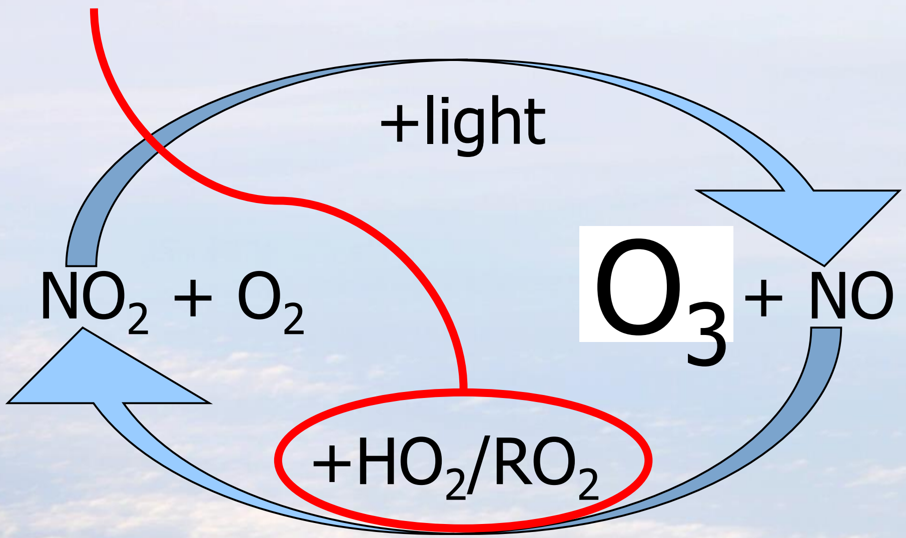
➔ ***Establishment of a photostationary state***

➔ ***No net formation of Ozone***

NO_2, O_3 and NO_2

Impact of NO_2 on the formation of ozone

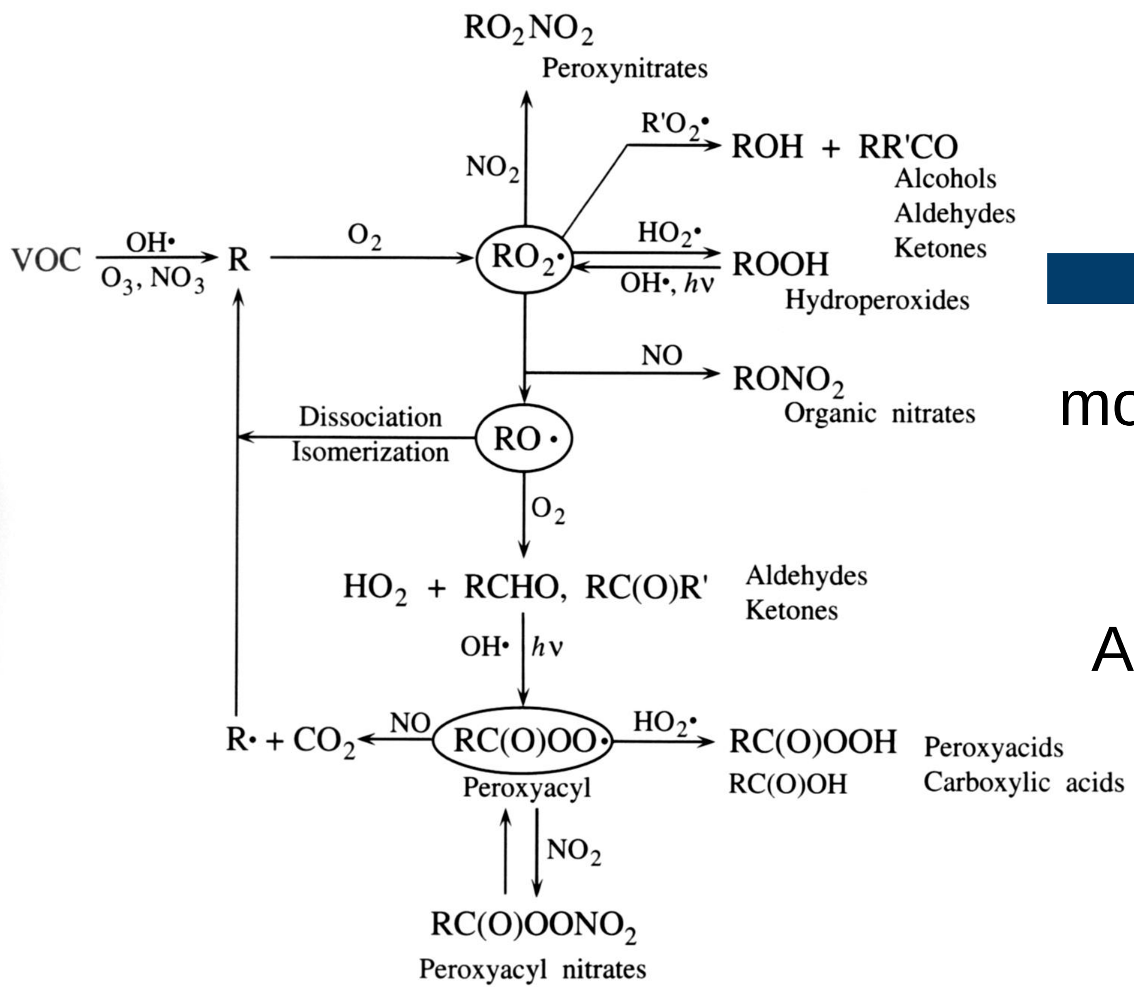
- *Adding hydrocarbons (VOCs)*



➔ ***Net production of Ozone***

➔ ***„summer smog"***

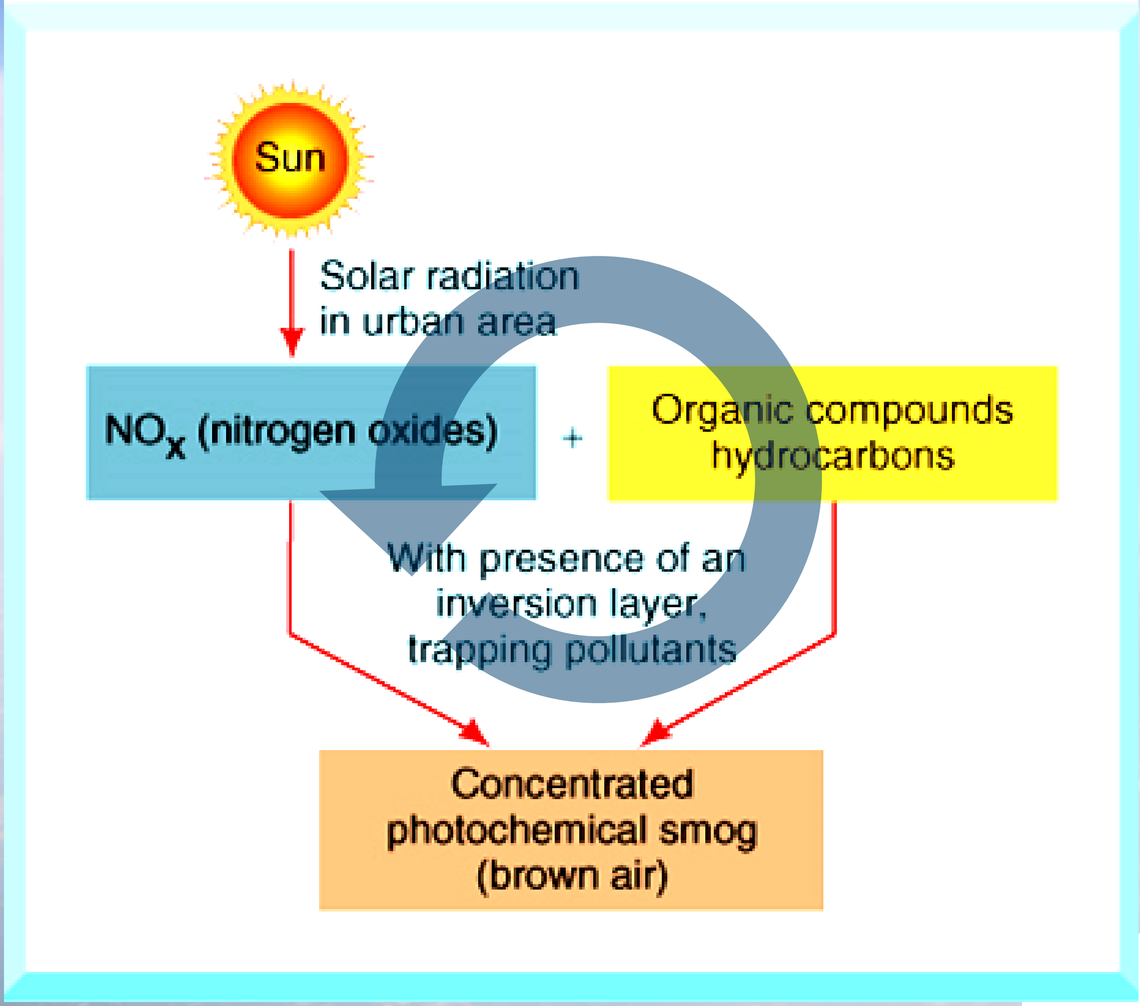
Formation of other products



more functional group

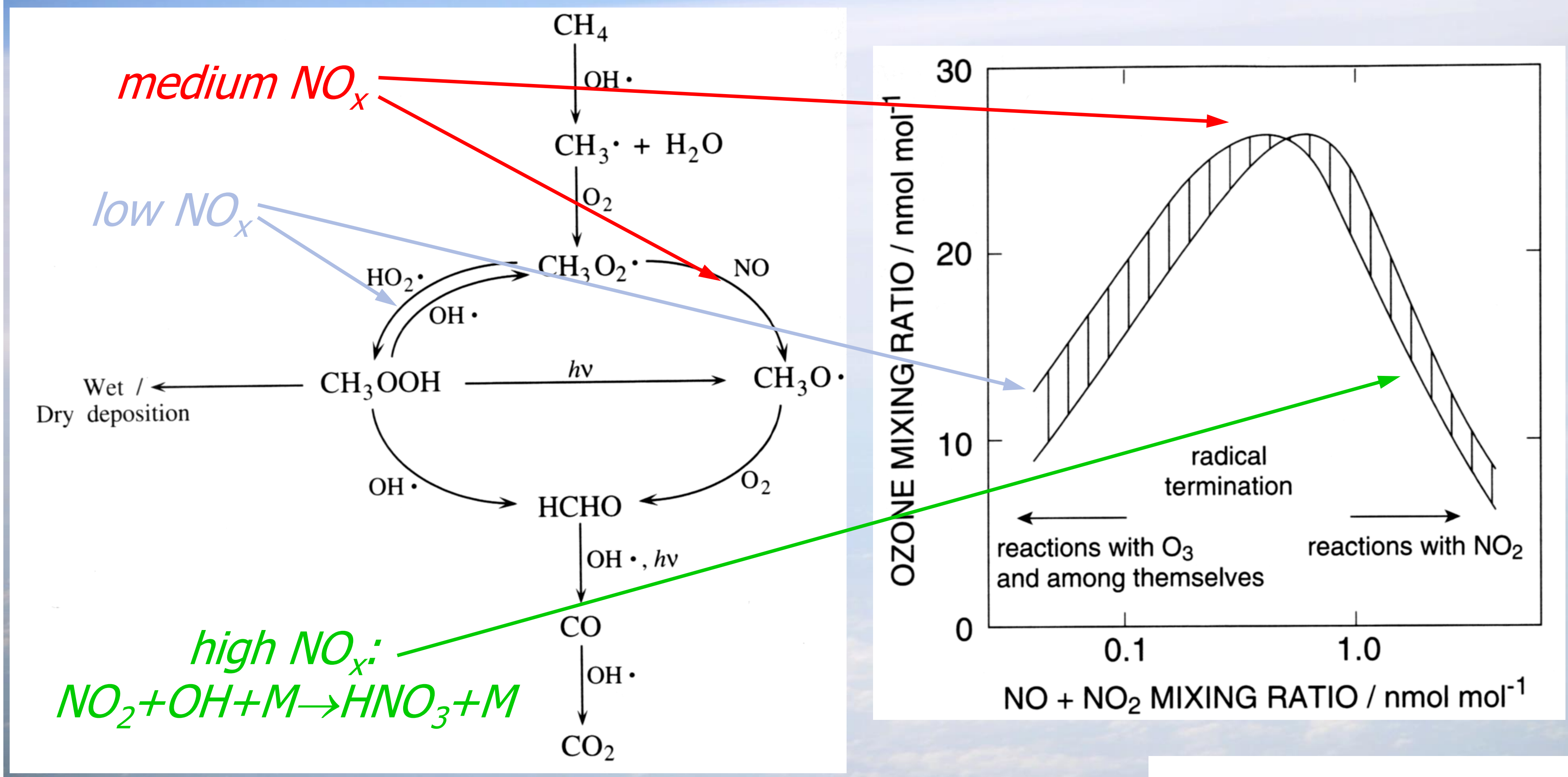
Arerosol formation

NO_2, O_3 and NO_2



Photochemistry also leads to aerosol production

NO_2, O_3 and NO_2



Ozone Production and NOx

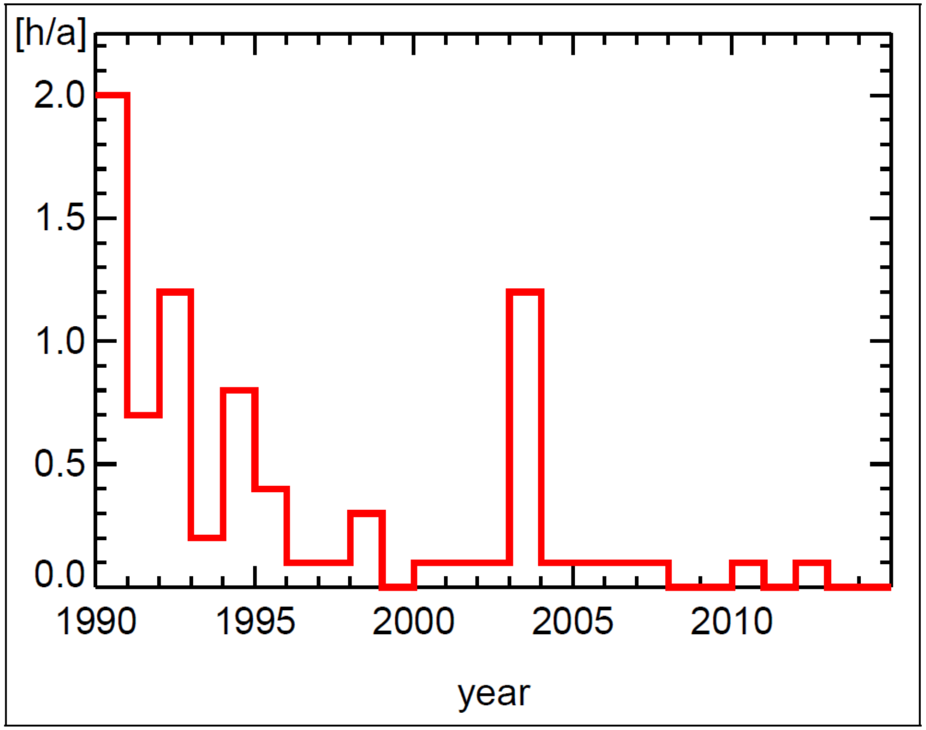
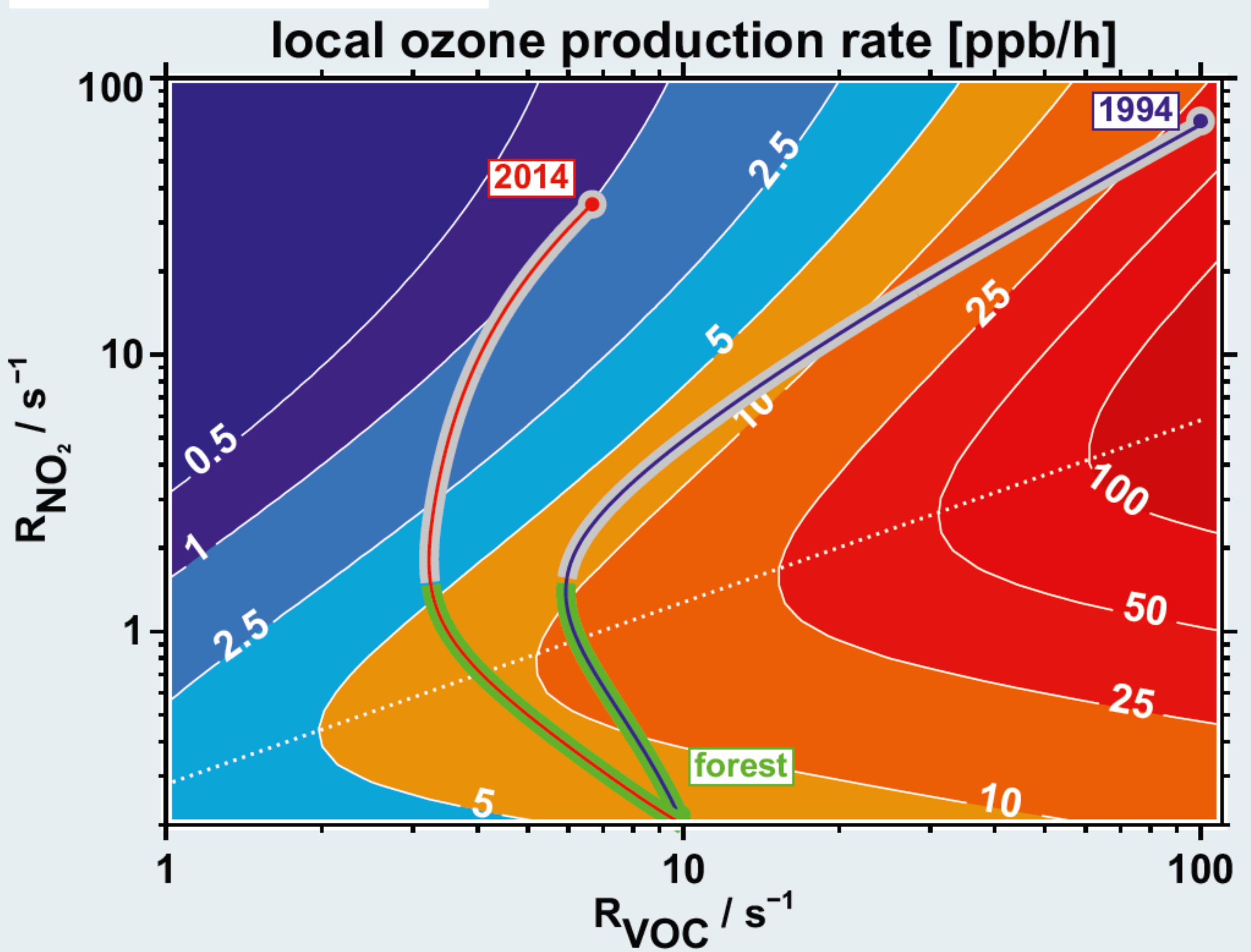


Fig. 1 Average number of hours/year for all survey stations in Germany[1] exceeding the European ozone alarm value of $240\mu g/m^3$

Numbers of ozone alarms decrease

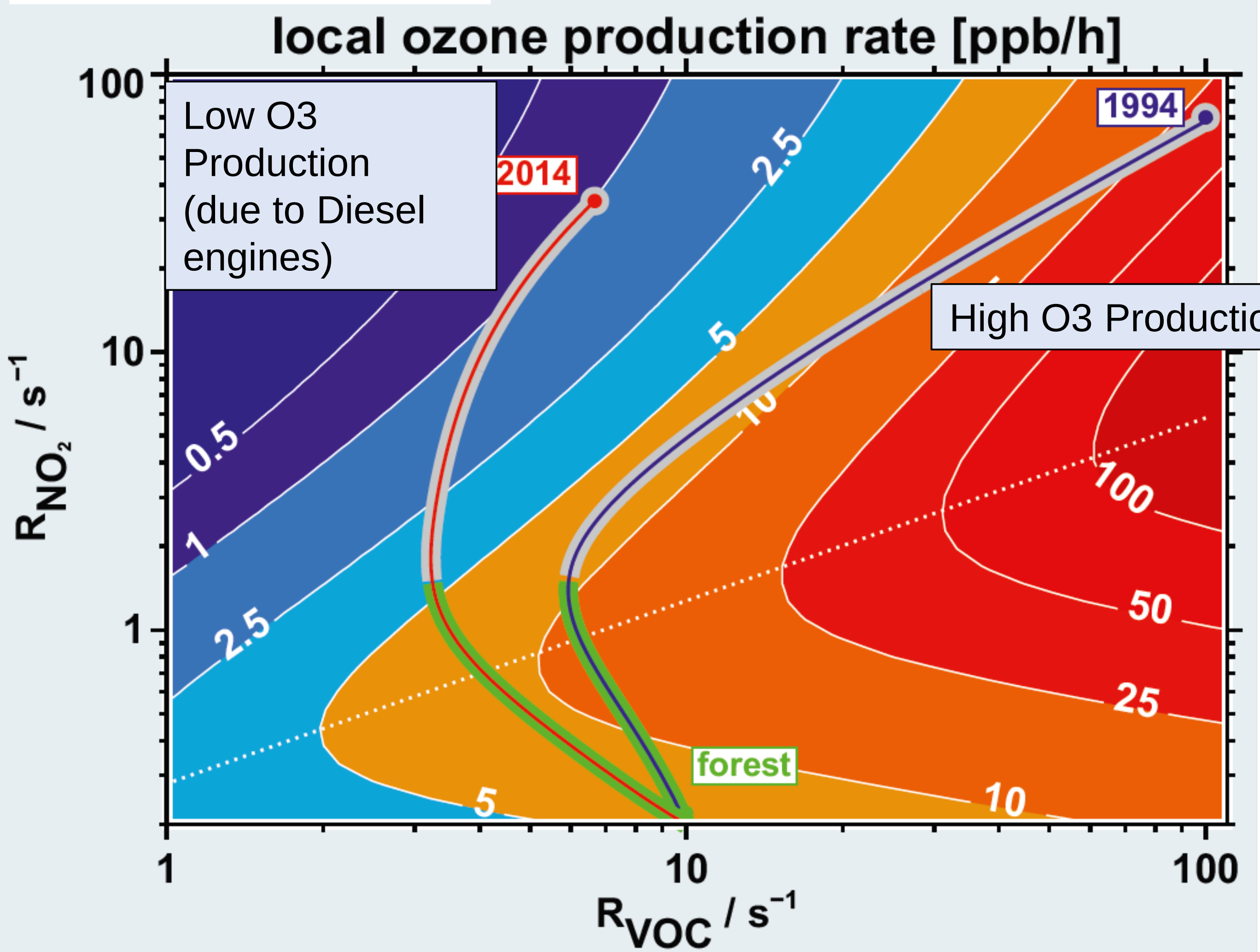
(except from 2003)

Ozone Production and NOx



Further details see: Ehlers et al., Twenty years of ambient observations of nitrogen oxides and specified hydrocarbons in air masses dominated by traffic emissions in Germany , *Faraday Discuss.*, ***2016***, 189, 407-437

Ozone Production and NOx



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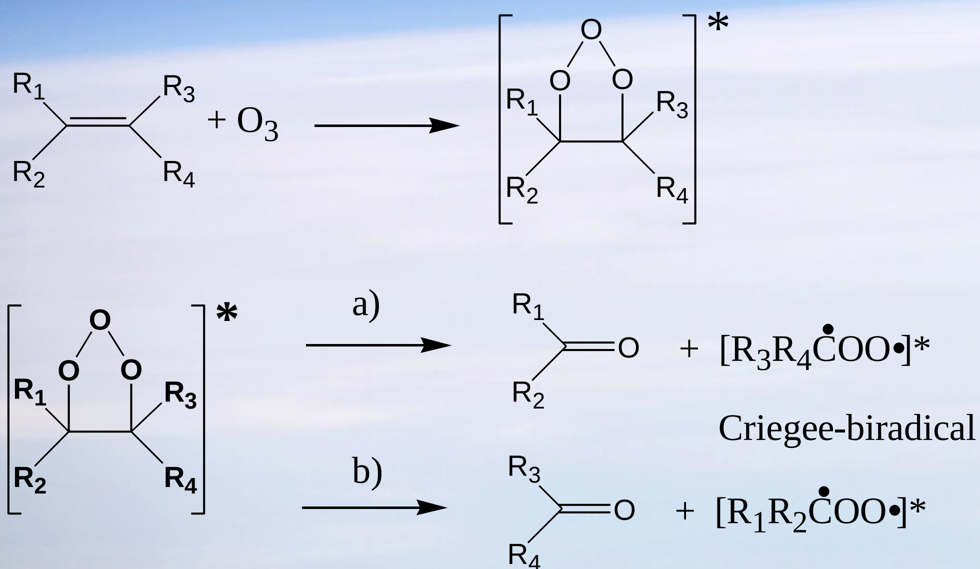
Reaction with ozone



$[\dot{C}H_2OO\bullet]^* \xrightarrow{+M} \dot{C}H_2OO\bullet$ (stabilisation)

$\longrightarrow CO_2 + H_2$

$\longrightarrow CO + H_2O$

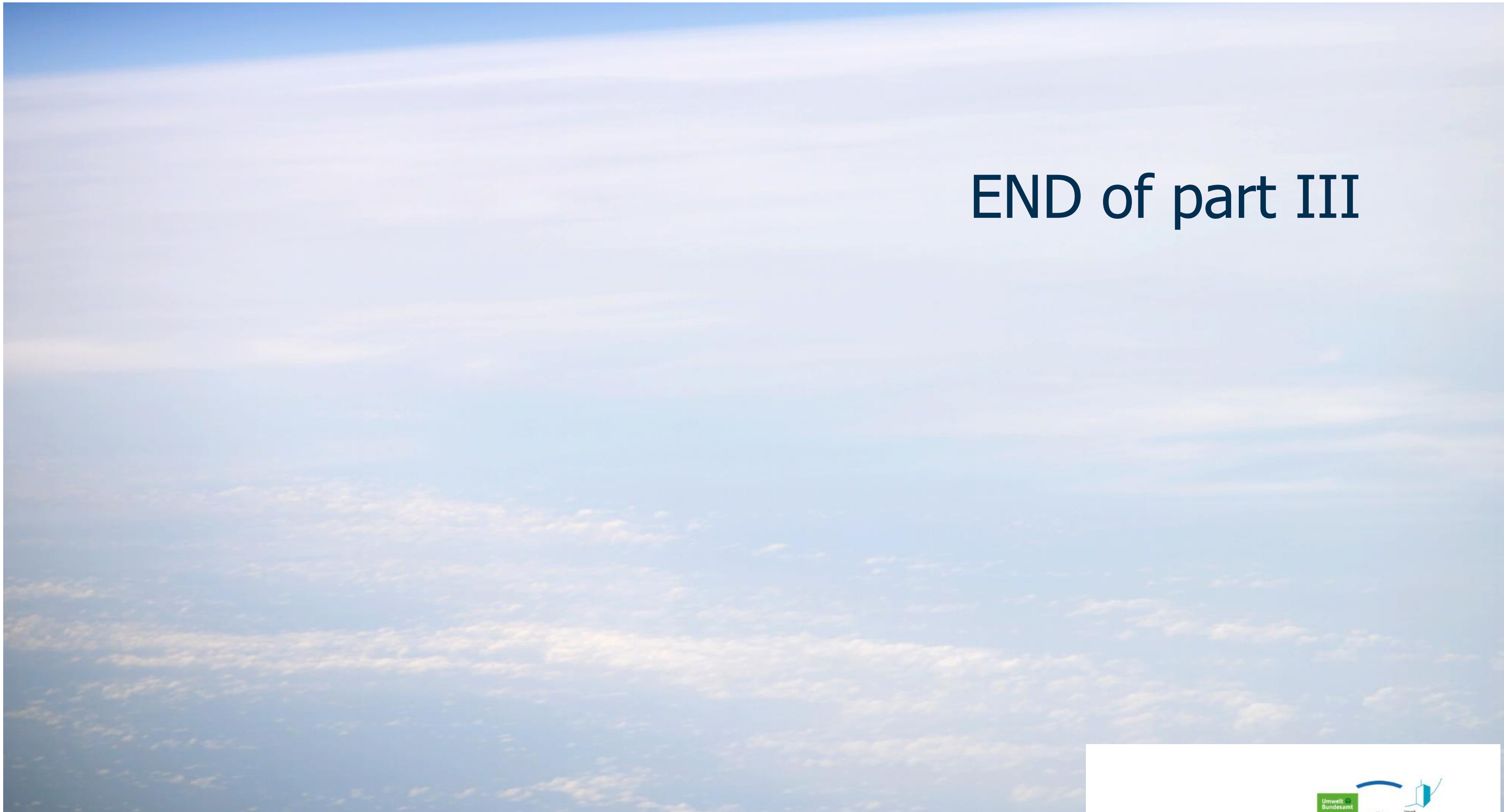
$\xrightarrow{+O_2} CO_2 + 2\ \mathbf{HO_2}$

$\longrightarrow HCO + \mathbf{OH}$

➔ Formation of oxygenated species

➔ Formation OH-radicals

Reaction with NO_3



END of part III

OH Balance Equation

$$\frac{\mathrm{d}\,[\mathrm{OH}]}{\mathrm{d}t} = P_{\mathrm{OH}} - D_{\mathrm{OH}} \approx 0$$

contributions
from transport, i.e., the flux divergence, are small

$$\begin{aligned} D_{\mathrm{OH}} &= [\mathrm{OH}] \cdot (k_7[\mathrm{CO}] + k_{14}[\mathrm{O_3}] + \cdots \\ &\quad + k_{17}[\mathrm{NO_2}] + k_{15}[\mathrm{HO_2}] + \cdots) \\ &= [\mathrm{OH}] \cdot \tau_{\mathrm{OH}}^{-1} \end{aligned}$$

contributions
from transport, i.e., the flux divergence, are small

Reactions of OH in Remote regions

NO > 0.1ppb	NO < 0.1ppb
$CO + OH \rightarrow CO_2 + H$	$CO + OH \rightarrow CO_2 + H$
$H + O_2 + M \rightarrow HO_2 + M$	$H + O_2 + M \rightarrow HO_2 + M$
$NO + HO_2 \rightarrow NO_2 + OH$	
$NO_2 + h\upsilon \rightarrow NO + O(^3P)$	$HO_2 + O_3 \rightarrow OH + 2O_2$
$O(^3P) + O_2 + M \rightarrow O_3 + M$	
Ozone Production	Ozone Loss
$CO + 2O_2 + h\upsilon \rightarrow CO_2 + O_3$	$CO + O_3 \rightarrow CO_2 + O_2$

Reactions of OH in Remote regions

NO > 0.1ppb

$$CO + OH \rightarrow CO_2 + H$$

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

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

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NO < 0.1ppb

$$CO + OH \rightarrow CO_2 + H$$

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

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

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

Reactions of OH in Remote regions

NO > 0.1ppb

$$CO + OH \rightarrow CO_2 + H$$

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

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

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

HEADLINE DER PRÄSENTATION

SUBLINE DER PRÄSENTATION

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Forschungszentrum

HEADLINE DER PRÄSENTATION

Subline der Präsentation bei umfänglicher Erläuterung

DATUM I NAME

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Forschungszentrum

HEADLINE

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HEADLINE

Subline

Bildunterschrift

Bildunterschrift