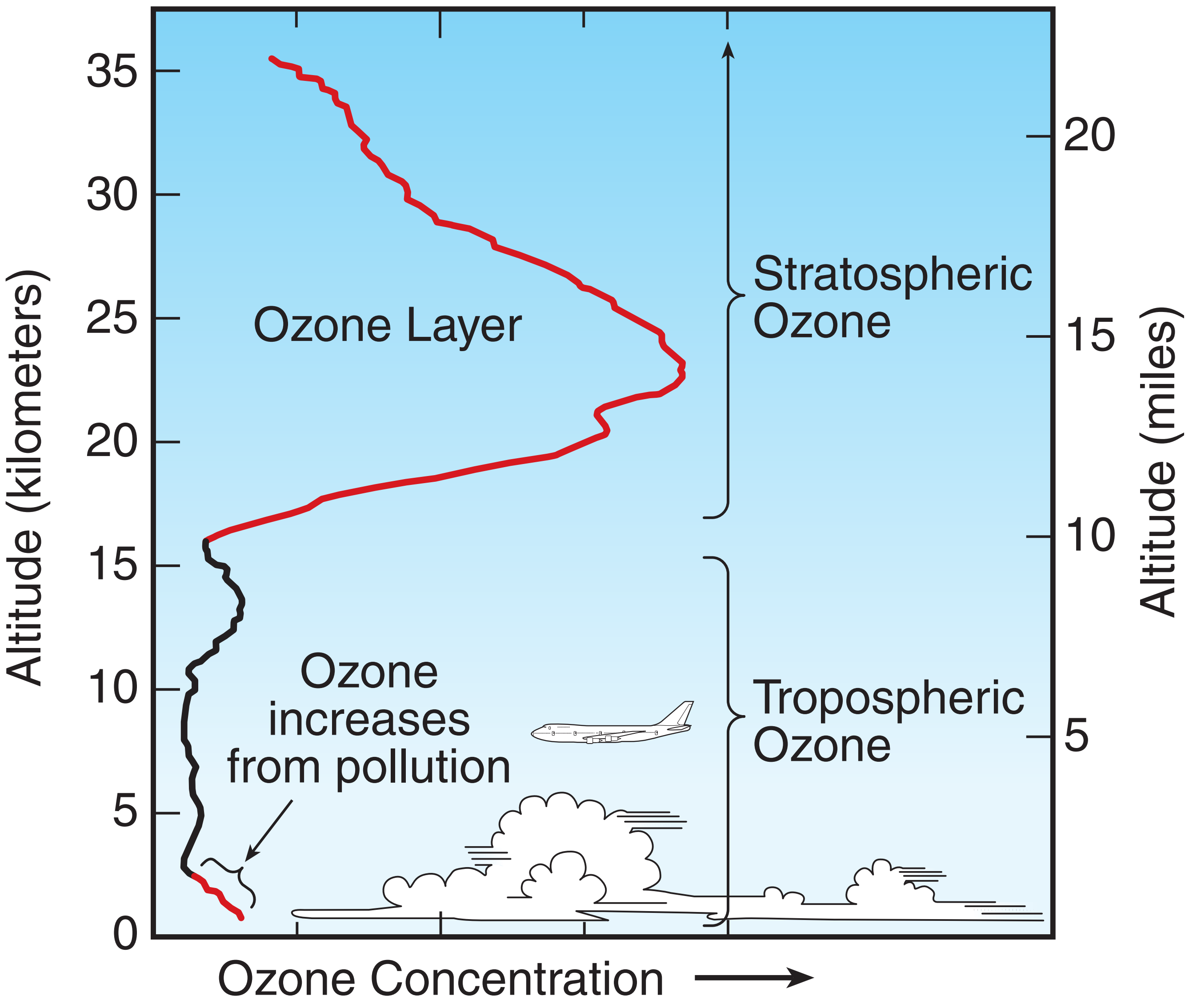
3 Tropospheric chemistry

3.1 Tropospheric ozone and hydrocarbon chemistry

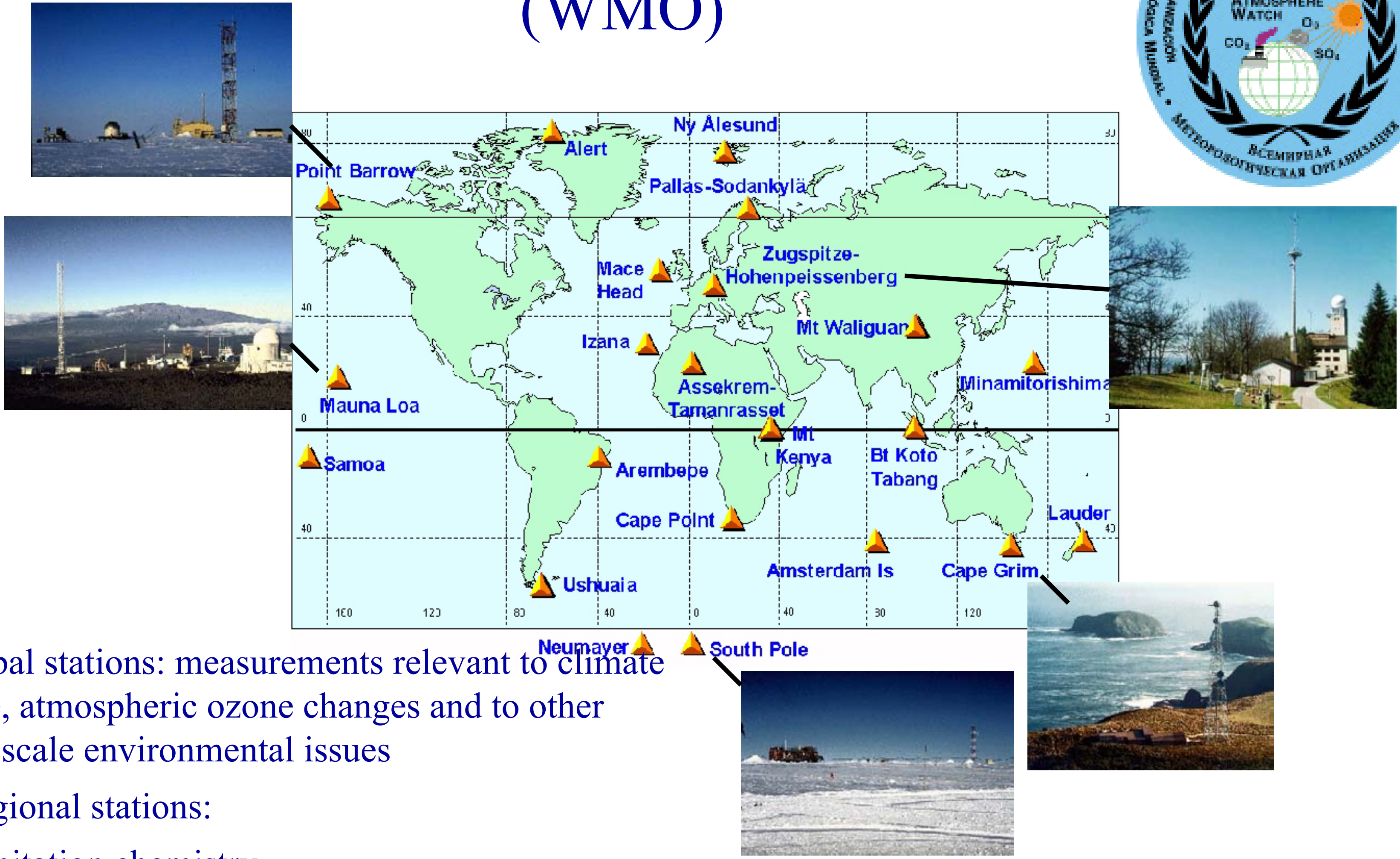


Ozone in the Atmosphere

Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

3.1.1 Tropospheric ozone trends

Global atmospheric chemistry monitoring (WMO)

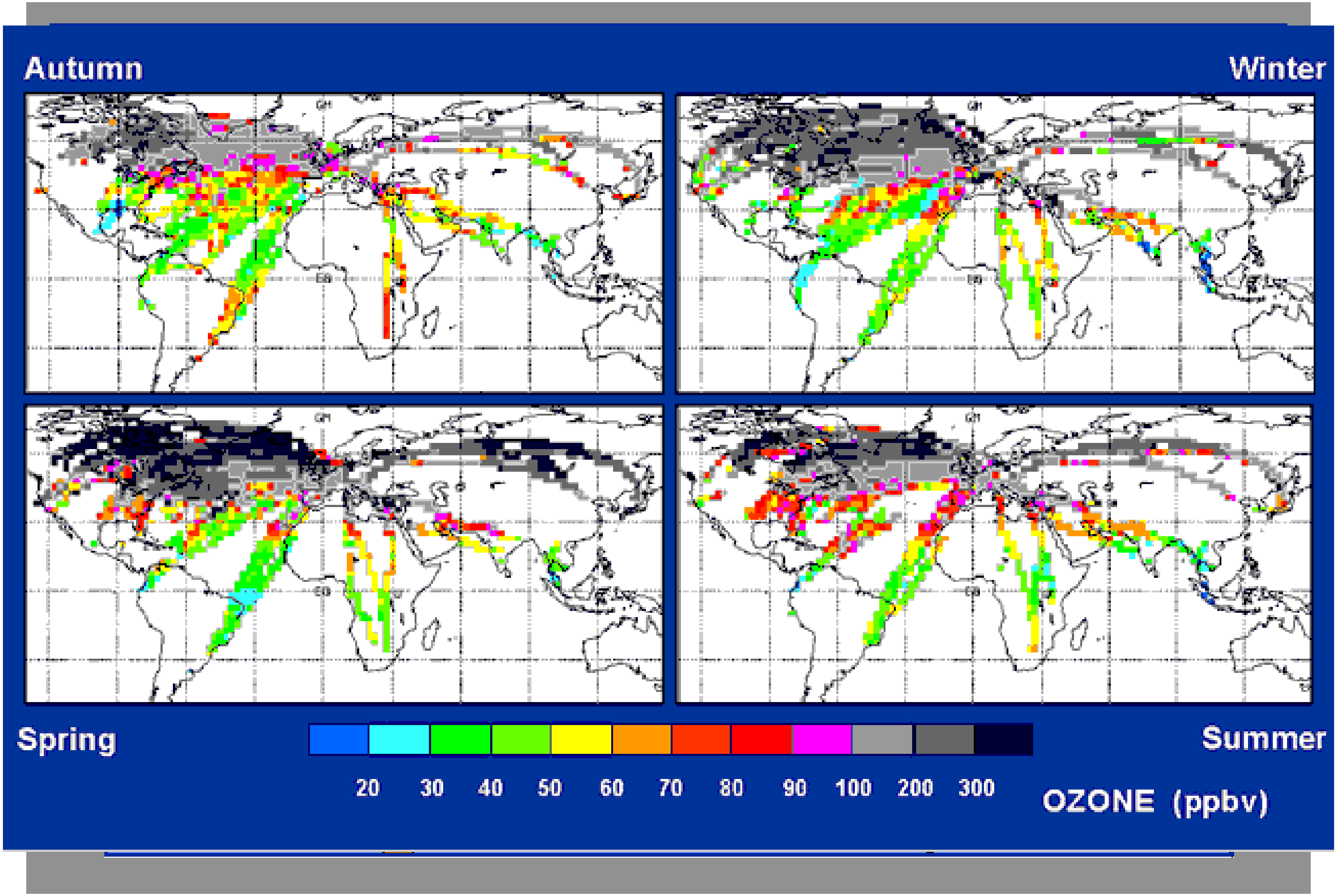


20 global stations: measurements relevant to climate change, atmospheric ozone changes and to other global-scale environmental issues

300 regional stations:

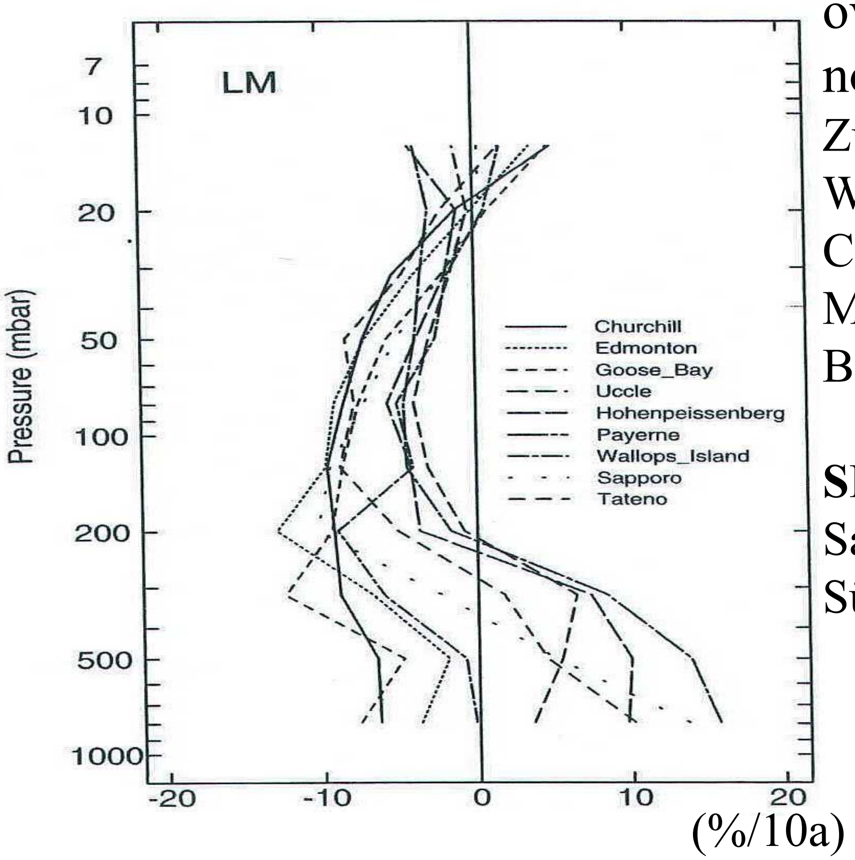
- precipitation chemistry
- radiation (visible and UV), O_3, CH_4, CO
- aerosol composition, black carbon
- meteorological parameters.

Ozone climatologies at 9-12 km altitude *(Thouret et al., 2006)*



Trends of ozone - stratospheric and tropospheric

36-59°N, 1996 vs. 1970

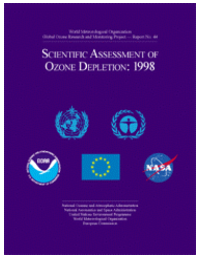


NH: Increases over Europa and Japan,
over Europe stagnation since mid 1980s
no significant trend over the USA (1980-95)

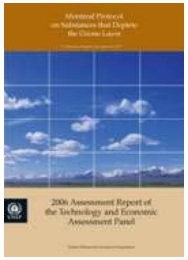
Zugspitze (47°N)	+14.8±5.1 %/10a [1978-9
Whiteface Mtn./USA (44°N)	+4.5±2.2 %/10a [1974-95]
Cape Grim/Tas (41°S)	+1.8±1.4 %/10a [1982-95]
Mauna Loa (20°N)	+0.1±2.8 %/10a [1980-97]
Barrow/AK (70°N)	- 0.6±3.4 %/10a [1980-97]

SH:

Samoa (14°S)	- 2.6±3.8 %/10a [1976-94]
Südpol (90°S)	- 8.3±2.4 %/10a [1980-97]



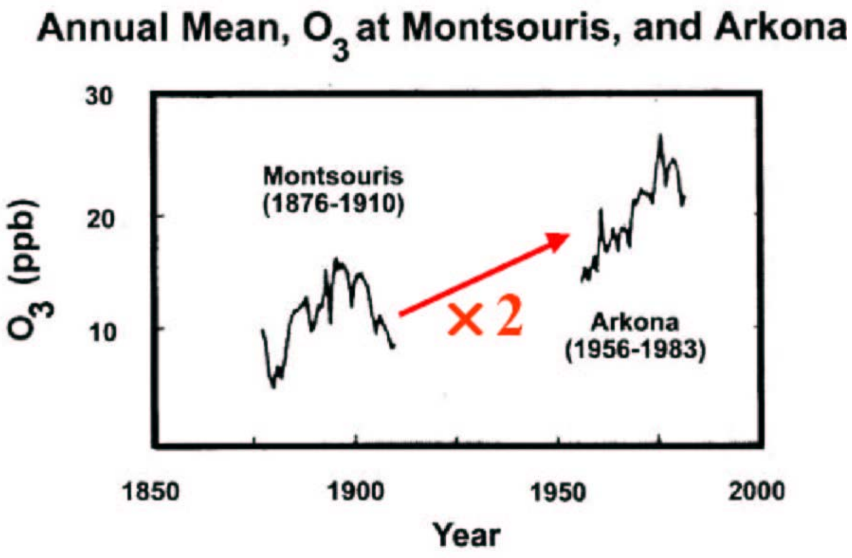
SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 1998



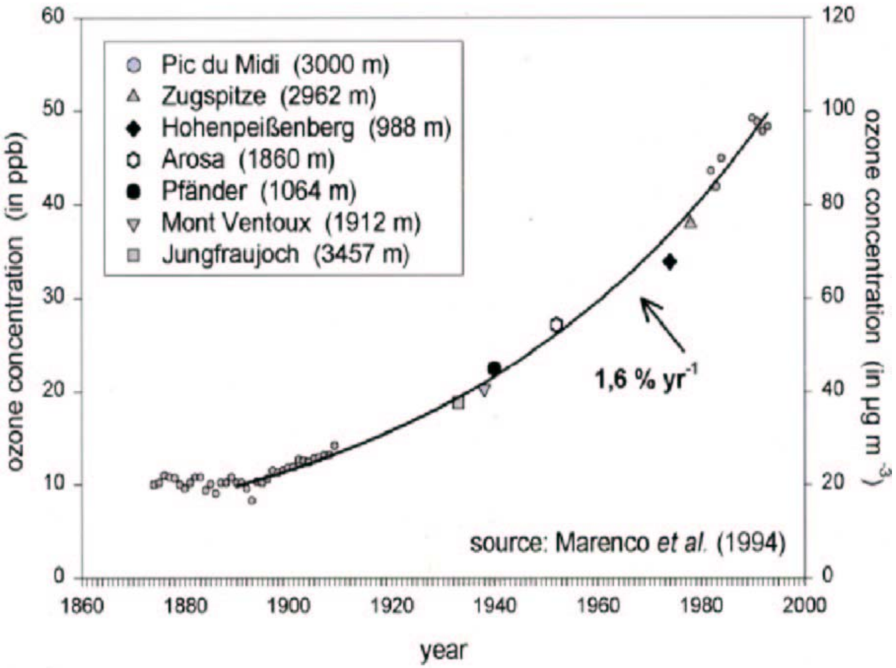
(WMO, 1998, after Logan & Megretskaia) http://ozone.unep.org/

Tropospheric ozone trends

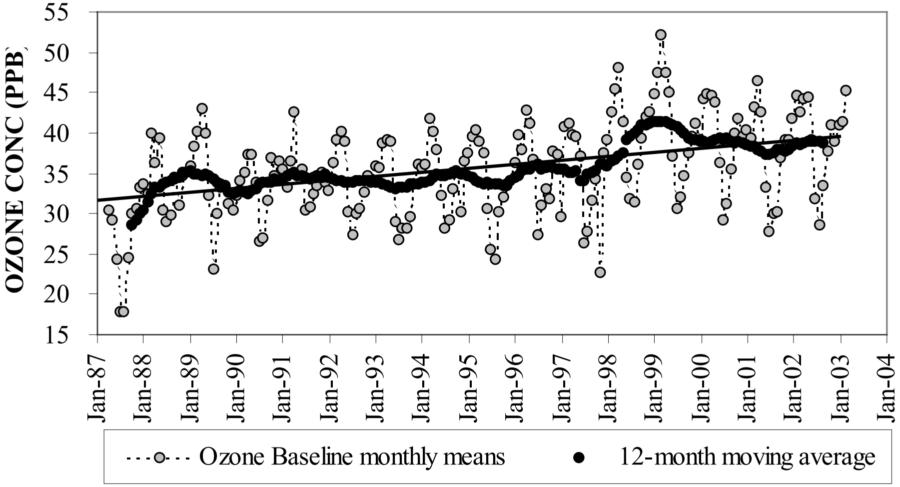
Background stations



Mountain stations



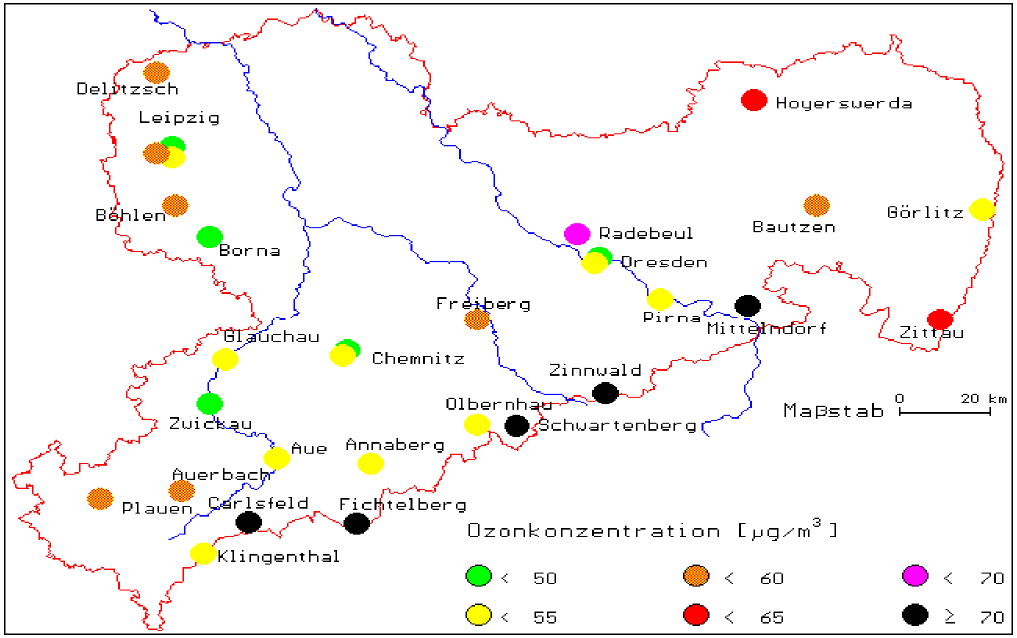
Mace Head, IRL *(Derwent, 2004)*

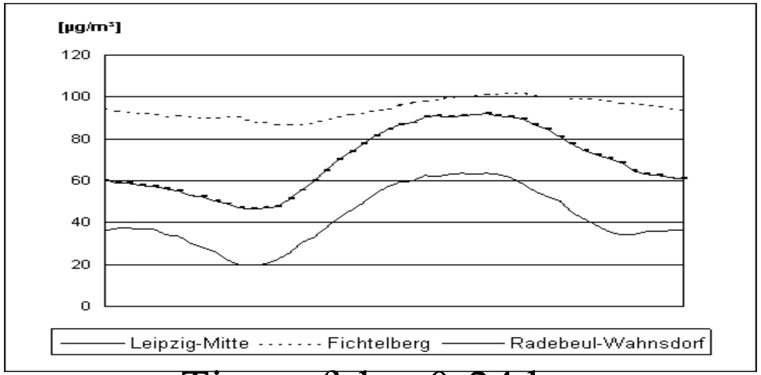


Tropospheric ozone:

Formation retarded upon precursor emissions

Distribution close and far from emissions





Time of day 0-24 h

(Saxonia state environmental agency, LfUG, 1999)

3.1.2 Ozone formation: Photosmog chemistry

Photosmog chemistry: urban atmosphere

vehicle emissions + hν → partly oxygenated HC_x + NO_2
($CO + NO + HC_x$) (carbonyls, ...)

CO does not accumulate - ?
no ozone - ?

Tropospheric O_3: Significance

Climate:

- absorption in the atmospheric ‚window‘ region near $\lambda = 9.6$ µm → $+0.35 \pm 0.15$ W m^{-2} since 1850

Ecotoxicology:

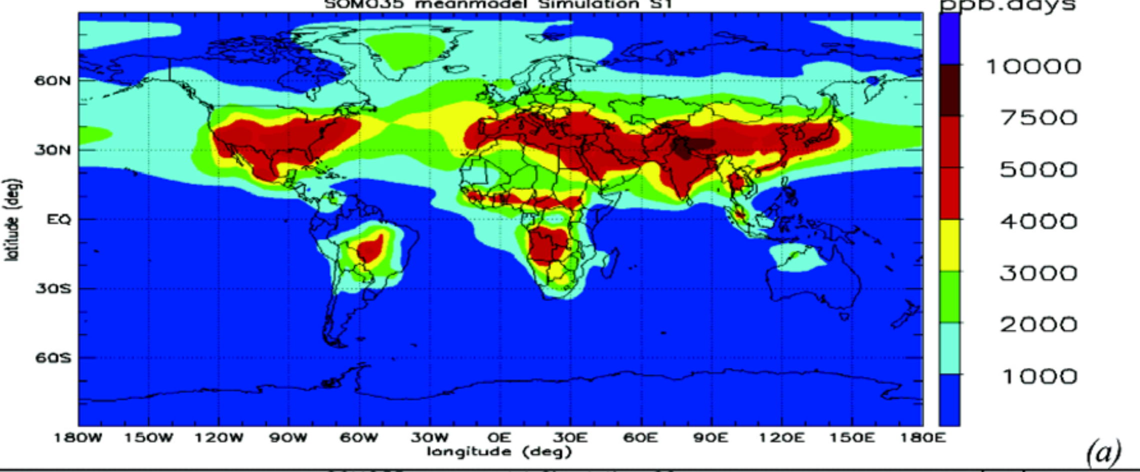
- toxic to plants (uptake through stomatae prevails, radical formation); sensitive crops (potato, wheat, rye, barley) and trees (larch, pine)
- for same dosis damage is highest under peak concentrations, synergistic effects with NO_2 and SO_2

Toxicology:

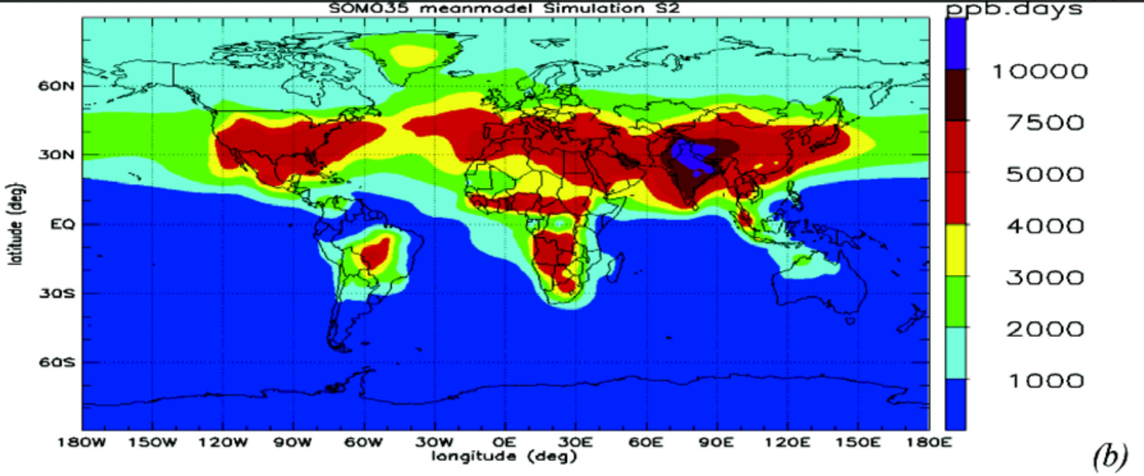
- concentrations > 120-150µg/m^3 are relevant, at least for sensitive persons. No epidemiological evidences.
- Significant loss of physical performance at higher concentrations, i.e. ca. 400 µg/m^3.

Example critical levels for natural and agroecosystems

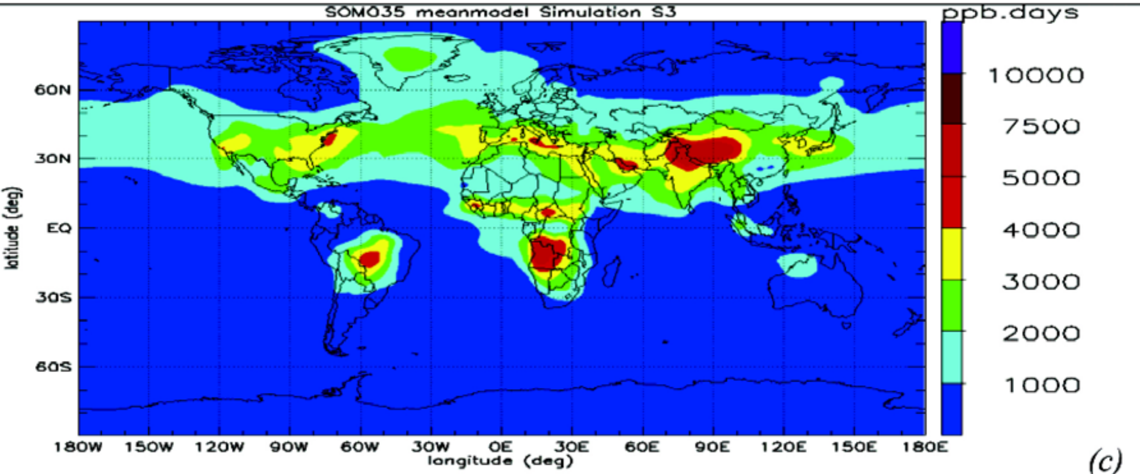
Losses of harvested wheat > 5%, if accumulated dose exceeding 40 ppbv > 3000 ppbv h;
similar: SOMO35 [ppbv d] – in 2000:



in 2030 under CL



in 2030 under MF
(Dentener et al., 2006)



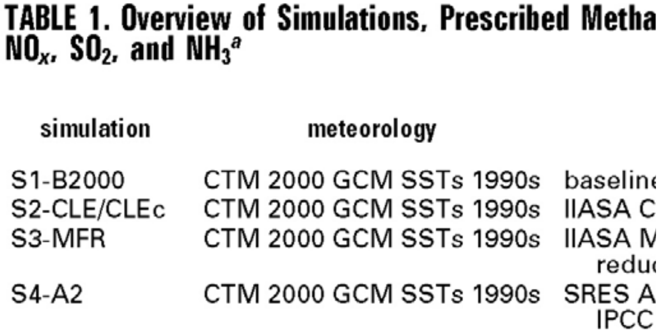
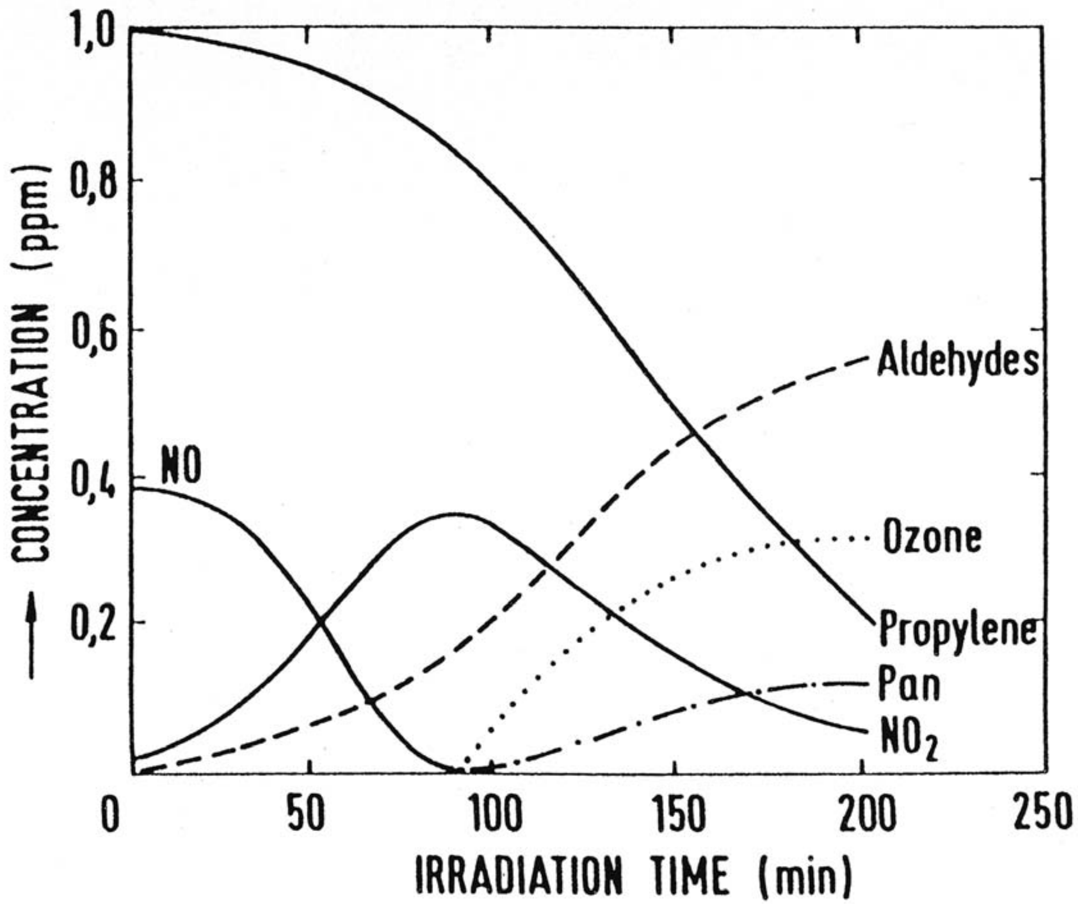


TABLE 1. Overview of Simulations, Prescribed Metha
NO_x, SO_2, and NH_3[a]

simulation	meteorology	
S1-B2000	CTM 2000 GCM SSTs 1990s	baselin
S2-CLE/CLEc	CTM 2000 GCM SSTs 1990s	IIASA C
S3-MFR	CTM 2000 GCM SSTs 1990s	IIASA M redu
S4-A2	CTM 2000 GCM SSTs 1990s	SRES A IPCC

Ozone formation in synthetic atmosphere



$NO_x + HC_x + \text{Light} \rightarrow \text{partly oxygenated } HC_x + O_3$

3.1.2.1 Ozone formation in CO oxidation

Ozone formation in the troposphere

(1) Why is CO not accumulating in urban air?

→ ‚discovery' of the OH radical

CO volume mixing ratio in the lower troposphere: 100-200 ppbv

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

Chemical fate of OH globally: 2/3 reacts with CO

(2) $H + O_2 \rightarrow HO_2$

Sum (1_2): **$CO + O_2 + OH \rightarrow HO_2 + CO_2$**

(3) $HO_2 + NO \rightarrow OH + NO_2$ $k = 220 \times 10^{-12}$ cm³/molec/s

(4) $NO_2 + h\nu$ (< 420 nm) $\rightarrow NO + O$ $j \approx 5 \times 10^{-3}/s$

(5) $O + O_2 + M \rightarrow O_3 + M$ $k^{(1)} \approx 10^{5}/s$

Sum (1-5): **$CO + 2\,O_2 \rightarrow CO_2 + O_3$**

(6) $O_3 + NO \rightarrow O_2 + NO_2$ $k^{(1)} \approx 10^{-2}/s$

Sum (1-6):

$CO + O_2 + NO \rightarrow CO_2 + NO_2$

Ozone formation in the troposphere

Leighton relationship

(4) $\mathbf{NO_2 + h\nu\ (< 420\ nm) \rightarrow NO + O}$ $j_4 \approx 5x10^{-3}/s$

(5) $\mathbf{O + O_2 + M \rightarrow O_3 + M}$ $k_5^{(1)} \approx 10^5/s$

(6) $\mathbf{O_3 + NO \rightarrow O_2 + NO_2}$ $k_6^{(2)} \approx 1x10^{-14}\ cm^3/molec/s$

ozone ‚titration' by NOx

$dc_{O3}/dt = 0 = k_2\ c_O\ c_{O2}\ c_M - k_3\ c_{NO}\ c_{O3}$ **equilibrium within 2 min**

hence: $c_{O3} = k_2\ c_O\ c_{O2}\ c_M\ /\ (k_3\ c_{NO})$ **quasi-constant ozone level (f(j_{NO2})**

c_O available from:

$dc_O/dt = 0 = j_1\ c_{NO2} - k_2\ c_O\ c_{O2}\ c_M$ (hence: $c_O = j_1\ c_{NO2}\ /(k_2\ c_{O2}\ c_M)$)

combined: $c_{O3} = k_2 c_{NO2}/(k_3 c_{NO})$ or: $(c_{O3}\ c_{NO})/c_{NO2} = \text{constant}$

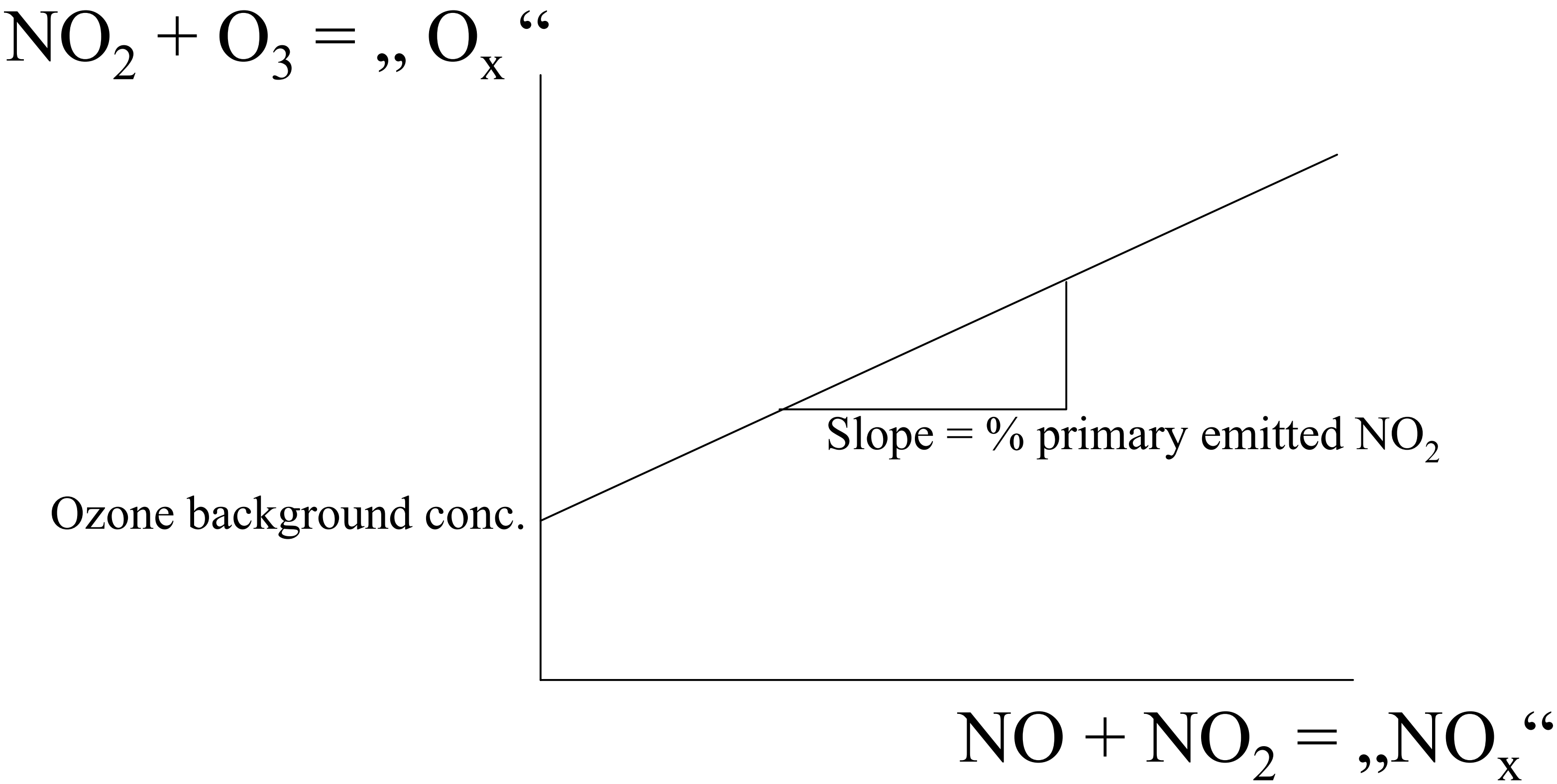
holds as long as there are no other O_3 loss reactions than (6)

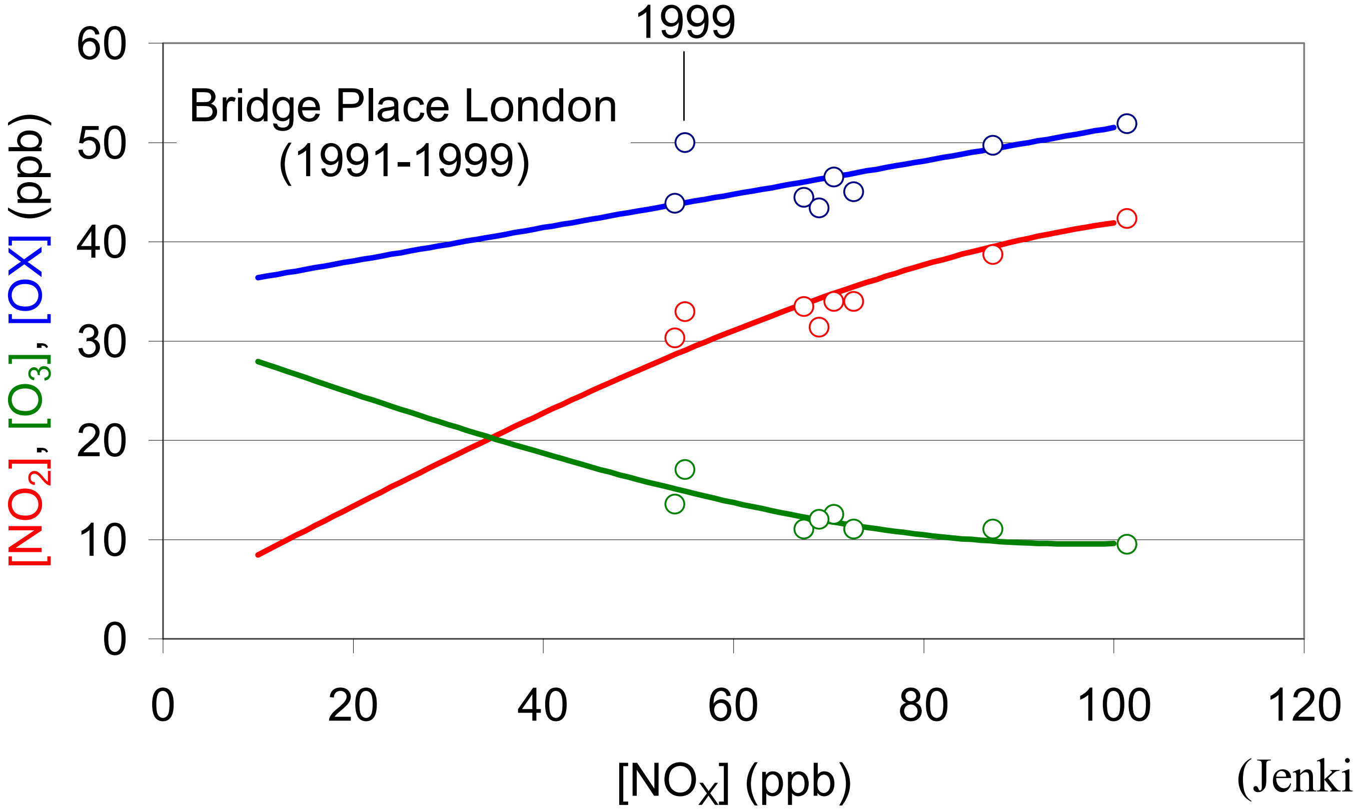
Ozone formation in the troposphere

Ozone depends on the background level, on NO_x and on the ratio NO_2/NO upon emission:

(4) $\mathbf{NO_2 + h\nu \rightarrow NO + O}$

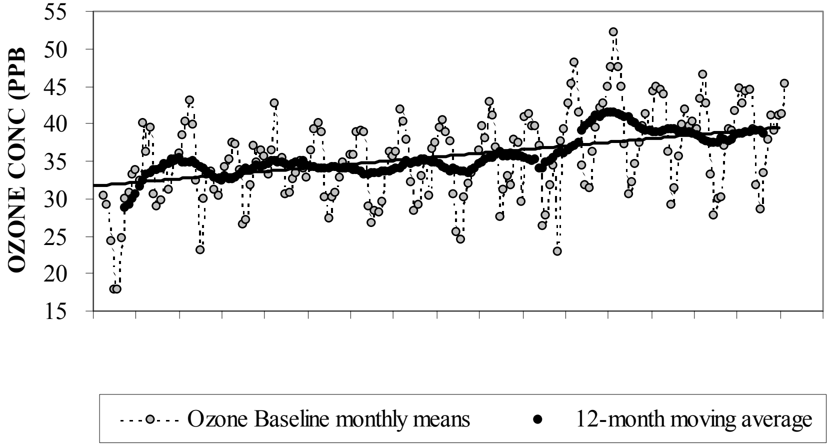
(5) $\mathbf{O + O_2 + M \rightarrow O_3 + M}$





(Jenkin et al 2004)

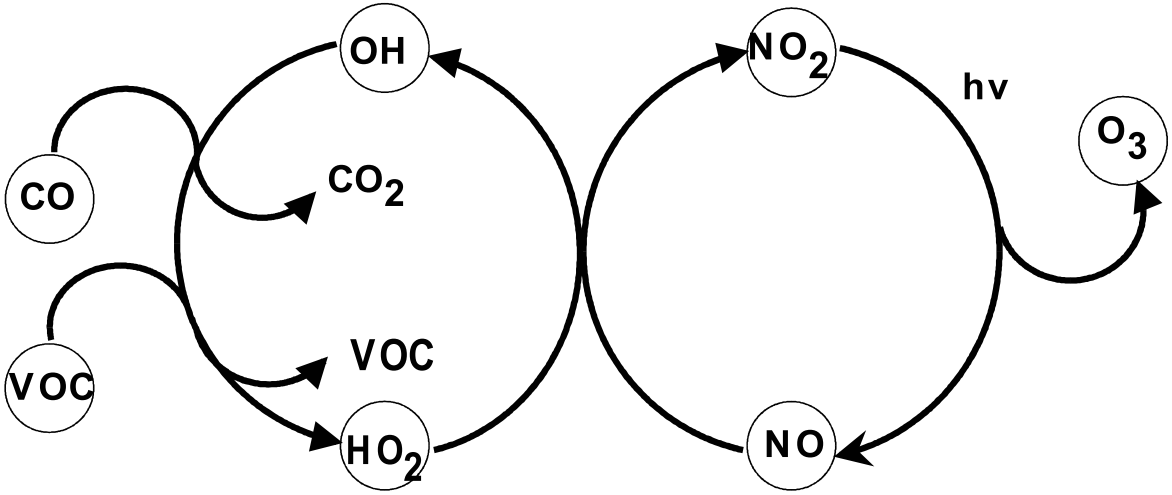
Ozone background at Mace Head, IRL *(Derwent, 2004)*



3.1.2.2 Ozone formation in aliphatic hydrocarbons oxidation

VOC = volatile organic carbon ($p_{sat} > 10^{-2}$ Pa)
(dt: flüchtige Kohlenwasserstoffe)
SOC = semivolatile organic carbon ($p_{sat} = 10^{-6}$-10^{-2} Pa)
(dt: mittelflüchtige Kohlenwasserstoffe)
NOC = non-volatile organic carbon ($p_{sat} < 10^{-6}$ Pa)
(dt: nichtflüchtige Kohlenwasserstoffe)
NMVOC = non-methane volatile organic carbon

2 main pathways: CO or VOC oxidation



(Möller, 2003)

Ozone formation from *hydrocarbons*, HC_x, and NO_x

(1a) $RCH_3 + OH \rightarrow RCH_2\cdot + H_2O$

(1b) $RCH_2\cdot + O_2 + M \rightarrow RCH_2OO\cdot + M$

(2) $RCH_2OO\cdot + NO \rightarrow RCH_2O\cdot + NO_2$

(3) $RCH_2O\cdot + O_2 \rightarrow RCHO + HO_2$

(4) $NO_2 + h\nu\ (< 430\ \mathrm{nm}) \rightarrow NO + O$ (source: NO_x)

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

Sum (1-5):

$RCH_3 + OH + 3\ O_2 \rightarrow RCHO + H_2O + HO_2 + O_3$

= catalyzed by NO and light

Sum (4-5):

$NO_2 + O_2 + h\nu \rightarrow NO + O_3$

(6) $HO_2 + NO \rightarrow OH + NO_2$ **= OH recycled**

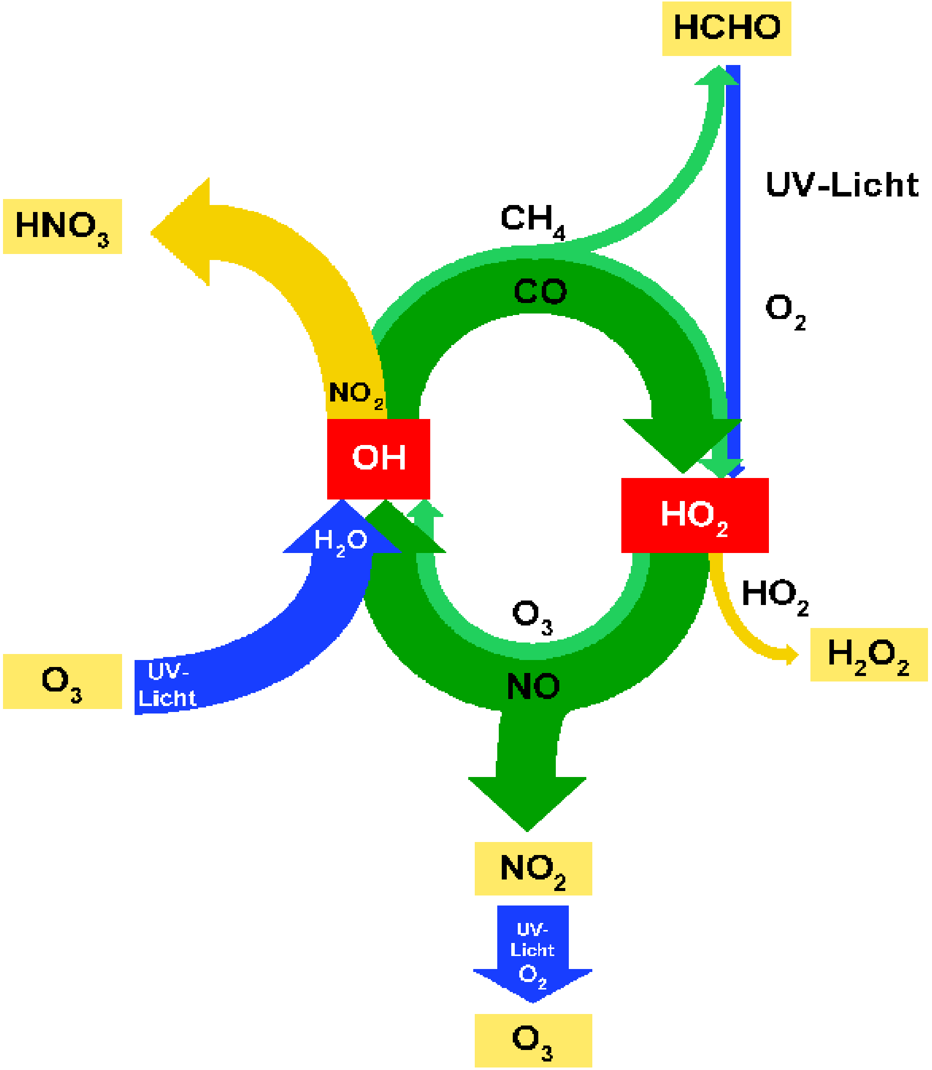
HC_x: alkanes, example methane

(1) $CH_4 + OH \rightarrow CH_3\cdot + H_2O$ (slow: $\tau_{CH4} \approx 8$ a)
(2) $CH_3\cdot + O_2 + M \rightarrow CH_3OO\cdot + M$
(3) $CH_3OO\cdot + NO \rightarrow CH_3O\cdot + NO_2$
(4) $CH_3O\cdot + O_2 \rightarrow HCHO + HO_2$

Sum:
$CH_4 + OH + 2\ O_2 \rightarrow HCHO + H_2O + HO_2$
$NO_2 + O_2 + h\nu \rightarrow NO + O_3$

- Although slow, CH_4 is a major chemical sink for OH (globally one third of OH reacts with CH_4)
- The so formed ozone is the major contribution to the background ozone.
- It increases with increasing methane emissions.

Tropospheric ozone formation from CO, CH_4: other products HCHO, H_2O_2, HNO_3 (radical sink reactions)



(Ehhalt, 1999)

HC_x: alkanes, example n-butane

(1a) $CH_3CH_2CH_2CH_3 + OH \rightarrow CH_3CH{\cdot}CH_2CH_3 + H_2O$ yd=85%

$CH_3CH{\cdot}CH_2CH_3 + O_2 + M \rightarrow CH_3CH(OO{\cdot})CH_2CH_3 + M$

(2a) $CH_3CH(OO{\cdot})CH_2CH_3 + NO \rightarrow CH_3CH(O{\cdot})CH_2CH_3 + NO_2$

(3aa) $CH_3CH(O{\cdot})CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_3 + HO_2$ yd=60%

(3ab) decomposition : $\rightarrow CH_3CO + {\cdot}CH_2CH_3$ yd=40%

${\cdot}CH_2CH_3 + O_2 \rightarrow CH_3CH_2OO{\cdot}$

(4ab) $CH_3CH_2OO{\cdot} + NO \rightarrow CH_3CH_2O{\cdot} + NO_2$

(5ab) $CH_3CH_2O{\cdot} + O_2 \rightarrow CH_3CHO + HO_2$

Sum: $CH_3CH_2CH_2CH_3 + OH + 2.8\ O_2 \rightarrow$

$0.6\ CH_3C(O)CH_2CH_3 + 0.8\ CH_3CHO + H_2O + HO_2 + 1.4\ NO_2$

HC_x: alkanes, example n-butane

(1a) $CH_3CH_2CH_2CH_3 + OH \rightarrow CH_3CH\cdot CH_2CH_3 + H_2O$ yd=85%

$CH_3CH\cdot CH_2CH_3 + O_2 + M \rightarrow CH_3CH(OO\cdot)CH_2CH_3 + M$

(2a) $CH_3CH(OO\cdot)CH_2CH_3 + NO \rightarrow CH_3CH(O\cdot)CH_2CH_3 + NO_2$

(3aa) $CH_3CH(O\cdot)CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_3 + HO_2$ yd=60%

(3ab) decomposition : $\rightarrow CH_3CO + \cdot CH_2CH_3$ yd=40%

$\cdot CH_2CH_3 + O_2 \rightarrow CH_3CH_2OO\cdot$

(4ab) $CH CH OO\cdot + NO \rightarrow CH CH O\cdot + NO$

(1b) $CH_3CH_2CH_2CH_3 + OH \rightarrow \cdot CH_2CH_2CH_2CH_3 + H_2O$ yd=15%

$CH_3CH_2CH_2CH_2\cdot + O_2 + M \rightarrow CH_3CH_2CH_2CH_2OO\cdot + M$

(2b) $CH_3CH_2CH_2CH_2OO\cdot + NO \rightarrow CH_3CH_2CH_2CH_2O\cdot + NO_2$

(3ba) $CH_3CH_2CH_2CH_2O\cdot + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2$ yd=?

(3bb) isomerization: $\rightarrow \cdot CH_2CH_2CH_2CH_2OH + HO$ yd=?

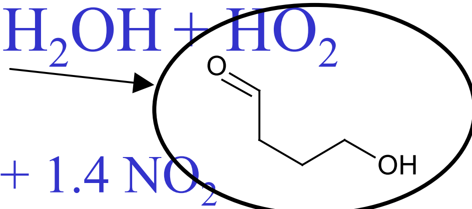
$\cdot CH_2CH_2CH_2CH_2OH + O_2 \rightarrow \cdot OOCH_2CH_2CH_2CH_2OH$

(4bb) $\cdot OOCH_2CH_2CH_2CH_2OH + NO \rightarrow \cdot OCH_2CH_2CH_2CH_2OH + NO_2$

(5bb) $\cdot OCH_2CH_2CH_2CH_2OH + O_2 \rightarrow CH(O)CH_2CH_2CH_2OH + HO_2$

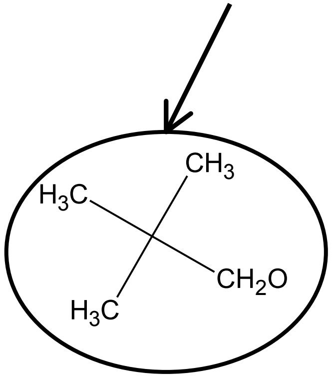
Sum: $CH_3CH_2CH_2CH_3 + OH + 2.8\ O_2 \rightarrow$

$0.6\ CH_3CH_2CH_2CHO + 0.8\ CH_2(OH)CH_2CH_2CHO + H_2O + HO_2 + 1.4\ NO_2$



Alkoxy radicals: reactivity overview

$RO^\bullet$	$k^{(1)}$ (10^3 s^{-1}) decomposition	H-abstraction by O_2	isomerization
$CH_3CH_2CH_2CH_2O^\bullet$	0.6	200	≈ 0
$CH_3CH_2CH_2CHO^\bullet CH_3$	17	40	200
$CH_3CH_2CHO^\bullet(CH_2)_2CH_3$	34	40	200
$CH_3CHO^\bullet(CH_2)_3CH_3$	28	40	2000
$CH_3C(CH_3)_2CH_2O^\bullet$	9.8	24	≈ 80



Nomenclature:
Saturated and unsaturated C chains: alkanes *(dt: Alkane)*, alkenes and alkynes *(dt: Alkene, Alkine)*
Partly oxygenated hydrocarbons: ROH alcohols *(dt: Alkohole)*, carbonyls: RCHO aldehydes *(dt: Aldehyde)* and R_2CO ketones *(dt: Ketone)*, RCOOH and $R(COOH)_2$ mono- and dicarboxylic acids *(dt: Mono- und Dicarbonsäuren)*
Multifunctional partly oxygenated hydrocarbons: RCHOHCHO α-hydroxyaldehydes, RCHOHCOOH α-hydroxyacids, ...

HC_x: alkene OH reaction, example propene

Alkenes are more reactive toward OH than alkanes: $k \leq 10^{-10}$ cm^3 $molec^{-1}$ s^{-1}

The higher substituted radical is more stable, hence, formed preferentially:

(1a) $CH_3CH{=}CH_2 + OH \rightarrow CH_3CH{\cdot}CH_2OH$ addition, yd=66%

$CH_3CH{\cdot}CH_2OH + O_2 + M \rightarrow CH_3CH(OO{\cdot})CH_2OH + M$

(2a) $CH_3CH(OO{\cdot})CH_2OH + NO \rightarrow CH_3CH(O{\cdot})CH_2OH + NO_2$

(3aa) $CH_3CH(O{\cdot})CH_2OH + O_2 \rightarrow CH_3C(O)CH_2OH + HO_2$ yd=3%

(3ab) decomposition: $\rightarrow CH_3C{\cdot}O + {\cdot}CH_2OH$ yd=97%

(4ab) ${\cdot}CH_2OH + O_2 \rightarrow HCHO + HO_2$

(1b) $CH_3CH{=}CH_2 + OH \rightarrow CH_3CH(OH)CH_2{\cdot}$ addition, yd=34%

$CH_3CH(OH)CH_2{\cdot} + O_2 + M \rightarrow CH_3CH(OH)CH_2(OO{\cdot}) + M$

(2b) $CH_3CH(OH)CH_2(OO{\cdot}) + NO \rightarrow CH_3CH(OH)CH_2O{\cdot} + NO_2$

(3ba) $CH_3CH(OH)CH_2O{\cdot} + O_2 \rightarrow CH_3CH(OH)CHO + HO_2$ yd=90%

(3bb) decomposition : $\rightarrow CH_3CH(OH){\cdot} + HCHO$ yd=10%

(4bb) $CH_3CH(OH){\cdot} + O_2 \rightarrow CH_3CHO + HO_2$

Sum: $CH_3CH{=}CH_2 + OH + 2.8\ O_2 \rightarrow 0.02\ CH_3C(O)CH_2OH + 0.65\ HCHO + 0.3\ CH_3CH(OH)CHO + 0.03\ CH_3CHO + H_2O + HO_2 + NO_2$

HC_x: alkene OH reaction

- Most alkenes react with OH addition to the double bond (positive p dependence of k_{OH}); only for the small alkenes the addition complex does not react further.
- H abstraction is more likely for large and branched alkenes.
- After the O_2 addition step ($\rightarrow$ ROO·), decomposition is the most probable path for $\leq C_4$ while isomerization dominates for $> C_4$
  (yields 0.04 for C_4 but 0.6 for C_8; Kwok et al., 1996)

Example n-butene:

(1) $CH_3CH_2CH{=}CH_2 + OH \rightarrow CH_3CH_2CH(OH)CH_2\cdot$

$CH_3CH_2CH(OH)CH_2\cdot + O_2 + M \rightarrow CH_3CH_2CH(OH)CH_2OO\cdot + M$

(2) $CH_3CH_2CH(OH)CH_2OO\cdot + NO \rightarrow CH_3CH_2CH(OH)CH_2O\cdot + NO_2$

(3) isomeriz.: $CH_3CH_2CH(OH)CH_2O\cdot \rightarrow \cdot CH_2CH_2CH(OH)CH_2OH$

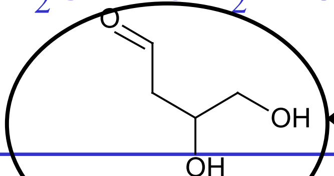
(4) $\cdot CH_2CH_2CH(OH)CH_2OH + O_2 \rightarrow \cdot OOCH_2CH_2CH(OH)CH_2OH$

(5) $\cdot OOCH_2CH_2CH(OH)CH_2OH + NO \rightarrow \cdot OCH_2CH_2CH(OH)CH_2OH + NO_2$

(6) $\cdot OCH_2CH_2CH(OH)CH_2OH + O_2 \rightarrow O{=}CHCH_2CH(OH)CH_2OH + HO_2$

Sum: $CH_3CH_2CH{=}CH_2 + OH + 2\ NO + 3\ O_2 \rightarrow$

$O{=}CHCH_2CH(OH)CH_2OH + H_2O + HO_2 + 2\ NO_2$



←←← dihydroxycarbonyl

HC_x: alkene OH reaction

Example isoprene (= 2-methylbutadiene):

1 or 2 addition 66%

(1a) $CH_2{=}C(CH_3)CH{=}CH_2 + OH$ → $HOCH_2C{\cdot}(CH_3)CH{=}CH_2$

→ $\cdot CH_2C(OH)(CH_3)C{=}CH_2$

$+ O_2 + NO$

→ → →

(4aa) decomposition: → HCHO + $CH_3COCH{=}CH_2$ yd ≈ 30%

methyl vinyl ketone

(4ab) isomerization: → $HC(O)C(CH_3)CH{=}CHOH$ yd ≈ 5%

γ-hydroxy-(2-methyl)butenal

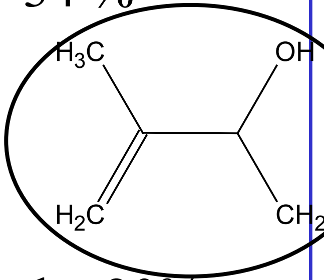
3 or 4 addition 34 %

(1b) $CH_2{=}C(CH_3)CH{=}CH_2 + OH$ → $CH_2{=}C(CH_3)CH{\cdot}CH_2OH$

→ $CH_2{=}C(CH_3)CHOHCH_2{\cdot}$

$+ O_2 + NO$

→ → →



(4ba) decomposition: → HCHO + $CH_2{=}C(CH_3)CHO$ yd ≈ 20%

methacrolein

(4bb) 5-ring closure: → $(C_4H_3O)(CH_3)$ yd < 5%

3-methylfuran

HC_x: OH reactivity, products overview

HC_x	k_{OH} $10^{-12}cm^3$ $molec^{-1}s^{-1}$ (298 K)	oxygenated intermediates formed	No. of NO converted		
			initial	from carbonyls	total
Alkanes:					
CH_4	0.006	HCHO	1	≈0.8	≈1.8
CH_3CH_3	0.25	CH_3CHO	2	4	6
$CH_3CH_2CH_3$	1.1	HCHO, CH_3CHO, CH_3COCH_3	3	5	8
$CH_3CH_2CH_2CH_3$	2.4	2 CH_3CHO	3	8	11
$CH_3CH(CH_3)CH_3$	2.2	HCHO, CH_3COCH_3	3	5	8
$CH_3(CH_2)_3CH_3$	4.0	HCHO, CH_3CHO, CH_3CH_2CHO, $CH_3(CH_2)\ _2CHO$	3	11	14
Alkenes:					
CH_2=CH_2	8.5	2 HCHO	2	2	4
CH_2=$CHCH_3$	26	HCHO, CH_3CHO	2	5	7
CH_2=$CHCH_2CH_3$	31	HCHO, CH_3CH_2CHO	2	8	10
cis-$CH_3CHCHCH_3$	56	2 CH_3CHO	2	8	10
trans-$CH_3CHCHCH_3$	64	2 CH_3CHO	2	8	10
CH_2=$C(CH_3)CH_3$	51	HCHO, CH_3COCH_3	2	5	7

Distributions - spatial

Alkanes, alkenes (pptv) at the ground, monitoring and campaign data

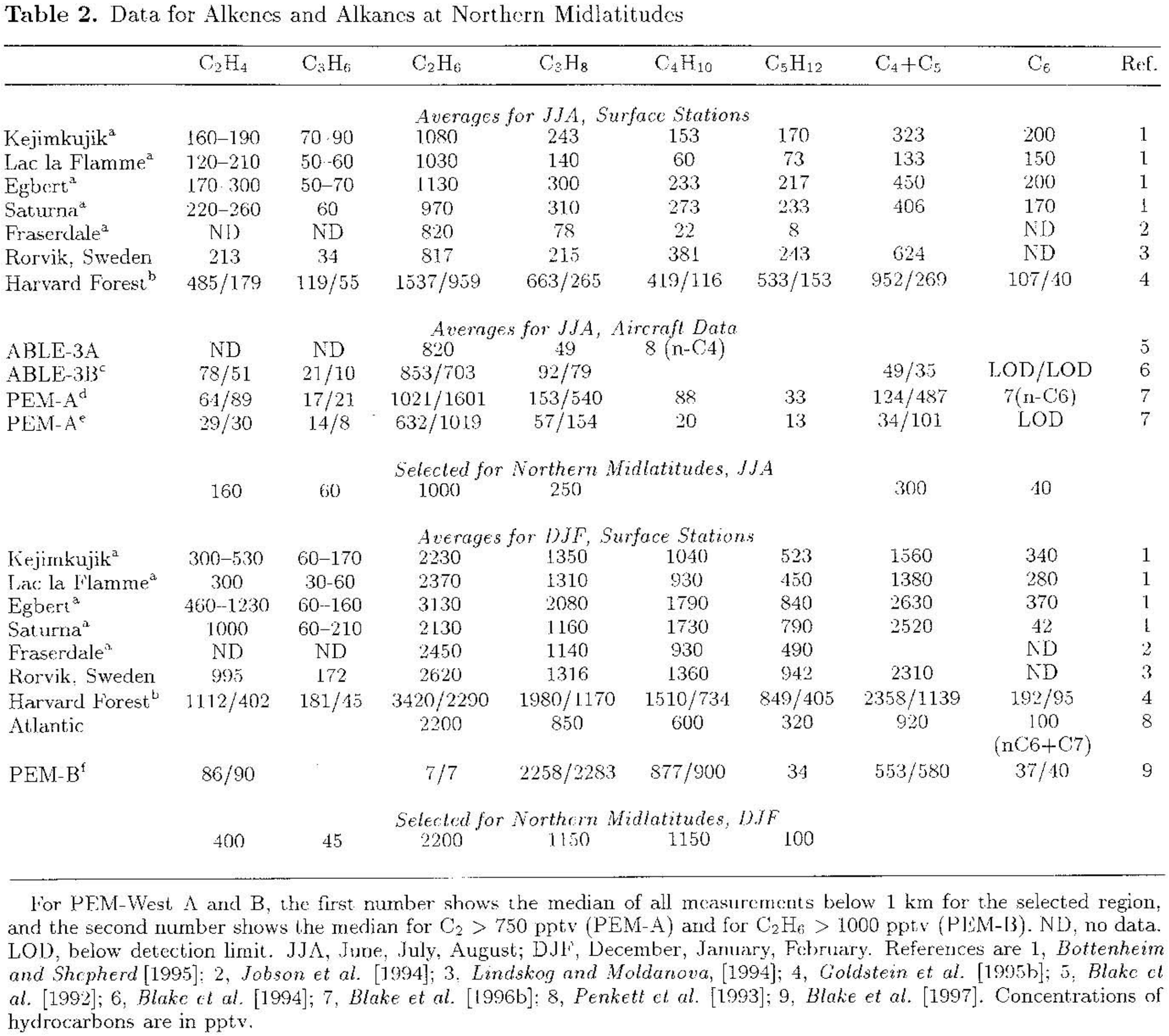


Table 2. Data for Alkenes and Alkanes at Northern Midlatitudes

	C_2H_4	C_3H_6	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_4+C_5	C_6	Ref.
			Averages for JJA, Surface Stations						
Kejimkujik[a]	160–190	70–90	1080	243	153	170	323	200	1
Lac la Flamme[a]	120–210	50–60	1030	140	60	73	133	150	1
Egbert[a]	170–300	50–70	1130	300	233	217	450	200	1
Saturna[a]	220–260	60	970	310	273	233	406	170	1
Fraserdale[a]	ND	ND	820	78	22	8		ND	2
Rorvik, Sweden	213	34	817	215	381	243	624	ND	3
Harvard Forest[b]	485/179	119/55	1537/959	663/265	419/116	533/153	952/269	107/40	4
			Averages for JJA, Aircraft Data						
ABLE-3A	ND	ND	820	49	8 (n-C4)				5
ABLE-3B[c]	78/51	21/10	853/703	92/79			49/35	LOD/LOD	6
PEM-A[d]	64/89	17/21	1021/1601	153/540	88	33	124/487	7(n-C6)	7
PEM-A[e]	29/30	14/8	632/1019	57/154	20	13	34/101	LOD	7
			Selected for Northern Midlatitudes, JJA						
	160	60	1000	250			300	40	
			Averages for DJF, Surface Stations						
Kejimkujik[a]	300–530	60–170	2230	1350	1040	523	1560	340	1
Lac la Flamme[a]	300	30-60	2370	1310	930	450	1380	280	1
Egbert[a]	460–1230	60–160	3130	2080	1790	840	2630	370	1
Saturna[a]	1000	60–210	2130	1160	1730	790	2520	42	1
Fraserdale[a]	ND	ND	2450	1140	930	490		ND	2
Rorvik, Sweden	995	172	2620	1316	1360	942	2310	ND	3
Harvard Forest[b]	1112/402	181/45	3420/2290	1980/1170	1510/734	849/405	2358/1139	192/95	4
Atlantic			2200	850	600	320	920	100 (nC6+C7)	8
PEM-B[f]	86/90		7/7	2258/2283	877/900	34	553/580	37/40	9
			Selected for Northern Midlatitudes, DJF						
	400	45	2200	1150	1150	100			

For PEM-West A and B, the first number shows the median of all measurements below 1 km for the selected region, and the second number shows the median for $C_2 > 750$ pptv (PEM-A) and for $C_2H_6 > 1000$ pptv (PEM-B). ND, no data. LOD, below detection limit. JJA, June, July, August; DJF, December, January, February. References are 1, *Bottenheim and Shepherd* [1995]; 2, *Jobson et al.* [1994]; 3, *Lindskog and Moldanova*, [1994]; 4, *Goldstein et al.* [1995b]; 5, *Blake et al.* [1992]; 6, *Blake et al.* [1994]; 7, *Blake et al.* [1996b]; 8, *Penkett et al.* [1993]; 9, *Blake et al.* [1997]. Concentrations of hydrocarbons are in pptv.

(Spivakovsky et al., 2000)

Further chemical fate of HC_x: aldehydes degradation, example CH_3CHO

Aldehydes are more reactive towards OH than alkanes

(1) $CH_3CHO + OH \rightarrow CH_3CO\cdot + H_2O$ $k=16x10^{-12}\ cm^3molec^{-1}s^{-1}$

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

(2) $CH_3C(O)OO\cdot + NO \rightarrow [CH_3C(O)O\cdot] \rightarrow CH_3\cdot + CO_2 + NO_2$

(3) $CH_3\cdot + O_2 \rightarrow CH_3OO\cdot$

(4) $CH_3OO\cdot + NO \rightarrow CH_3O\cdot + NO_2$

(5) $CH_3O\cdot + O_2$ [α-hydroxyl radical $\cdot CH_2OH$?]$\rightarrow HCHO + HO_2$

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

Sum: $CH_3CHO + 3\ NO + 3\ O_2 \rightarrow HCHO + 3\ NO_2 + CO_2 + H_2O$

OH is regenerated

3 O_3 are formed

General (5) $RCH_2O\cdot + O_2 \rightarrow RCHO + HO_2$

Time scale: 1 sunny day is not long enough for all aldehydes to react

→ Most of the ozone is formed the following day

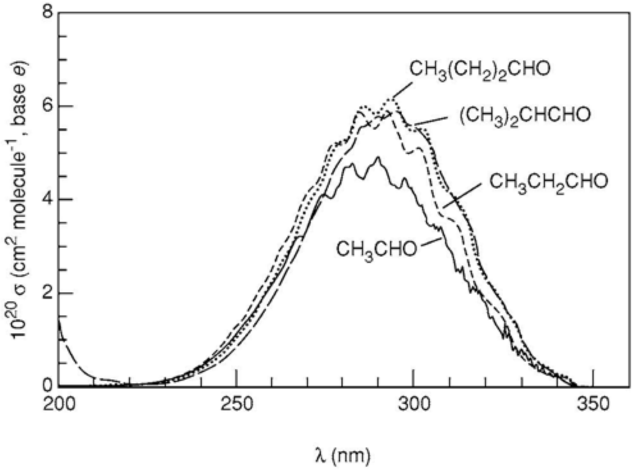
Further oxygenation lowers the partial pressure such that condensable products are formed → reduced ozone yield

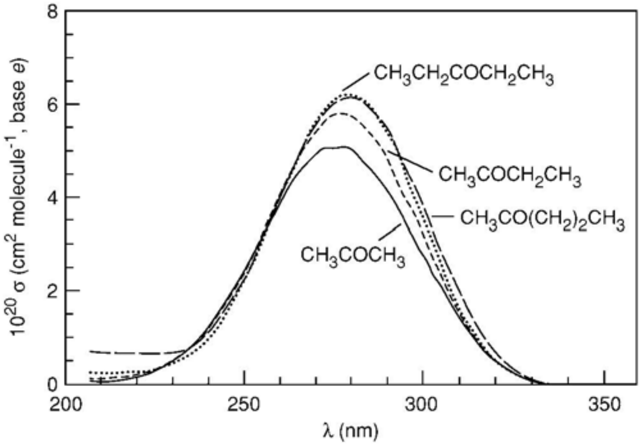
Photolysis of aldehydes and ketones

Aldehydes and ketones may undergo photolysis

$CH_3CHO + h\nu\ (\leq 340\ \text{nm}) \rightarrow CH_3^{\cdot} + HCO^{\cdot}$

$CH_3C(O)CH_3 + h\nu\ (\leq 330\ \text{nm}) \rightarrow CH_3^{\cdot} + CH_3C^{\cdot}O$





(Martinez et al., 1992)

OH reactions of other oxygenated HC_x

Alcohols, example ethanol (3 options, 1a-c):

The alkyl hydrogen is predominantly abstracted:

(1a) $CH_3CH_2OH + OH \rightarrow CH_3CH{\cdot}OH + H_2O$ 90%

(1b) $\rightarrow CH_3CH_2O{\cdot} + H_2O$ 5%

(1c) $\rightarrow {\cdot}CH_2CH_2OH + H_2O$ 5%

$k=3.2\text{x}10^{-12}$ $cm^3molec^{-1}s^{-1}$

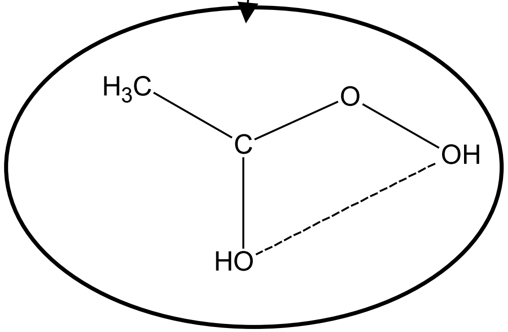
Carboxylic acids, example acetic acid (= ethanoic acid):

OH is first added, then the carboxylic H is abstracted:

(1) $CH_3COOH + OH \rightarrow [CH_3C{\cdot}(OH)OOH] \rightarrow$ [5-ring intermediate]

(2) $\rightarrow CH_3COO{\cdot} + H_2O$

$k=0.8\text{x}10^{-12}$ $cm^3molec^{-1}s^{-1}$



Chain termination (and propagation)

Fate of $ROO^{\cdot}$ (5 options, 3a-e)

(3a) $ROO^{\cdot} + HO_2 \rightarrow ROOH + O_2$

(3b) $\rightarrow ROH + O_3$

(3c) $\rightarrow RO^{\cdot} + OH + O_2$

(3d) $\rightarrow R'CHO + H_2O + O_2$

(3e) $+ ROO^{\cdot} \rightarrow$ *various classes of compounds*

Radicals can be recycled via (3c). This channel is significant for R's containing a carbonyl group in α or β position. This OH source may be significant for low NO_x conditions or aged air masses (high carbonyl fractions).

Branching yields (%)

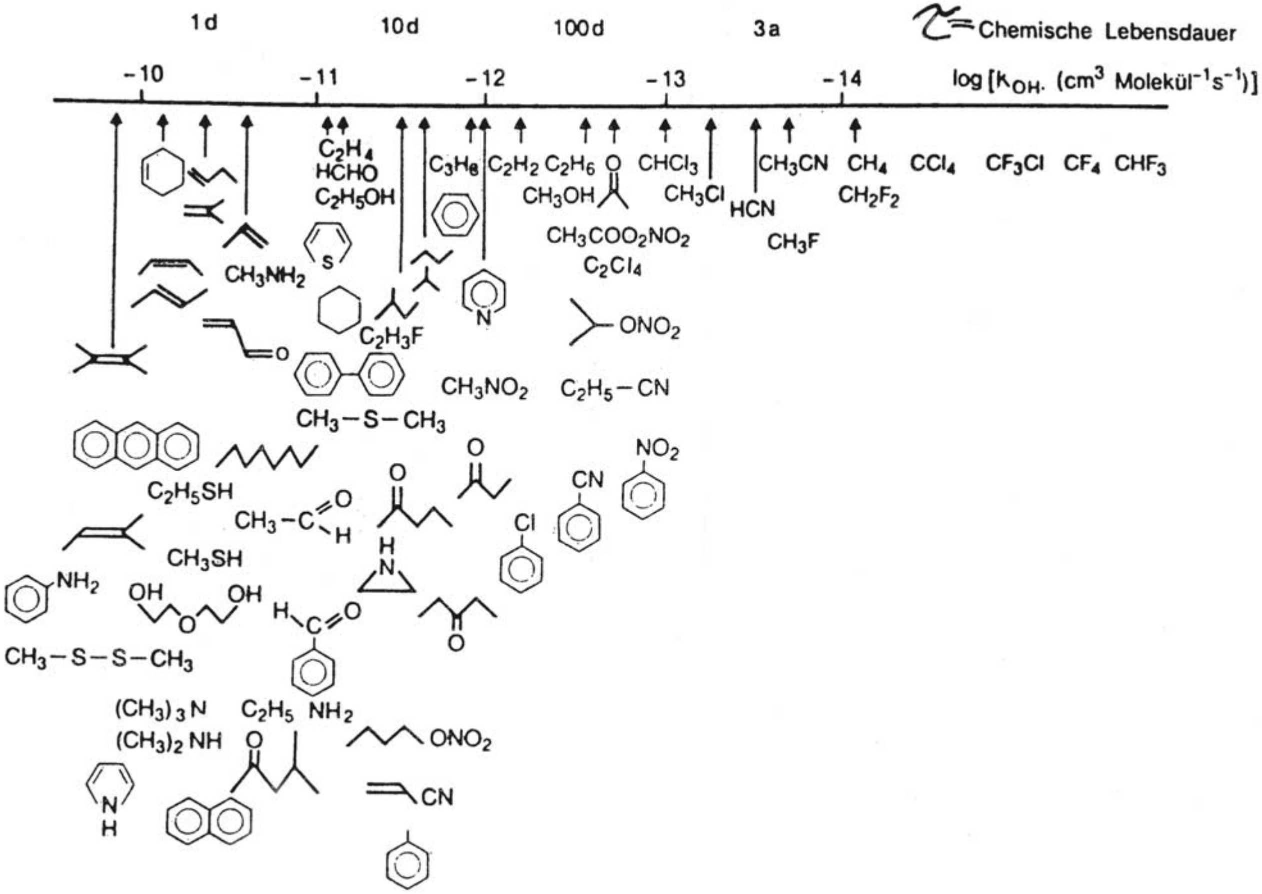
$ROO^{\cdot}$	3a	3b	3c	3d	
$CH_3CH_2OO^{\cdot}$	> 0.93	0	0	0	
$CH_3C(O)OO^{\cdot}$	0.4	0.2	0.4	0	→ high OH yield
$CH_3C(O)CH_2OO^{\cdot}$	0.33	0	0.67	0	→ high OH yield

(Hasson et al., 2004)

HC_x, oxygenated, halogenated HC_x, and hetero atom organics OH reactivity overview

$$-\frac{dc_x}{dt} = k_{OH}\, c_{OH}\, c_x = \frac{c_x}{\tau}$$

Chemical residence time of organic substances in the atmosphere



3.1.2.3 Ozone formation in aromatic hydrocarbons oxidation

HC_x: Aromatics OH initiated chemistry

- Aromatic hydrocarbons have anthropogenic sources
- they contribute 20-30% to total NMVOC in urban air
- degradation: → oxygenated C_4 (e.g. *cis/trans*-HOOCCH=CHCOOH) and C_2 products (e.g. HOOCCOOH)
- high ozone formation potential – incompletely understood

Nomenclature:

Aromatic hydrocarbons *(dt: aromatische Kohlenwasserstoffe)*:

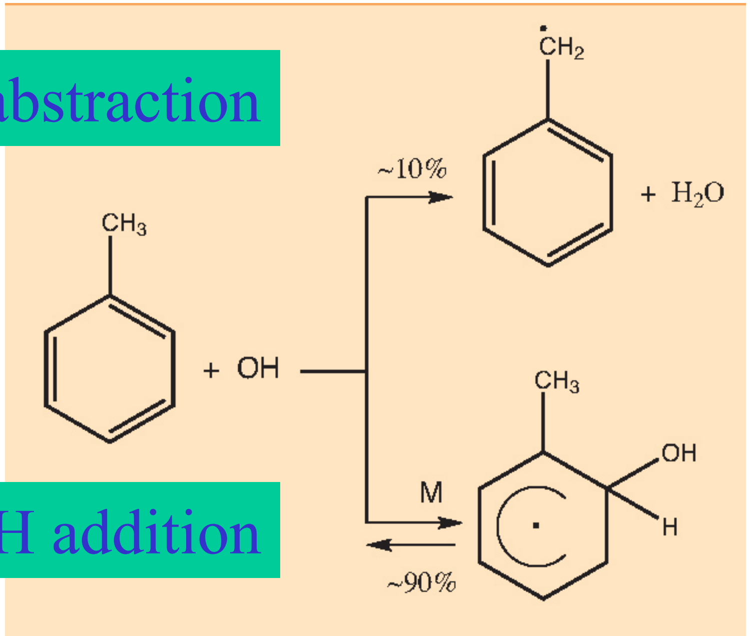
benzene $C_6H_6 = \phi H$ *(dt.: Benzol)*

Substituted: toluene ϕCH_3 *(dt.: Toluol)*, *o-, m-, p*-xylene *(dt.: Xylol)* $\phi(CH_3)_2$, phenol ϕOH *(dt.: Phenol)*, ...

Hetero atom aromatic hydrocarbons: furan C_4H_4O, pyridin C_5H_5N...

Polycyclic aromatic hydrocarbons (PAH) *(dt: mehrkernige oder polyzyklische aromatische Kohlenwasserstoffe)*: naphthalene *(dt.: Naphthalin)*, ...

HC$_x$: Aromatics OH initiated chemistry, example toluene



1a. H abstraction

1b. OH addition

(1a ff) $\phi CH_3 + OH \xrightarrow{-H_2O} \phi CH_2\cdot \xrightarrow{+O_2} \phi CH_2OO\cdot \xrightarrow{+NO} \phi CH_2O\cdot \xrightarrow{+O_2} \phi CHO$

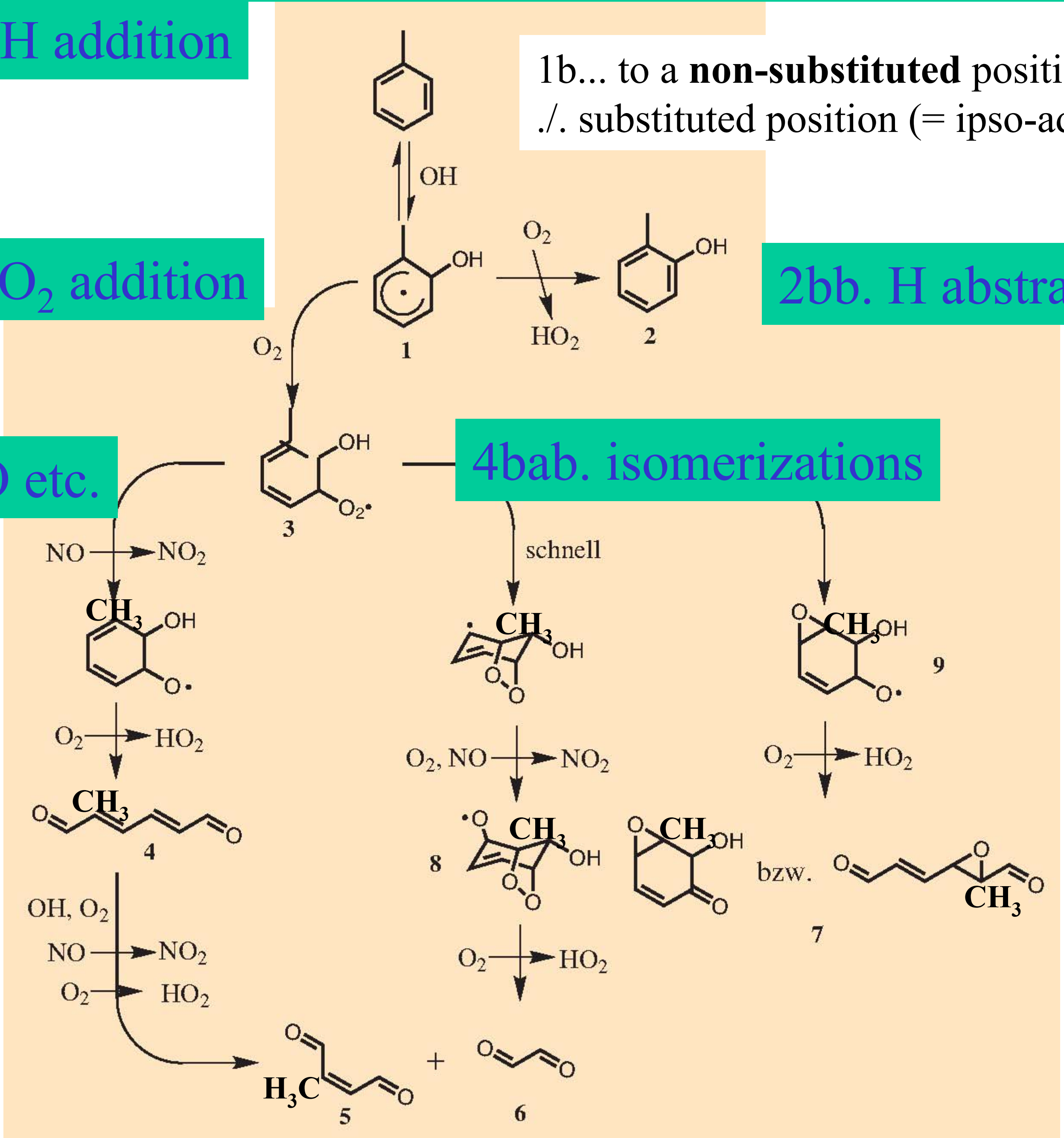
$+NO_2 \qquad\qquad +O_2$

(1a ff) $\rightarrow \phi CH_2ONO_2$

(1b ff) $\phi CH_3 + OH = \phi\cdot(OH)CH_3 \xrightarrow{+O_2} \phi CH_3(OH)(OO\cdot) \rightarrow \rightarrow \rightarrow$

HC_x: Aromatics OH initiated chemistry, example toluene (2) – 1b. OH addition

1b... to a **non-substituted** position
./. substituted position (= ipso-addition) < 10%



2ba. O_2 addition

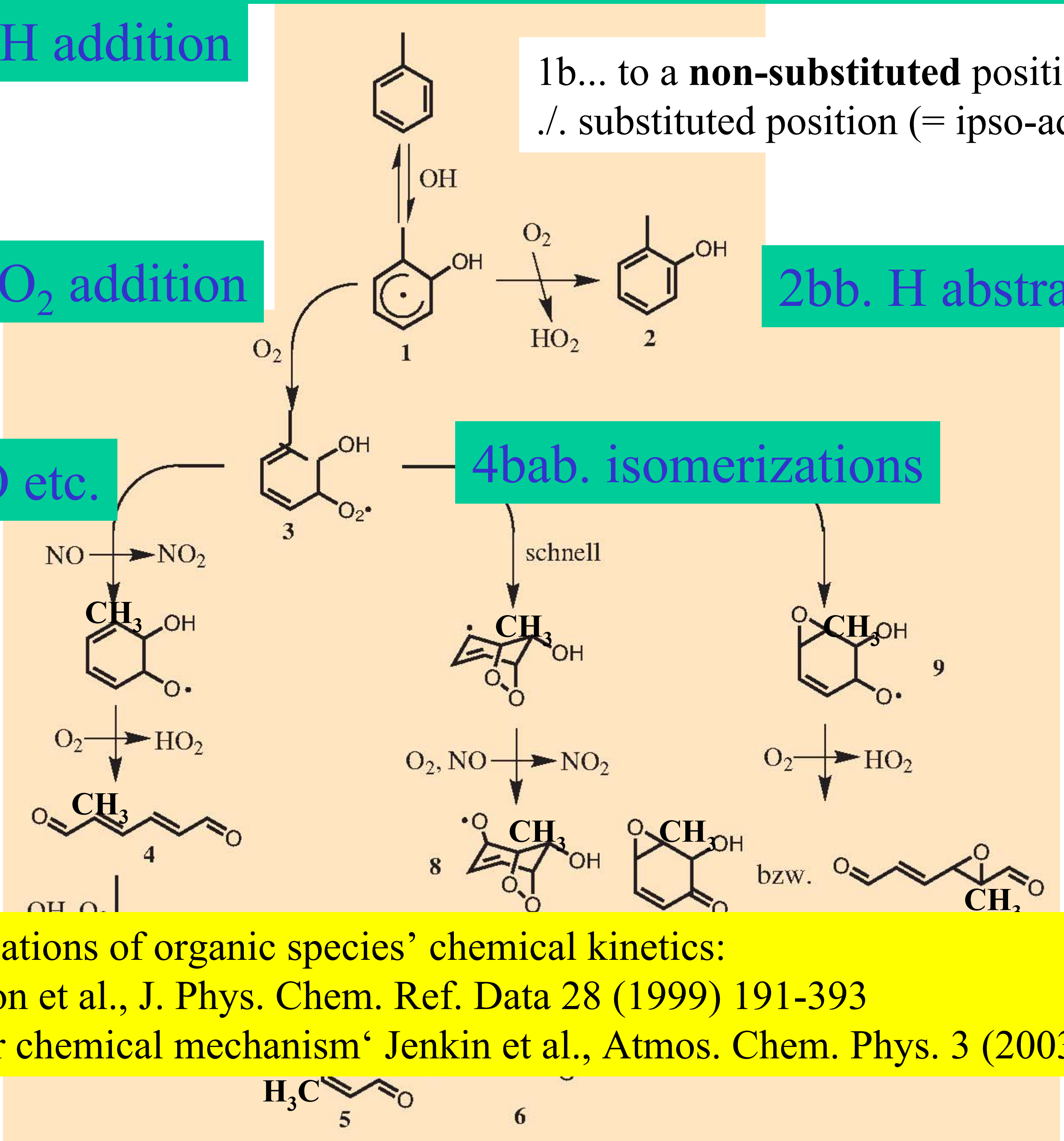
2bb. H abstraction by O_2

3baa. NO etc.

4bab. isomerizations

HC_x: Aromatics OH initiated chemistry, example toluene (2) – 1b. OH addition

1b... to a **non-substituted** position
./. substituted position (= ipso-addition) < 10%



2ba. O_2 addition

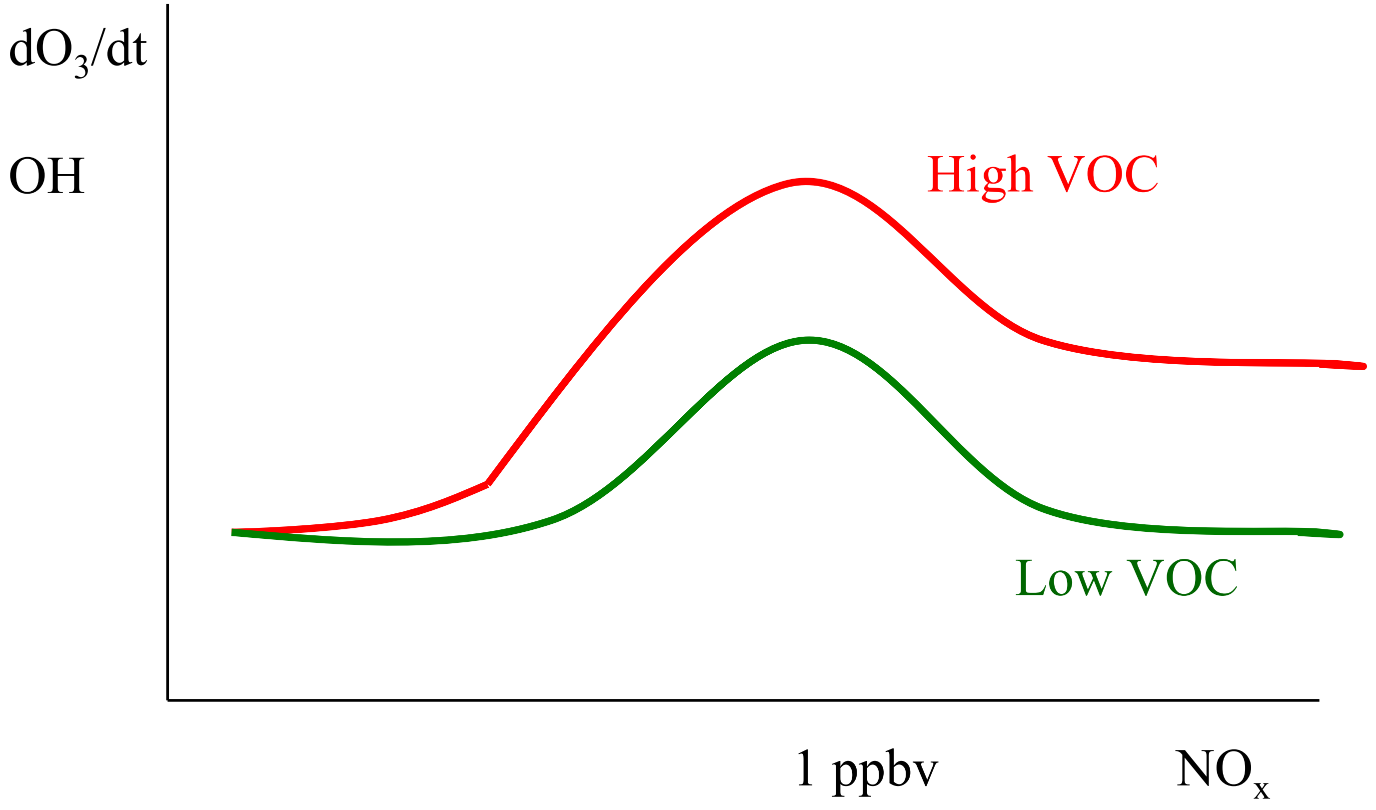
2bb. H abstraction by O_2

3baa. NO etc.

4bab. isomerizations

Compilations of organic species' chemical kinetics:
Atkinson et al., J. Phys. Chem. Ref. Data 28 (1999) 191-393
‚Master chemical mechanism' Jenkin et al., Atmos. Chem. Phys. 3 (2003) 161-193

Tropospheric ozone:
Dependence on NO_x



(FZJ-ICG3, 1998; Brune et al., 2000)

Ozone formation efficiency of various hydrocarbons

Characterisation of VOCs according to their POCP
photochemical ozone creation potential:
POCP : = $\Delta m_{O3} / \Delta F_{VOCi}$
under defined conditions (ozone formation during several days, NO_x poor) *(Carter, 1994; EK, 1994)*

	POCP
C_2H_4	100
CH_4	0.7
C_6H_6	18.9
CH_3OH	12.3
HCHO	42.1

3.1.3 Radical sources

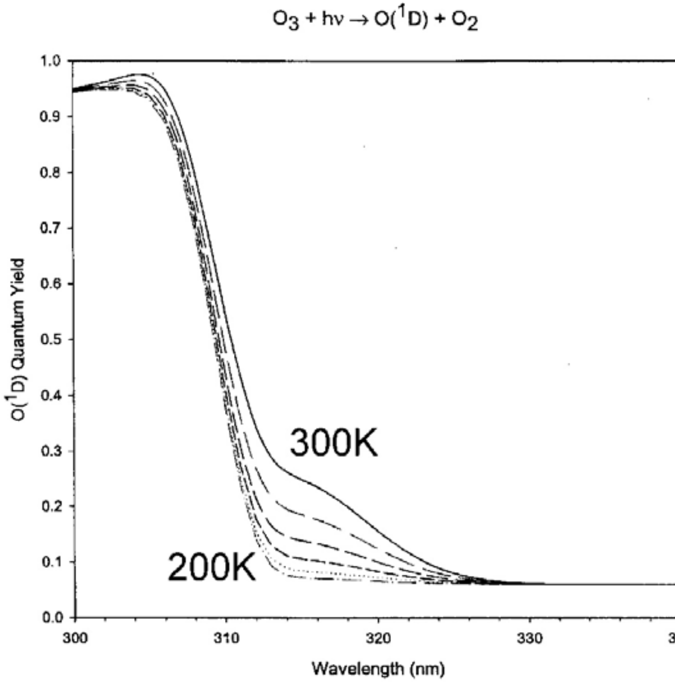
3.1.3.1 Radical source ozone

(1a) $O_3 + h\nu$ (320-800 nm) $\rightarrow O_2 + O(^3P)$

(-1a) $O(^3P) + O_2 \rightarrow O_3$ net effect: none

(1b) $O_3 + h\nu$ (310-336 nm) $\rightarrow O_2 + O(^1D)$

quantum yield
$\phi(T,\lambda)$ = 5-25%:



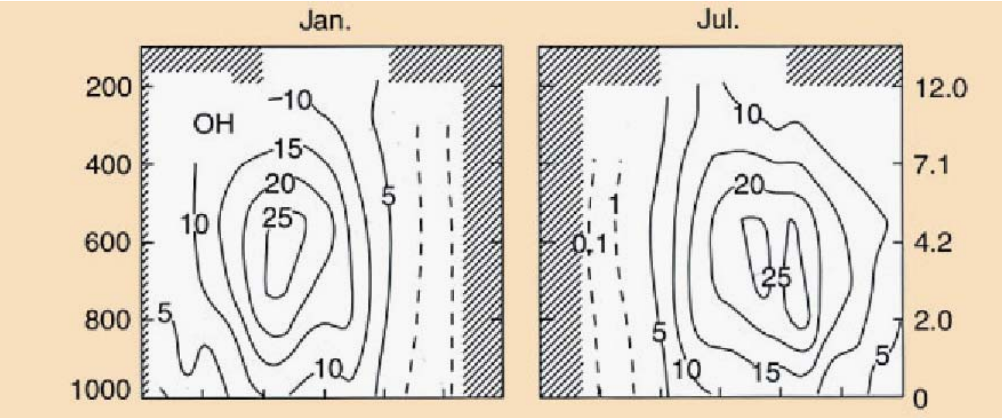
(2ba) + M $\rightarrow O(^3P)$ + M k=26x10^{-12} cm^3/molec/s (N_2)
k=40x10^{-12} cm^3/molec/s (O_2)

net effect: none

(2bb) $O(^1D)$ + $H_2O \rightarrow$ 2 OH k=220x10^{-12} cm^3/molec/s

net effect: **radical formation**

Radical distributions – spatial: OH



Zonally and monthly averaged data
(10^5 molec cm^{-3}; Spivakovsky et al., 2000)

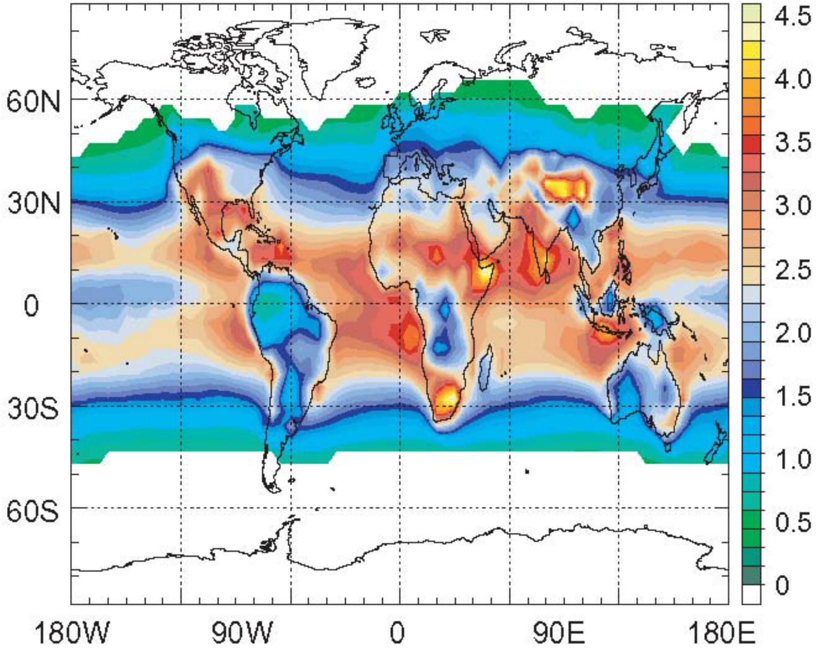


Fig. 1. Annual mean OH concentrations near the earth's surface, calculated with a chemistry-transport model (Lelieveld et al., 2002). The units are 10^6 radicals/cm^3. These results refer to OH in the

where mean OH con-

l et al., 2003)

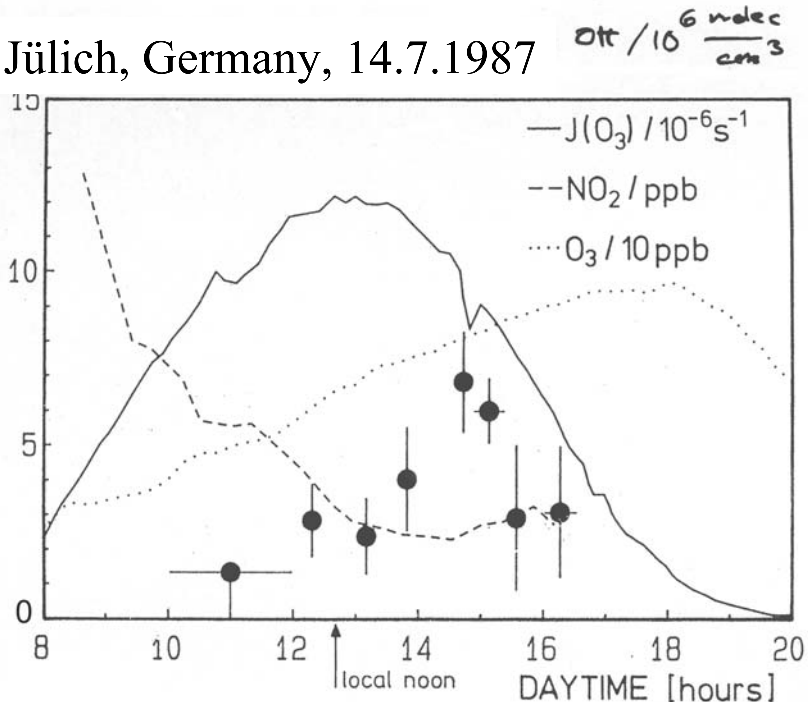
Common acronyms for hydrogen compounds:

$HO_x = HO + HO_2 + H\cdot + CH_3O\cdot + CH_3OO\cdot + HOCH_2OO\cdot$

$\text{Odd-H} = HO_x + 2\ H_2O_2 + 2\ CH_3OOH + HNO_2 + HNO_4$

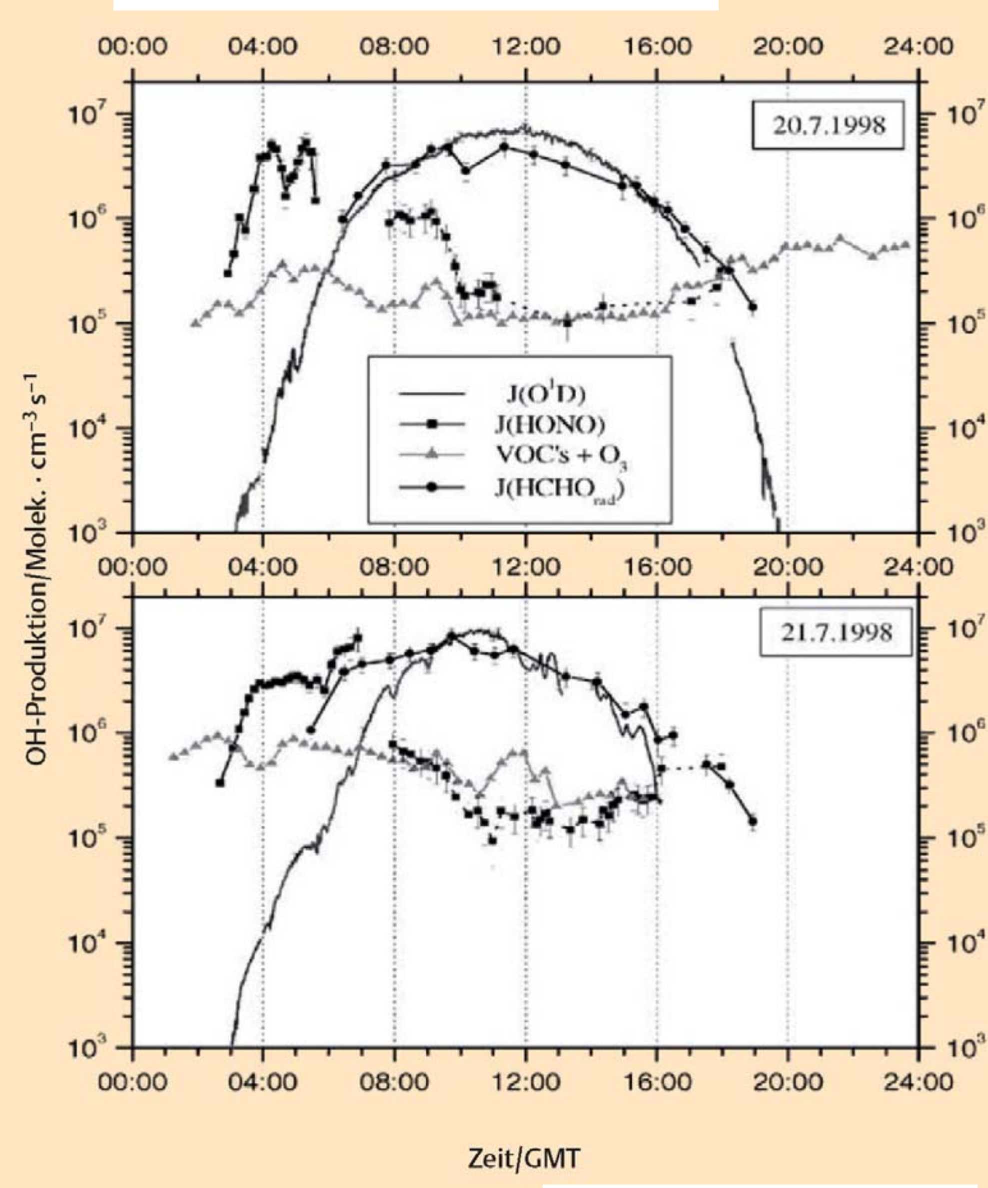
Radical distributions - temporal

Jülich, Germany, 14.7.1987



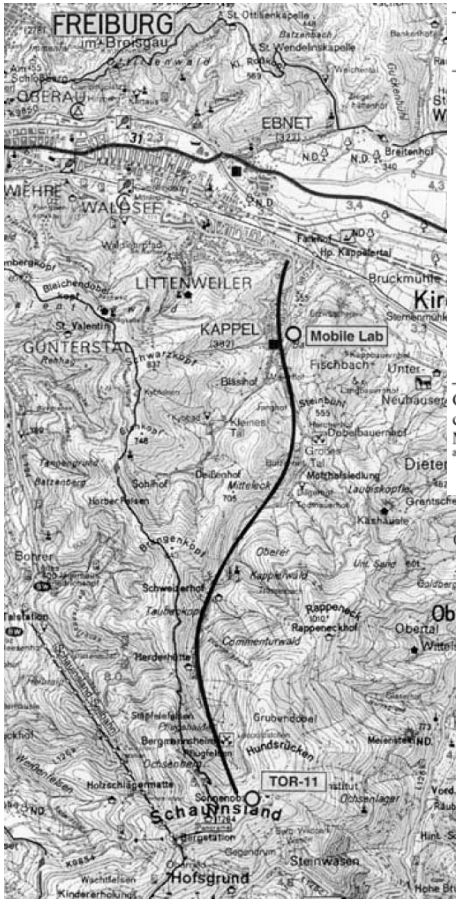
(Dorn et al., 1988)

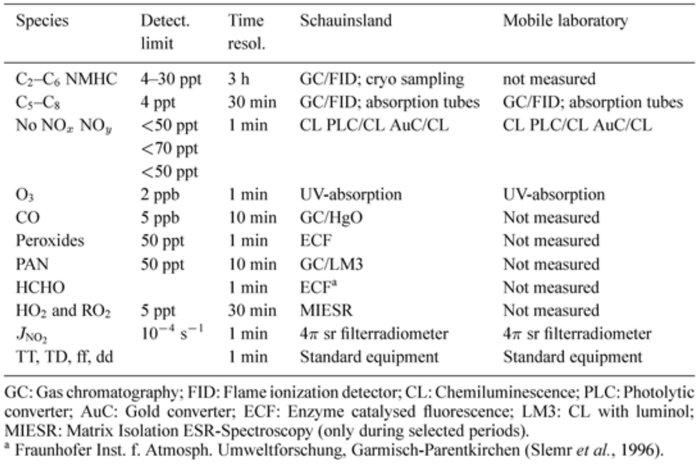
Berlin, Germany, 20.-21.7.98



(Barnes et al., 2007)

Measuring c_{HCx} decay: Indirect determination of c_{OH}





Species	Detect. limit	Time resol.	Schauinsland	Mobile laboratory
C_2–C_6 NMHC	4–30 ppt	3 h	GC/FID; cryo sampling	not measured
C_5–C_8	4 ppt	30 min	GC/FID; absorption tubes	GC/FID; absorption tubes
No NO_x NO_y	<50 ppt <70 ppt <50 ppt	1 min	CL PLC/CL AuC/CL	CL PLC/CL AuC/CL
O_3	2 ppb	1 min	UV-absorption	UV-absorption
CO	5 ppb	10 min	GC/HgO	Not measured
Peroxides	50 ppt	1 min	ECF	Not measured
PAN	50 ppt	10 min	GC/LM3	Not measured
HCHO		1 min	ECF[a]	Not measured
HO_2 and RO_2	5 ppt	30 min	MIESR	Not measured
J_{NO_2}	10^{-4} s^{-1}	1 min	4π sr filterradiometer	4π sr filterradiometer
TT, TD, ff, dd		1 min	Standard equipment	Standard equipment

GC: Gas chromatography; FID: Flame ionization detector; CL: Chemiluminescence; PLC: Photolytic converter; AuC: Gold converter; ECF: Enzyme catalysed fluorescence; LM3: CL with luminol; MIESR: Matrix Isolation ESR-Spectroscopy (only during selected periods).

[a] Fraunhofer Inst. f. Atmosph. Umweltforschung, Garmisch-Parentkirchen (Slemr *et al.*, 1996).

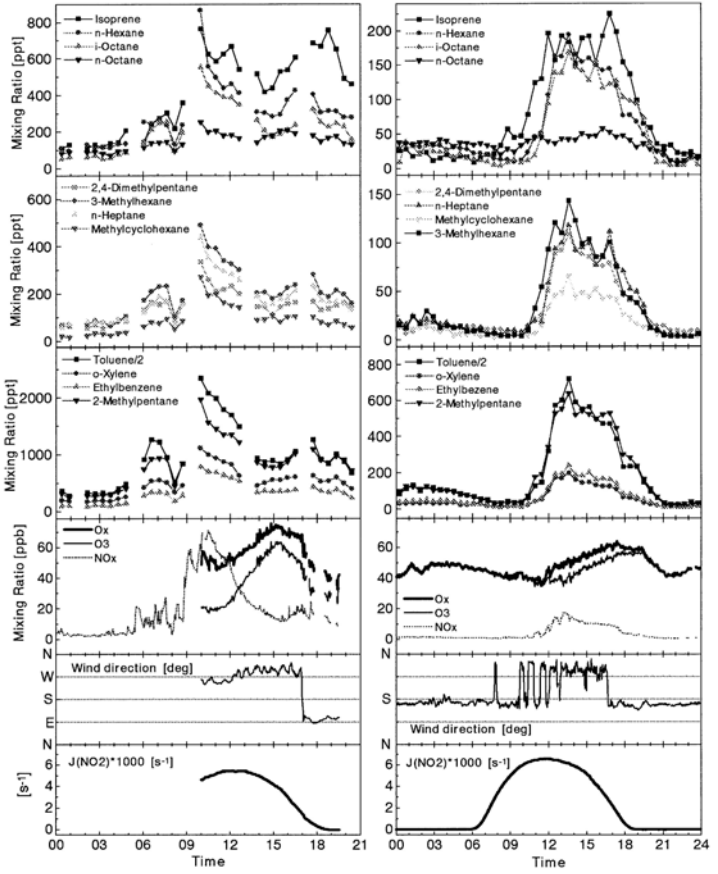


Figure 3. Diurnal variation of hydrocarbons, NO_x, O_3, O_x, wind direction and J_{NO_2} on 17 Sept. 1992. *Left:* Kappel; *Right:* Schauinsland.

$$-\frac{d[RH_i]}{dt} = [RH_i] \cdot [OH] \cdot k_i$$

$$\ln\left(\frac{[RH_i]_{t_2}}{[RH_i]_{t_1}}\right) = -k_i[\overline{OH}]\Delta t$$

without reaction:

$[RH_i]_{t2} = [RH_i]_{t1}\, e^{-k_D t}$

$\ln([RH_i]_{t1}/[RH_i]_{t2}) = k_D t$

After integration over the travel time between the two measurement sites, $\Delta t = t_1 - t_2$, and with the averages $[\overline{OH}] = \int_{\Delta t}[OH]\, dt/\Delta t$ and $\overline{k}_D = \int_{\Delta t} k_D\, dt/\Delta t$, we obtain with the above assumptions

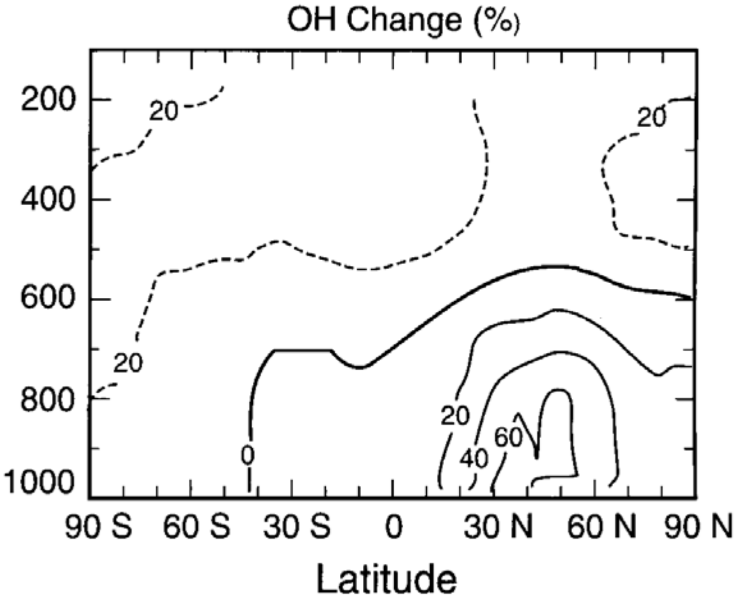
$$\ln([RH_i]_{t1}/[RH_i]_{t2}) = [\overline{OH}]k_i\Delta t + \overline{k}_D\Delta t$$

(Kramp & Volz-Thomas, 1995)

Radical distributions – spatial, temporal trend: OH

- Because of increased short-wave light intensity (actinic flux): Mid latitudes NH: +1.5%/a at 300 nm, +0.8%/a at 305 nm (1997 vs. 1989, observations at ground), stronger effects in the SH (observations from satellite only) at 40° some 20%, at 60° some 100% higher.

- 1994 vs. 1979 2D model results (Granier, 2003):



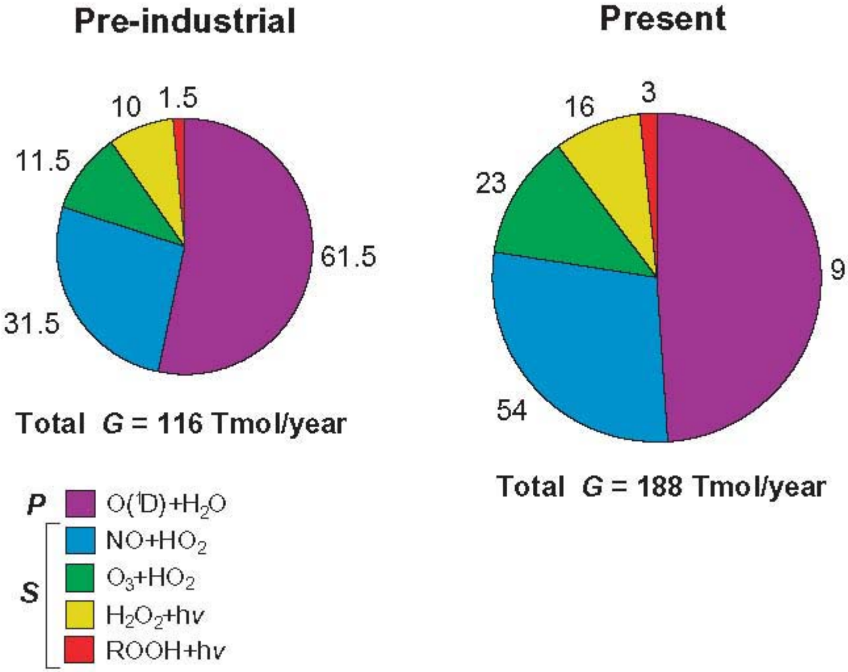
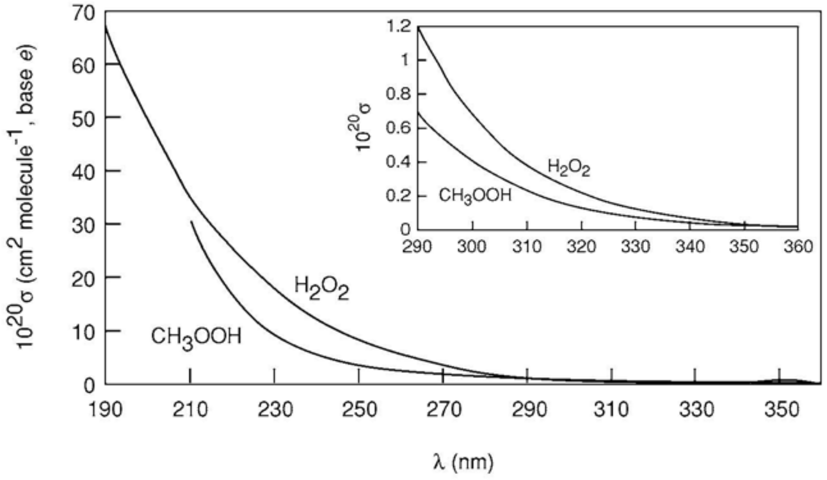


Fig. 3. Model calculated annual OH formation rates (Tmol/year) through the main chemical pathways, based on present-day and pre-industrial emissions of natural and anthropogenic origin.

(Lelieveld et al., 2002)

3.1.3.2 Radical source peroxides

(1) $H_2O_2 + h\nu \rightarrow 2\ OH\cdot$



(Vaghjiani & Ravishankara, 1989)

(1-2) $RCH_3 \rightarrow \rightarrow RCH_2OO\cdot$

(3) $RCH_2OO\cdot + HO_2\cdot \rightarrow RCH_2OOH + O_2$

(Instead of: $RCH_2OO\cdot + NO \rightarrow RCH_2O\cdot + NO_2$)

(4) $RCH_2OOH + O_2 + h\nu \rightarrow OH\cdot + HO_2\cdot + RCHO$

HC_x: Peroxides formation and reactions between peroxides

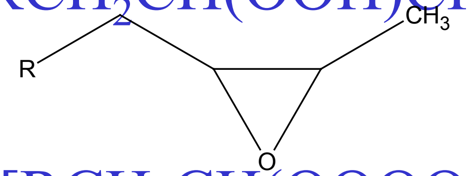
(1a) $RCH_2CH_2CH_3 + OH \rightarrow RCH_2CH{\cdot}CH_2CH_3 + H_2O$

$RCH_2CH{\cdot}CH_2CH_3 + O_2 + M \rightarrow RCH_2CH(OO{\cdot})CH_2CH_3 + M$

(2aa) $RCH_2CH(OO{\cdot})CH_2CH_3 + NO \rightarrow RCH_2CH(O{\cdot})CH_2CH_3 + NO_2$

(2ab) $+ NO \rightarrow RCH_2CH(ONO_2)CH_2CH_3$

(2ba) $+ HO_2 \rightarrow RCH_2CH(OOH)CH_2CH_3 + O_2$ major

(2bb) $+ HO_2 \rightarrow$  $+ H_2O + O_2$

(2c) $+ R'O_2 \rightarrow [RCH_2CH(OOOOR')CH_2CH_3] \rightarrow$

(3ca) $\rightarrow RCH_2CH(O{\cdot})CH_2CH_3 + R'O{\cdot} + O_2 \rightarrow \rightarrow \rightarrow$

(3cb) $\rightarrow RCH_2CH(OH)CH_2CH_3 + R'CHO + O_2$

(3cc) $\rightarrow RCH_2CH(OOR')CH_2CH_3 + O_2$

R	k_{3c} $10^{-12} cm^3 molec^{-1} s^{-1}$ (T = 298 K)	$k_{3ca}/(k_{3ca}+k_{3cb}+k_{3cc})$	$k_{3cb}/(k_{3ca}+k_{3cb}+k_{3cc})$	$k_{3cc}/(k_{3ca}+k_{3cb}+k_{3cc})$
CH_3	0.37	0.33	0.67	≈0.0
CH_2CH_3	0.06	0.63	0.32	≈0.05
$CH_2(CH_3)_2$	0.001	0.56	0.44	≈0.0

3.1.3.3 Radical source aldehydes

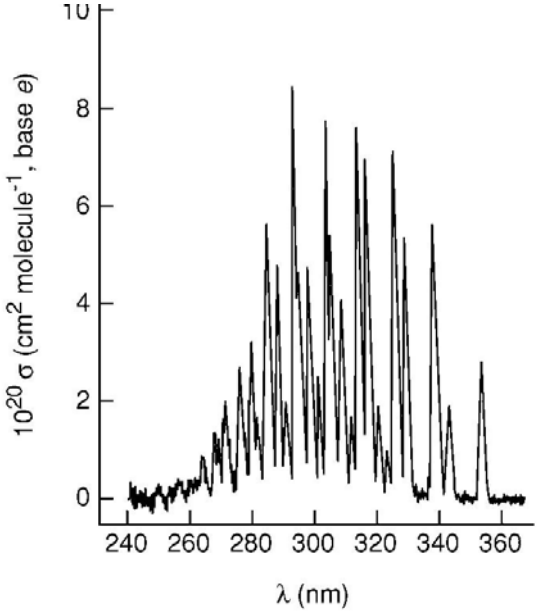
(1a) $HCHO + h\nu\ (\lambda \leq 360\text{nm}) \rightarrow CO + H_2$

(1b) $+ h\nu \rightarrow CHO\cdot + H\cdot$ yd(1b+1c)≈80%

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

(1c) $HCHO + OH\cdot \rightarrow CHO\cdot + H\cdot$

(2c) $HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$



(Rogers, 1990)

TABLE 4.25 Recommended Quantum Yields for Photolysis of HCHO[a]

Wavelength (nm)	H + HCO	H_2 + CO
240	0.27	0.49
250	0.29	0.49
260	0.30	0.49
270	0.38	0.43
280	0.57	0.32
290	0.73	0.24
300	0.78	0.21
301.25	0.749	0.251
303.75	0.753	0.247
306.25	0.753	0.247
308.75	0.748	0.252
311.25	0.739	0.261
313.75	0.724	0.276
316.25	0.684	0.316
318.75	0.623	0.368
321.25	0.559	0.423
323.75	0.492	0.480
326.25	0.420	0.550
328.75	0.343	0.634
331.25	0.259	0.697
333.75	0.168	0.739
336.25	0.093	0.728
338.75	0.033	0.667
341.25	0.003	0.602
343.75	0.001	0.535
346.25	0	0.469
348.75	0	0.405
351.25	0	0.337
353.75	0	0.265
356.25	0	0.197

[a] IUPAC recommendations from 240 to 300 nm (Atkinson *et al.*, 1997a) and NASA recommendations from 301 to 356 nm (DeMore *et al.*, 1997), where the latter are for 2.5 nm intervals centered on the indicated wavelength based on Horowitz and Calvert, *Int. J. Chem. Kinet.*, *10*, 805 (1978); Moortgat and Warneck, *J. Chem. Phys.*, *70*, 3639 (1979); and Moortgat *et al.*, *ibid.*, *78*, 1185 (1983).

3.1.3.4 Radical source NO_2

(1) $NO_2 + h\nu\ (\lambda > 420nm) \rightarrow NO_2^*$

(2a) $NO_2^* + M \rightarrow NO_2 + M$

(2b) $NO_2^* + H_2O \rightarrow HNO_2 + OH\cdot$

nitrous acid $k_{2b}/k_{2a} \approx 10^{-4}$

$k_{2b}=0.17\times10^{-12}$ cm^3/molec/s (Li et al., 2008)

However:

- Leads to overestimates of ozone production in urban areas

(Wennberg & Dabdub, 2008)

- Is k_{2b} a factor of 10 lower ?

(Crowley & Carl, 1997)

3.1.3.5 Radical source nitrous acid

$HNO_2 + h\nu \rightarrow OH\cdot + NO$ → *2.2*

3.1.4 Sinks of tropospheric ozone

3.1.4.1 Hydrocarbon and CO chemistry in the absence of NO_x

Degradation of RH in NO-poor areas

(1) $RCH_3 + OH\cdot \rightarrow RCH_2\cdot + H_2O$

(2) $RCH_2\cdot + O_2 + M \rightarrow RCH_2OO\cdot + M$

(3a) $NO_2 + h\nu \nrightarrow NO + O$

(4a) $O + O_2 + M \nrightarrow O_3 + M$

(3b) $RCH_2OO\cdot + \cancel{NO} + O_3 \rightarrow RCH_2O\cdot + 2\,O_2$

(4b) $RCH_2O\cdot + O_2 \rightarrow RCHO + HO_2\cdot$

Sum (1-4): $RCH_3 + OH\cdot + O_3 \rightarrow RCHO + H_2O + HO_2\cdot$

→ *Ozone loss. The threshold NO level for formation vs. loss is 5-10 pptv near the ground and ≈ 20 pptv near the tropopause*

Degradation of methane in NO-poor areas

(1) $CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O$

(2) $CH_3\cdot + O_2 + M \rightarrow CH_3OO\cdot + M$

(3) $CH_3OO\cdot + HO_2\cdot \rightarrow CH_3OOH + O_2$

(4a) $CH_3OOH + h\nu\ (< 330\text{nm}) \rightarrow CH_3O\cdot + OH\cdot$

(5) $CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot$

Sum (1-5): $CH_4 + O_2 \rightarrow HCHO + H_2O$

(4b) $CH_3OOH + OH\cdot \rightarrow HCHO + H_2O + OH\cdot$

Sum (1-4b): $CH_4 + OH\cdot + HO_2 \rightarrow HCHO + 2\ H_2O$

→ *neutral with regard to ozone*

Much of the CH_3OOH is washed out ($\tau \approx$ week)

→ *no oxidation to HCHO and CO, radical sink:*

Sum (1-3): $CH_4 + OH\cdot + HO_2\cdot \rightarrow CH_3OOH + H_2O$

Degradation of CO in NO-poor areas

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

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

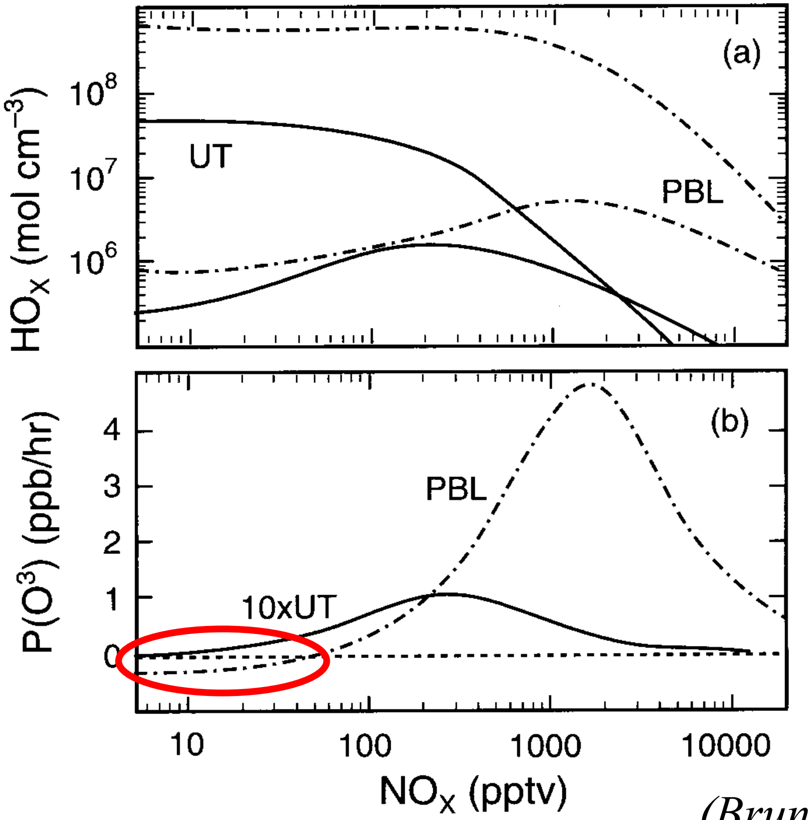
(3a) $HO_2\cdot + O_3 \rightarrow OH\cdot + 2\ O_2$

Sum (1-3a): $CO + O_3 \rightarrow CO_2 + O_2$

(3b) $HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$

Sum (1-3b): $CO + OH\cdot + HO_2\cdot \rightarrow CO_2 + H_2O_2$

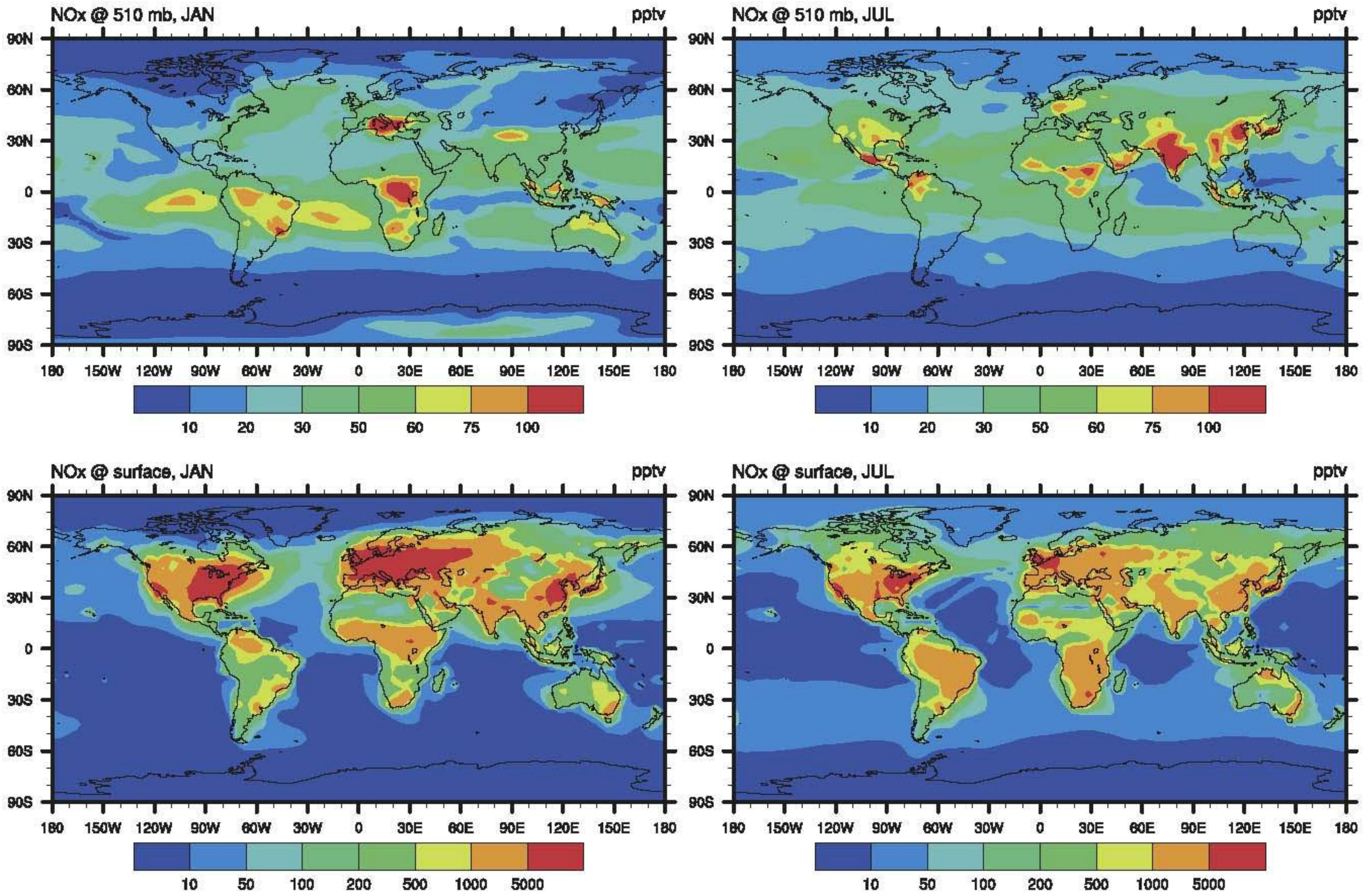
Tropospheric Ozone, HO_x, NO_x



(Brune et al., 2000)

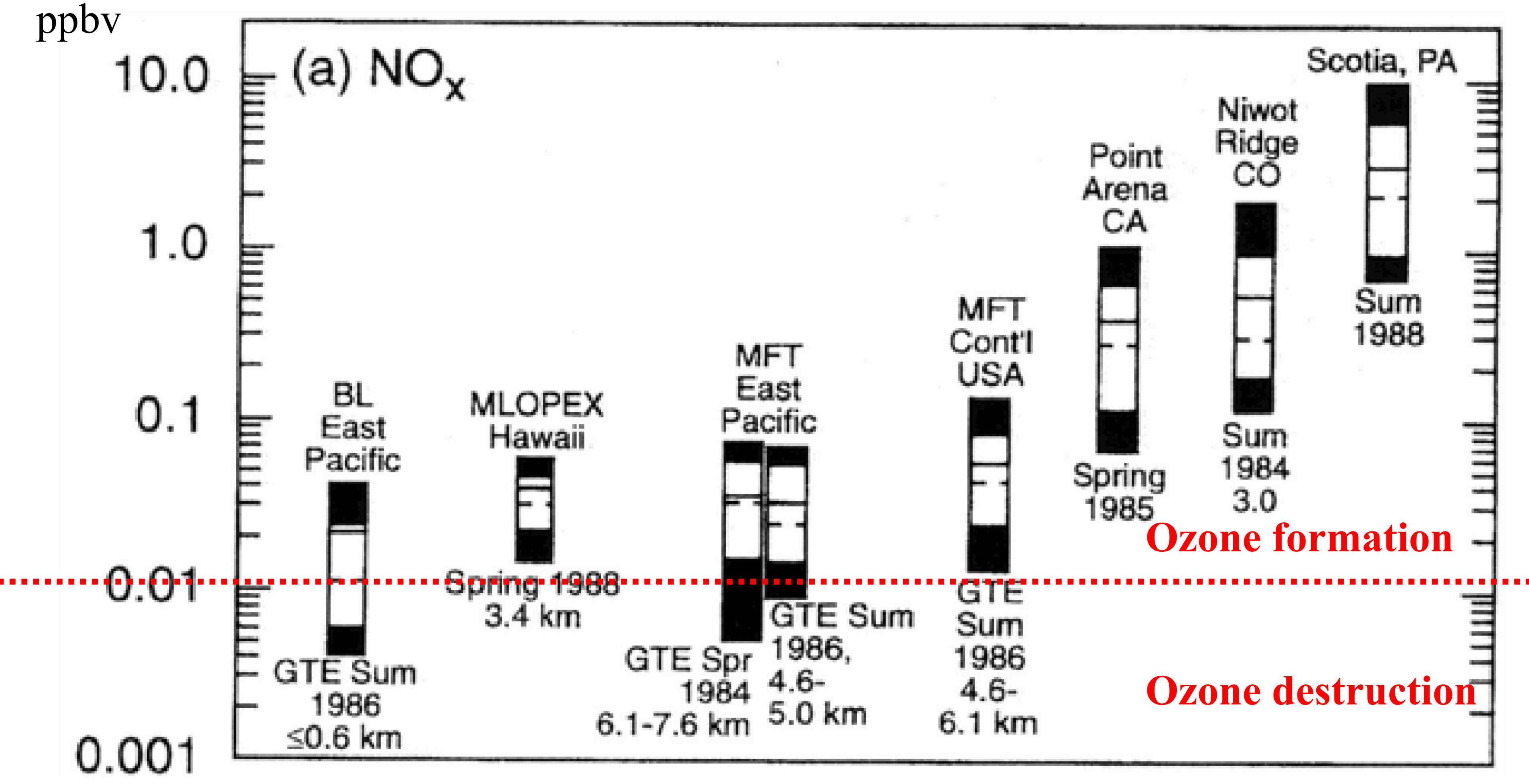
Ozone depletion!

Distributions of NO_x (pptv) @ 510 and 970 hPa, monthly mean



(Model results MOZART2; Horowitz et al., 2003)

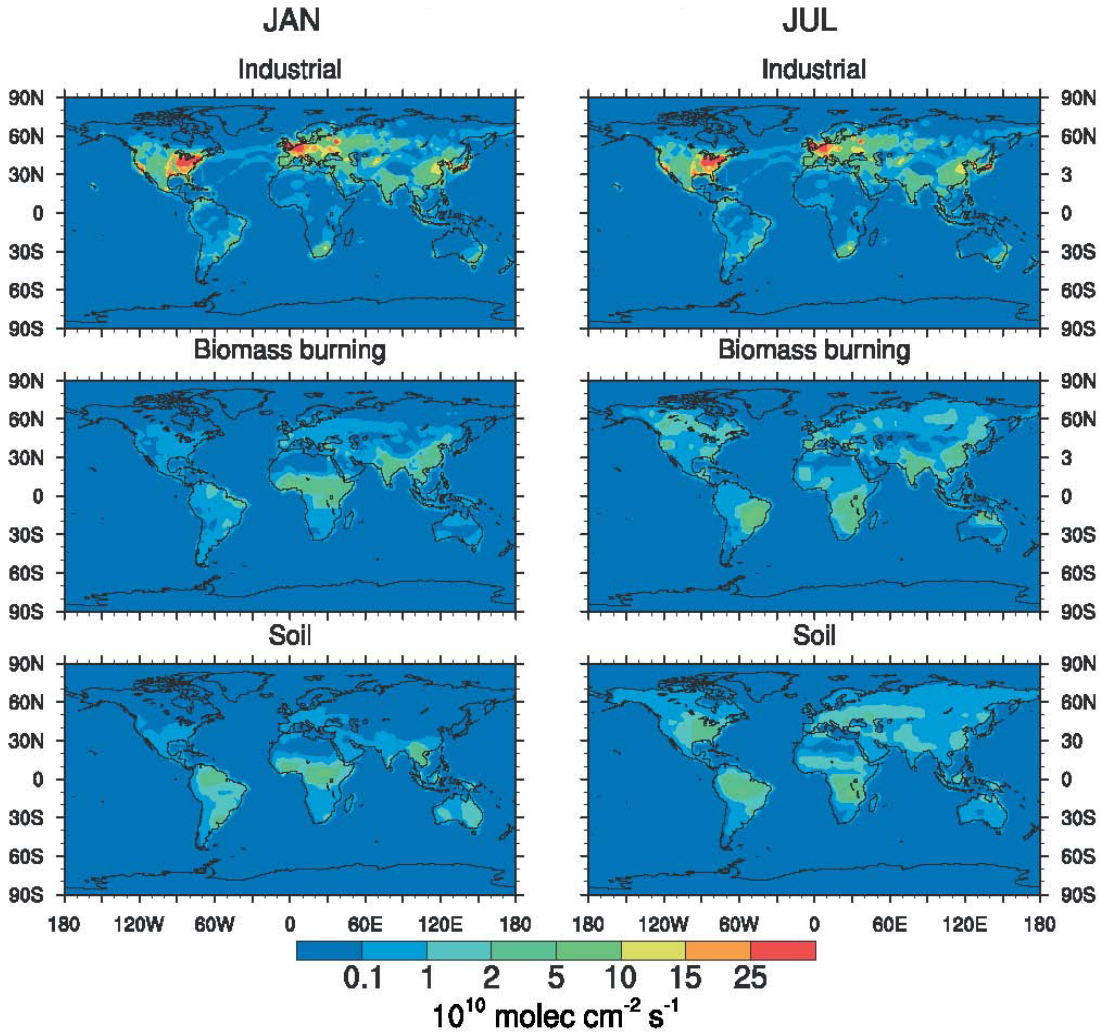
NO_x distribution: NO_x-poor ?



(Ridley, 1991)

→ **Most regions of the planetary boundary layer are above the NO_x threshold.**

Global sources for N oxides, NO_x



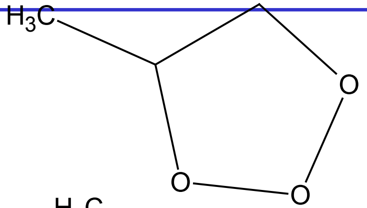
1990 (Tg N/a)	Natural	Anth
Lightning	3.0 (2-6)	
Soils and vegetation	3.2 (1.9-4.5)	
Agriculture (*)		2.3 (1.4-3.2)
Biomass burning	0.3	3.3 (2.1-5.5)
Fossil fuel burning		21 (20-23)
Sum	***6.5 (4.2-11)***	***26.6 (23-32)***

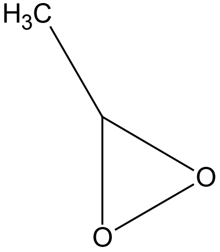
(*) Animal and plant production, without biomass burning

3.1.4.2 Ozone as oxidizer

3.1.4.2.1 Alkene ozonations

example propene





Alkenes react readily with ozone: $k \leq 10^{-10}$ cm^3 $molec^{-1}$ s^{-1}

(1) $CH_3CH{=}CH_2 + O_3 \rightarrow$ [primary ozonide]

(2a) [primary ozonide] $\rightarrow CH_3CH(OO\cdot)CH_2O\cdot$ 55%

(3a) decomposition: $\rightarrow CH_3CHOO\cdot + HCHO$

(4a) 3-ring closure: $\rightarrow [CH_3(CHOO)]$

(5a) decomposition: $\rightarrow H_3CC\cdot O + OH\cdot$ major

(6a) $H_3CC\cdot O + O_2 \rightarrow H_3CC(O)OO\cdot$

(7a) $H_3CC(O)OO\cdot + NO \rightarrow H_3C\cdot + CO_2 + NO_2$

$CH_3\cdot + O_2 + M \rightarrow CH_3OO\cdot + M$

(8a) $CH_3OO\cdot + NO \rightarrow CH_3O\cdot + NO_2$

(9a) $CH_3O\cdot + O_2 \rightarrow HCHO + HO_2$

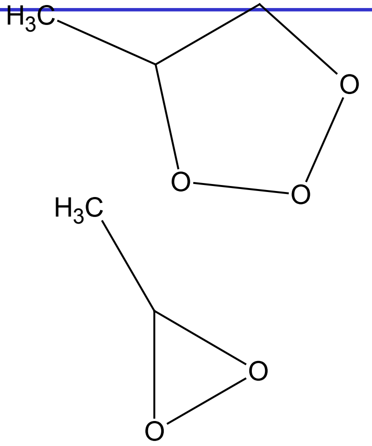
Sum: $CH_3CH{=}CH_2 + 2\ O_2 + O_3 + 2\ NO \rightarrow 2\ HCHO + CO_2 + OH + HO_2 + 2\ NO_2$

so far 1 O_3 formed (+ 2 NO_2 – 1 O_3)

3.1.4.2 Ozone as oxidizer

3.1.4.2.1 Alkene ozonations

example propene



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(7a) $H_3CC(O)OO\cdot + NO \rightarrow H_3C\cdot + CO_2 + NO_2$

$CH_3\cdot + O_2 + M \rightarrow CH_3OO\cdot + M$

(8a) $CH_3OO\cdot + NO \rightarrow CH_3O\cdot + NO_2$

(2b) [primary ozonide] $\rightarrow CH_3CH(O\cdot)CH_2OO\cdot$ 45%

(3b) decomposition: $\rightarrow CH_3CHO + \cdot CH_2COO\cdot$

(4b) 3-ring closure: $\rightarrow [(CH_2OO)]$

(5ba) decomposition: $\rightarrow H_2 + CO_2$

(5bb) decomposition: $\rightarrow H_2O + CO$

(5bc) decomposition: $\rightarrow OH\cdot + HC\cdot O$ major

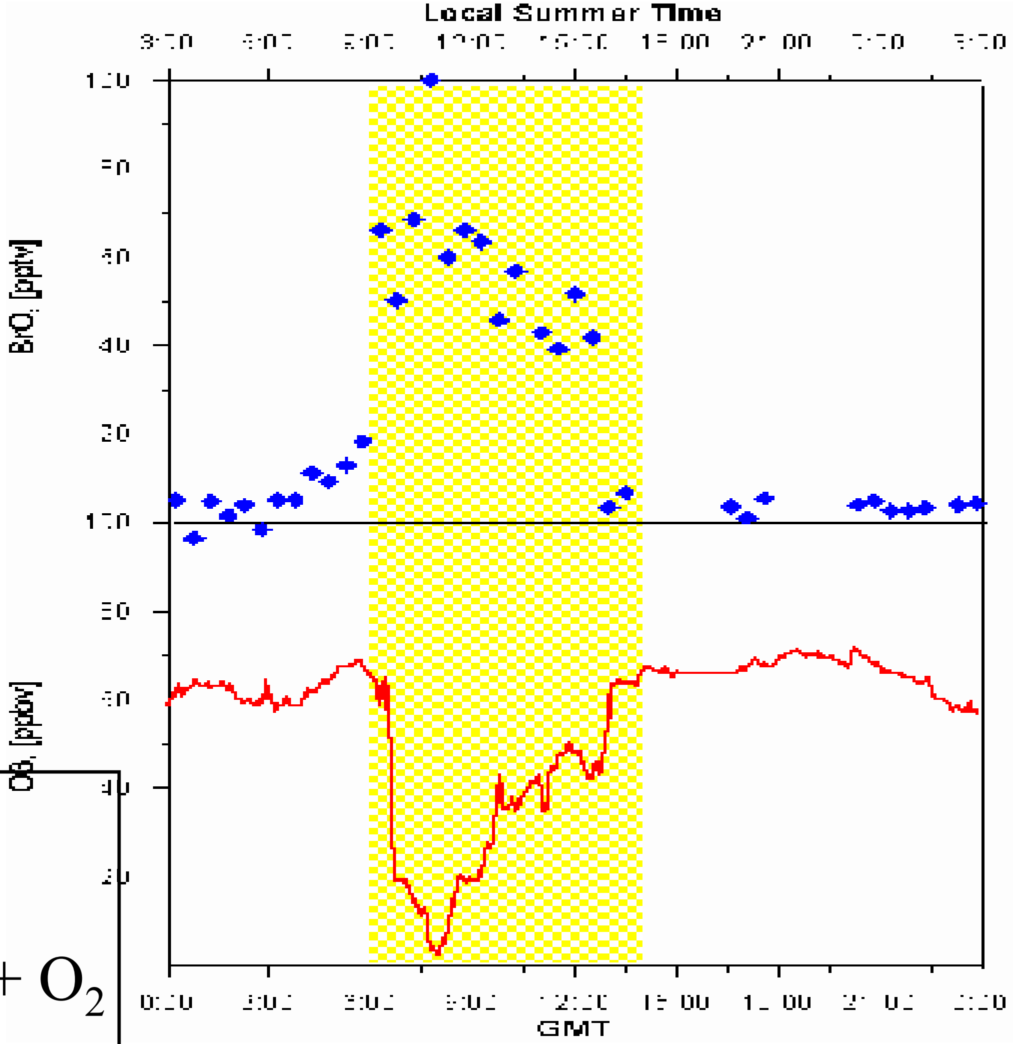
(6bc) $HC\cdot O + O_2 \rightarrow CO + HO_2\cdot$

Sum: $CH_3CH{=}CH_2 + O_3 + O_2 \rightarrow CH_3CHO + CO + OH\cdot + HO_2\cdot$

so far 1 O_3 consumed

3.1.4.2.2 Halogen oxidation

over a Br-rich area, the Dead Sea,
June 1997
(Luria et al., 1998; Hebestreit et al., 1999)



(1) $Br\cdot + O_3 \rightarrow BrO\cdot + O_2$
(2, Strat.) $BrO\cdot + O \rightarrow Br\cdot + O_2$
(2, Trop.) $BrO\cdot + HO_2\cdot \rightarrow HOBr + O_2$
(3) $HOBr + h\nu \rightarrow OH\cdot + Br\cdot$

Sum:
(1-3 Trop.) $O_3 + HO_2\cdot \rightarrow OH\cdot + 2\ O_2$

Chemistry of ground-level ozone in polar regions

- Ozone depletion events, 1-7 days, occur coinciding with elevated levels of filterable Br (Oltmans et al., 1981; Barrie et al., 1988)
- Obviously, O_3 is catalytically destroyed. Elevated BrO during months in the boundary layer of the winter polar regions are regularly observed (from satellite; van Rozendael et al., 1999)
- Parallelly: Hg(g) disappears, although its lifetime should be 6-24 months (‚Hg depletion events‘; Schroeder et al., 1998)

Stratosphere: The sink reaction $O + O_3 \rightarrow 2\ O_2$ can be catalyzed:

$X + O_3 \rightarrow XO + O_2$

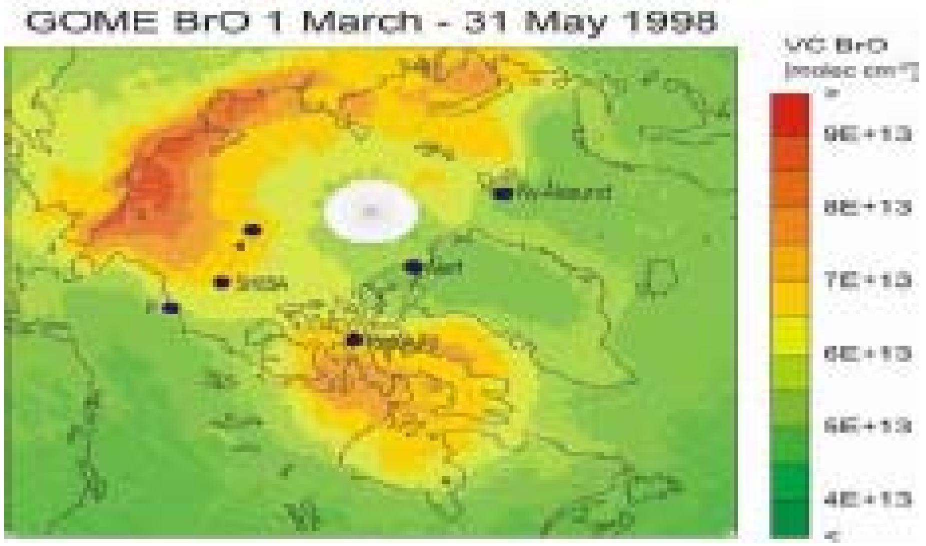
$XO + O \rightarrow X + O_2$

Sum:

$O_3 + O \rightarrow 2\ O_2$

X = Cl, Br (anthropogenic),

X = OH, NO (natural) *



Chemistry of ground-level ozone in polar regions (2)

(1a) $HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$

(2) $Br_2 + h\nu \rightarrow 2\ Br\cdot$

(3) $Br\cdot + O_3 \rightarrow BrO\cdot + O_2$

(4a) $BrO\cdot + HO_2\cdot \rightarrow HOBr + O_2$

Sum:

(1-4) $H^+ + Br^- + HO_2\cdot + O_3 \rightarrow Br\cdot + H_2O + 2\ O_2$

(1ba) $HOBr + Cl^- + H^+ \rightarrow H_2O + BrCl$

(1bb) $BrCl + Br^- \rightarrow Br_2Cl^-$

(1bc) $Br_2Cl^- \rightarrow Br_2 + Cl^-$

Sum:

(1b = 1a) $HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$

(4ba) $2\ BrO\cdot \rightarrow 2\ Br\cdot + O_2$

(4bb) $\rightarrow Br_2 + O_2$

(4c) $BrO\cdot + XO\cdot \rightarrow XBr + O_2$

- Exponential growth of BrO (‚Br explosion‘)
- source of Br^- is seasalt, solid or aqueous (brine)

Chemistry of ground-level ozone in polar regions (3)

Br · formed upon photolysis reactions:

(1) $BrO\cdot + h\nu \rightarrow Br\cdot + O$

(2) $Br_2 + h\nu \rightarrow 2\ Br\cdot$

(3) $BrI + h\nu \rightarrow Br\cdot + I\cdot$

- XO (X=Cl,Br,I) cross reactions (4c) are faster than (4a) $BrO+HO_2$, but much less significant. IO was recently observed, however.
- It is not clear how sea salt ions reach the snow surfaces (sea spray, upward migration from sea ice, or from frost flowers)

Destruction of ozone on surfaces

→ **4. *Budgets/4.3.2 Dry deposition***