Block-Kurs Luftchemie

TNO | Knowledge for business

Freie Universität Berlin, FB Geowissenschaften
Institut für Meteorologie

Arbeitsgruppe TRUMF – TRoposphärische UMweltForschung

13-17 März 2006

9.00 - 11.00 / 12.00 - 14.00

Peter Builtjes

Fokus des Kurses

- Atmosphärische chemische Zusammensetzung der Troposphäre und der Stratosphäre
- Welche Phenomäne bestimmen die chemische Zusammensetzung
- Geowissenschaften – Meteorologie – Atmosphärische Chemie
- Atmosphärische Chemie ist wichtig für:
  - Strahlungsbilanz und Klimaänderung
  - Luftqualität

Struktur des Kurses

Montag : Einführung / Basisprinzipen / Stratosphäre I

Dienstag : Stratosphäre II / Troposphäre I

Mittwoch : Troposphäre II und III

Donnerstagmorgen : Zusammenfassung / Einführung in die Artikeln

Donnerstagmittag : Studieren Artikeln

Freitag : Presentationen

- **Teilnahme Schein : 80 % Teilnahme**
- **Seminar Schein : 80 % Teilnahme + Präsentation**

I) Einführung und einige Basisprinzipen

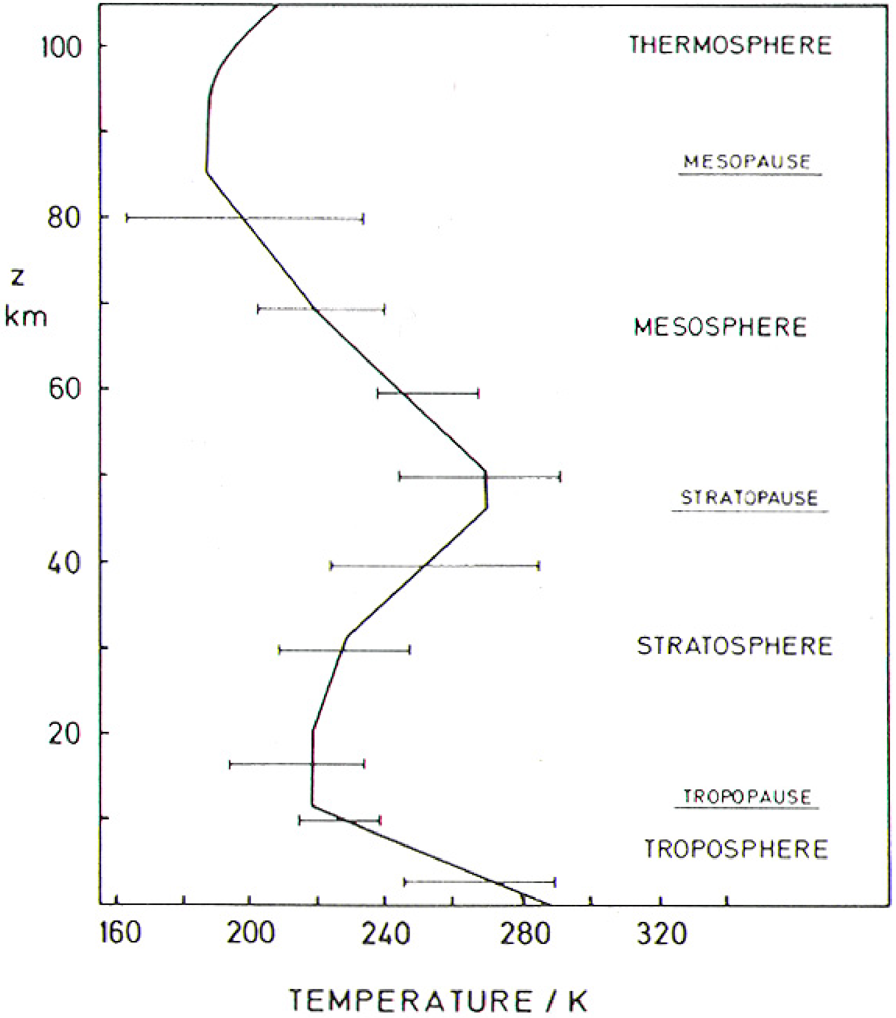

Fig. 1-5. Vertical temperature structure of the atmosphere. The solid curve represents the U.S. Standard Atmosphere, and the horizontal bars indicate the range of monthly means observed between equator and north pole. [Adapted from U.S. Standard Atmosphere (1976).]

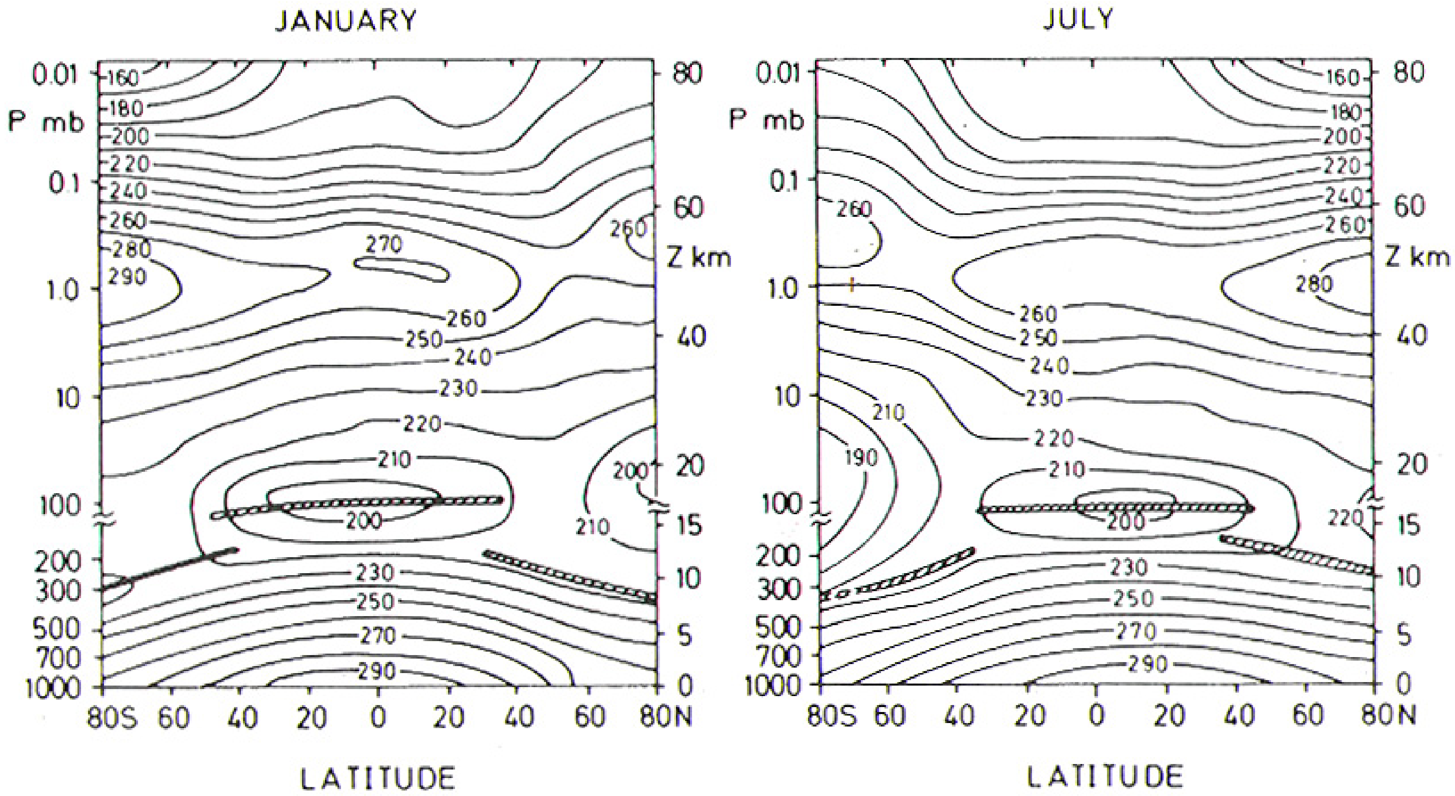

Fig. 1-4. Atmospheric distribution of zonal mean temperatures (in K) for January and July. [Data from Newell *et al.* (1972) for the lower 20 km and from Labitzke and Barnett (1979) for the upper atmosphere are combined.] The tropopause levels are indicated by shaded bars.

Literatur

Peter Warneck, Chemistry of the Natural Atmosphere, Acadamic Press, Inc., 1988

E. Meszaros, Atmospheric Chemistry, Elsevier, 1981

John Seinfeld and Spyros Pandis, Atmospheric Chemistry and Physics, John Wileyd Sons, 1998

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Richard Wayne, Chemistry of Atmospheres, Clarendon Press, 1993

Peter Hobbs, Basic physical Chemistry for the Atmospheric Sciences, Cambridge Univ. Press, 1995

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Formation and evolution of the atmosphere

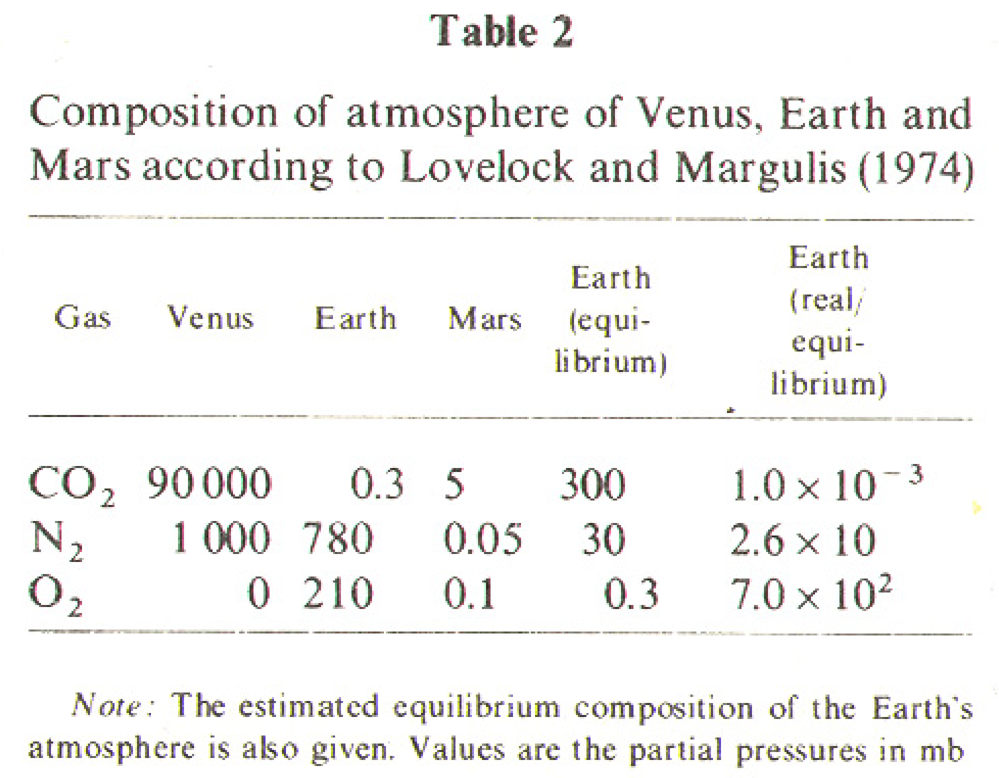

Table 2

Composition of atmosphere of Venus, Earth and Mars according to Lovelock and Margulis (1974)

Gas	Venus	Earth	Mars	Earth (equi-librium)	Earth (real/ equi-librium)
CO_2	90 000	0.3	5	300	1.0×10^{-3}
N_2	1 000	780	0.05	30	2.6×10
O_2	0	210	0.1	0.3	7.0×10^{2}

Note: The estimated equilibrium composition of the Earth's atmosphere is also given. Values are the partial pressures in mb

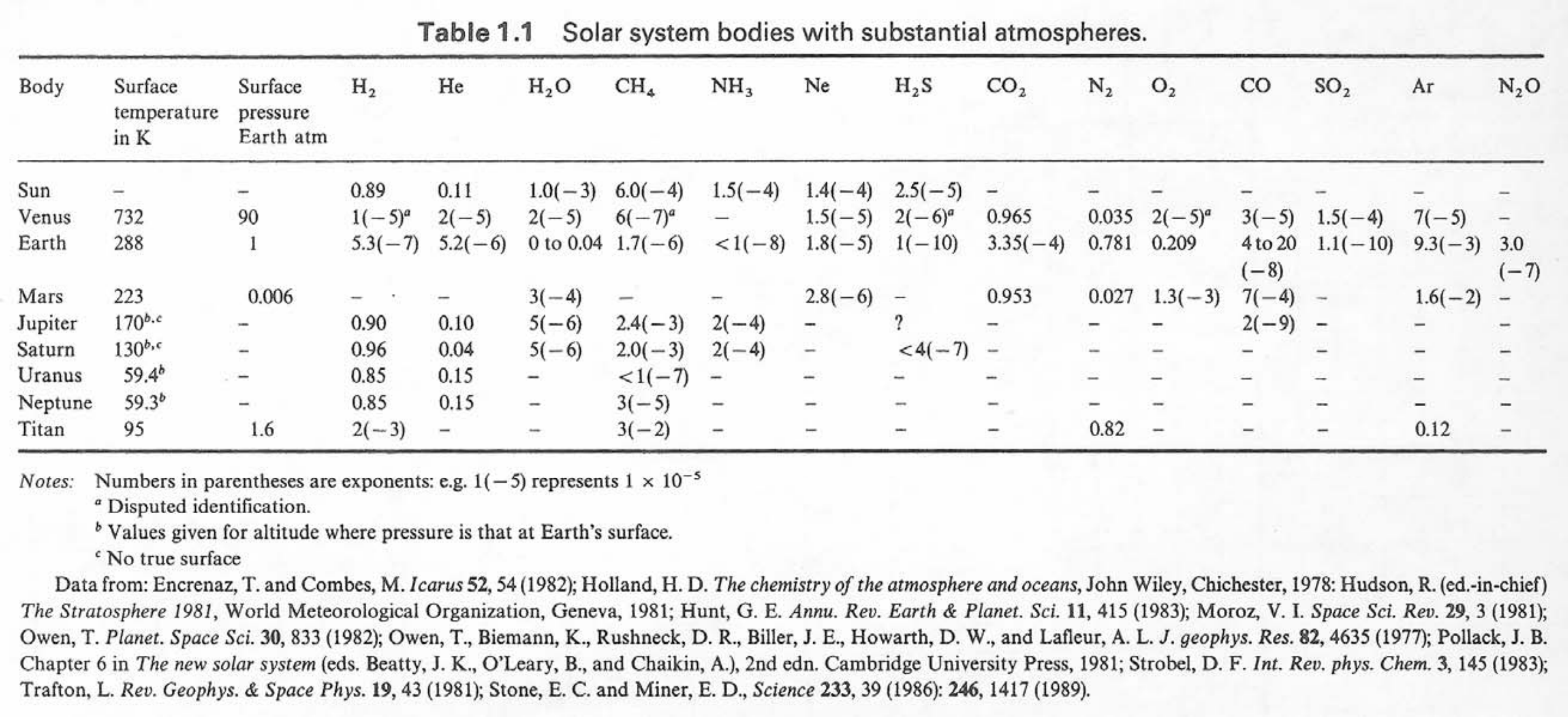

Table 1.1 Solar system bodies with substantial atmospheres.

Body	Surface temperature in K	Surface pressure Earth atm	H_2	He	H_2O	CH_4	NH_3	Ne	H_2S	CO_2	N_2	O_2	CO	SO_2	Ar	N_2O
Sun	–	–	0.89	0.11	1.0(−3)	6.0(−4)	1.5(−4)	1.4(−4)	2.5(−5)	–	–	–	–	–	–	–
Venus	732	90	1(−5)[a]	2(−5)	2(−5)	6(−7)[a]	–	1.5(−5)	2(−6)[a]	0.965	0.035	2(−5)[a]	3(−5)	1.5(−4)	7(−5)	–
Earth	288	1	5.3(−7)	5.2(−6)	0 to 0.04	1.7(−6)	<1(−8)	1.8(−5)	1(−10)	3.35(−4)	0.781	0.209	4 to 20 (−8)	1.1(−10)	9.3(−3)	3.0 (−7)
Mars	223	0.006	–	–	3(−4)	–	–	2.8(−6)	–	0.953	0.027	1.3(−3)	7(−4)	–	1.6(−2)	–
Jupiter	170[b,c]	–	0.90	0.10	5(−6)	2.4(−3)	2(−4)	–	?	–	–	–	2(−9)	–	–	–
Saturn	130[b,c]	–	0.96	0.04	5(−6)	2.0(−3)	2(−4)	–	<4(−7)	–	–	–	–	–	–	–
Uranus	59.4[b]	–	0.85	0.15	–	<1(−7)	–	–	–	–	–	–	–	–	–	–
Neptune	59.3[b]	–	0.85	0.15	–	3(−5)	–	–	–	–	–	–	–	–	–	–
Titan	95	1.6	2(−3)	–	–	3(−2)	–	–	–	–	0.82	–	–	–	0.12	–

Notes: Numbers in parentheses are exponents: e.g. 1(−5) represents 1×10^{-5}

[a] Disputed identification.

[b] Values given for altitude where pressure is that at Earth's surface.

[c] No true surface

Data from: Encrenaz, T. and Combes, M. *Icarus* **52**, 54 (1982); Holland, H. D. *The chemistry of the atmosphere and oceans*, John Wiley, Chichester, 1978: Hudson, R. (ed.-in-chief) *The Stratosphere 1981*, World Meteorological Organization, Geneva, 1981; Hunt, G. E. *Annu. Rev. Earth & Planet. Sci.* **11**, 415 (1983); Moroz, V. I. *Space Sci. Rev.* **29**, 3 (1981); Owen, T. *Planet. Space Sci.* **30**, 833 (1982); Owen, T., Biemann, K., Rushneck, D. R., Biller, J. E., Howarth, D. W., and Lafleur, A. L. *J. geophys. Res.* **82**, 4635 (1977); Pollack, J. B. Chapter 6 in *The new solar system* (eds. Beatty, J. K., O'Leary, B., and Chaikin, A.), 2nd edn. Cambridge University Press, 1981; Strobel, D. F. *Int. Rev. phys. Chem.* **3**, 145 (1983); Trafton, L. *Rev. Geophys. & Space Phys.* **19**, 43 (1981); Stone, E. C. and Miner, E. D., *Science* **233**, 39 (1986): **246**, 1417 (1989).

Richard Wayne

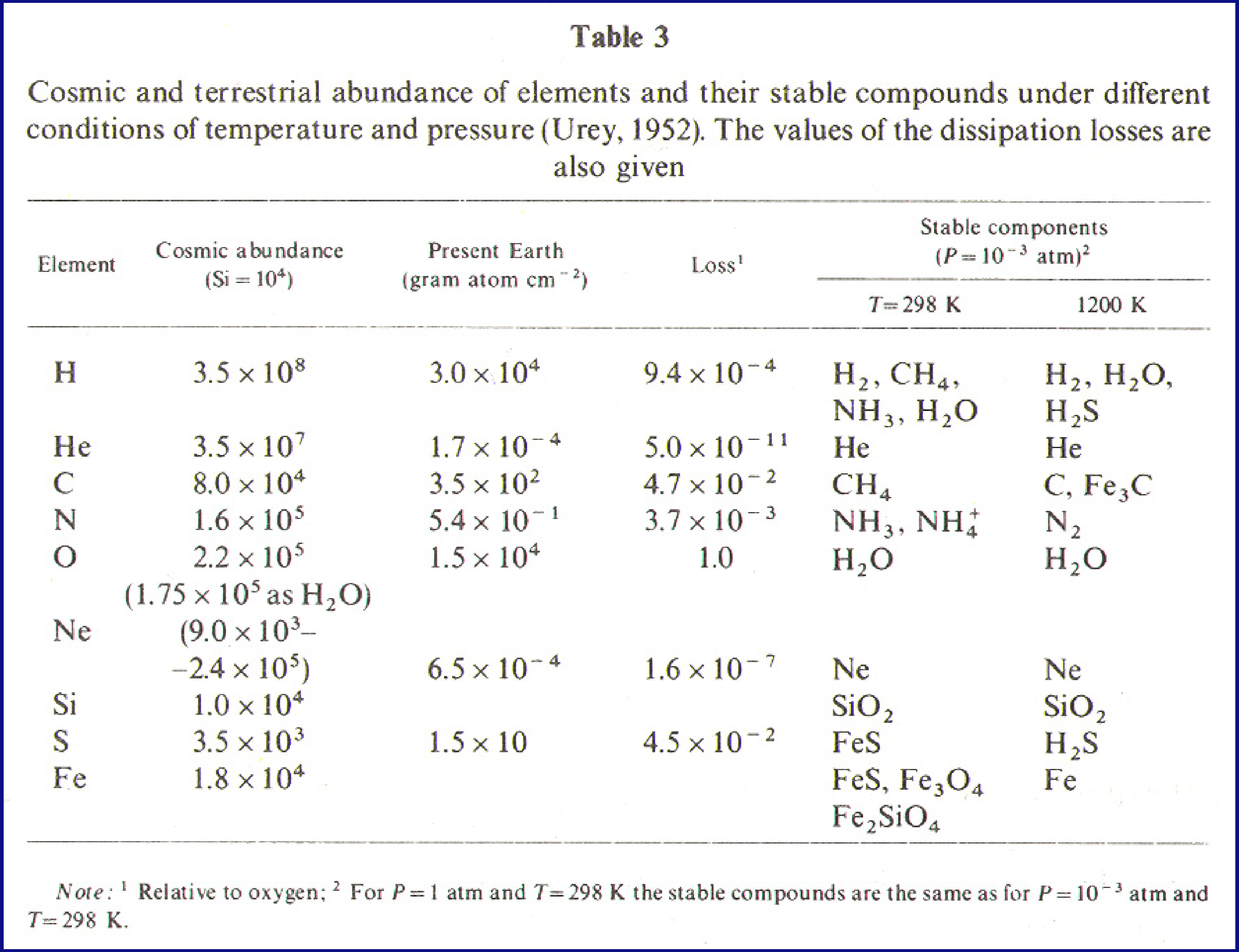

Table 3

Cosmic and terrestrial abundance of elements and their stable compounds under different conditions of temperature and pressure (Urey, 1952). The values of the dissipation losses are also given

Element	Cosmic abundance ($Si = 10^4$)	Present Earth (gram atom cm^{-2})	Loss[1]	Stable components ($P = 10^{-3}$ atm)[2]	
				$T = 298$ K	1200 K
H	3.5×10^8	3.0×10^4	9.4×10^{-4}	H_2, CH_4, NH_3, H_2O	H_2, H_2O, H_2S
He	3.5×10^7	1.7×10^{-4}	5.0×10^{-11}	He	He
C	8.0×10^4	3.5×10^2	4.7×10^{-2}	CH_4	C, Fe_3C
N	1.6×10^5	5.4×10^{-1}	3.7×10^{-3}	NH_3, NH_4^+	N_2
O	2.2×10^5 (1.75×10^5 as H_2O)	1.5×10^4	1.0	H_2O	H_2O
Ne	(9.0×10^3–2.4×10^5)	6.5×10^{-4}	1.6×10^{-7}	Ne	Ne
Si	1.0×10^4			SiO_2	SiO_2
S	3.5×10^3	1.5×10	4.5×10^{-2}	FeS	H_2S
Fe	1.8×10^4			FeS, Fe_3O_4 Fe_2SiO_4	Fe

Note: [1] Relative to oxygen; [2] For $P = 1$ atm and $T = 298$ K the stable compounds are the same as for $P = 10^{-3}$ atm and $T = 298$ K.

Development of the earth atmosphere

1) Proto-planet, gasphase H_2, He (little CH_4, H_2O, NH_3, H_2S)

followed by dissipation of the leighter atoms
Development of gravitation field and of temperature
(by radioactive heating + solar radiation)

followed by condensation of H_2O, binding of H

2) Solid surface, secondairy elements: gases from the solid earth, outgassing + volcano’s

CH_4, NH_3, H_2O, a reducing atmosphere with H

proof: Old (3.000 - 1000 million years) Fe-layers are reduced, not oxidised

vulcano’s lead to CO_2, H_2O, N_2, a reducing atmosphere with O

Averaged composition of volcanic gas

H_2O	20 - 97	%
CO_2	1 - 48	%
N_2	1 - 38	%
SO_2	1 - 30	%
SO_3	0 - 8	%
H_2	0 - 4	%
Cl_2	0 - 4	%

3) Surface temperature at the edge between reducing and oxidysing atmosphere: T ~ -10 / -15 °C

With increasing amount of CO_2 and H_2O (greenhouse effect) T increases to above 0 °C, liquid water

Formation of O_2 in the atmosphere

$H_2O + h\nu \rightarrow H + OH \quad \lambda < 195$ nm

$H_2O + h\nu \rightarrow H_2 + O$

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

But, O_2 absorbs at $\lambda < 195$ nm, blocking

Estimated equilibrium at $O_2 \sim 0.02$ %, 10^{-3} PAL (present atmospheric level)

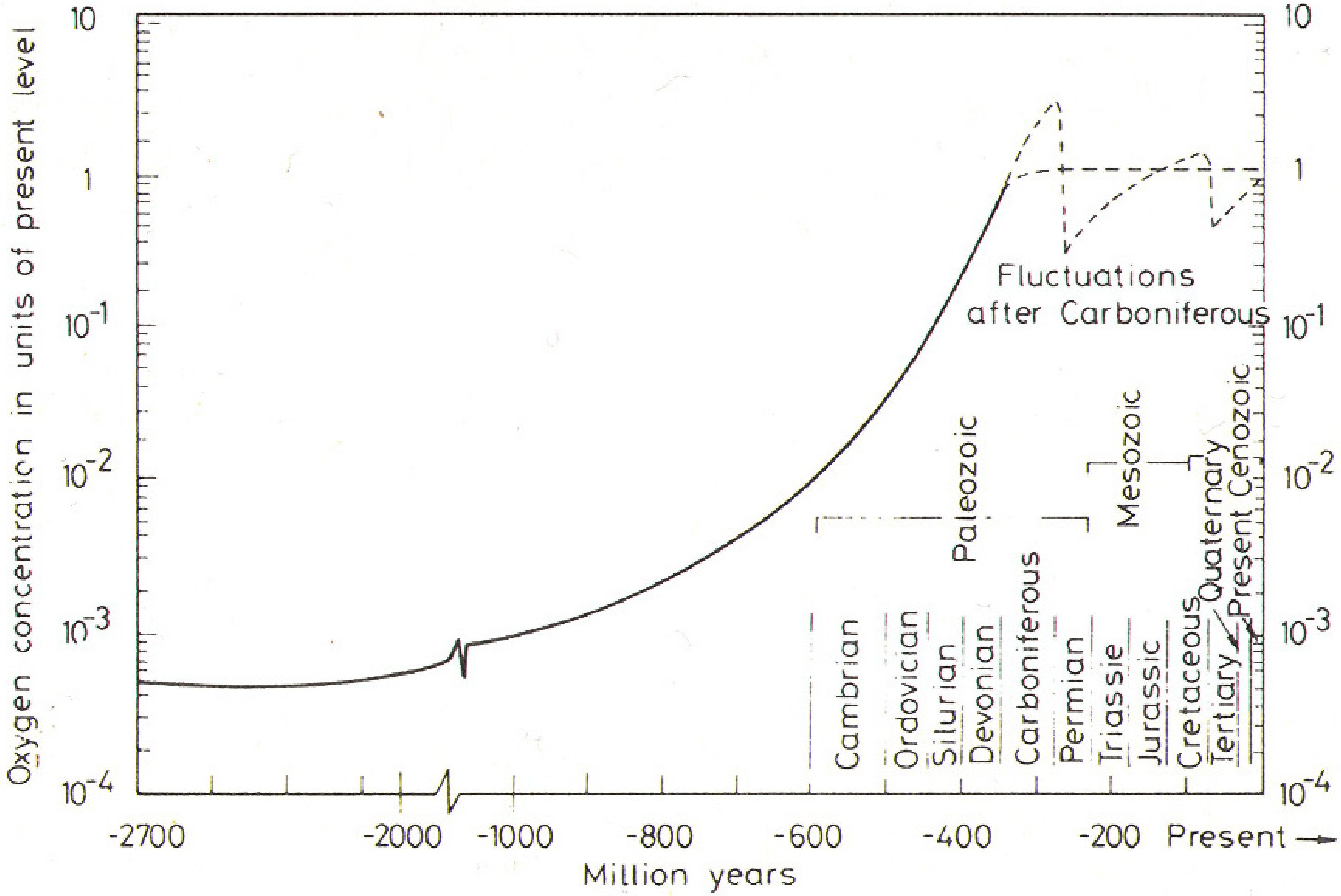

Fig. 3

Variation of the oxygen level in the Earth's atmosphere during geological time (Berkner and Marshall, 1967). (By courtesy of Academic Press)

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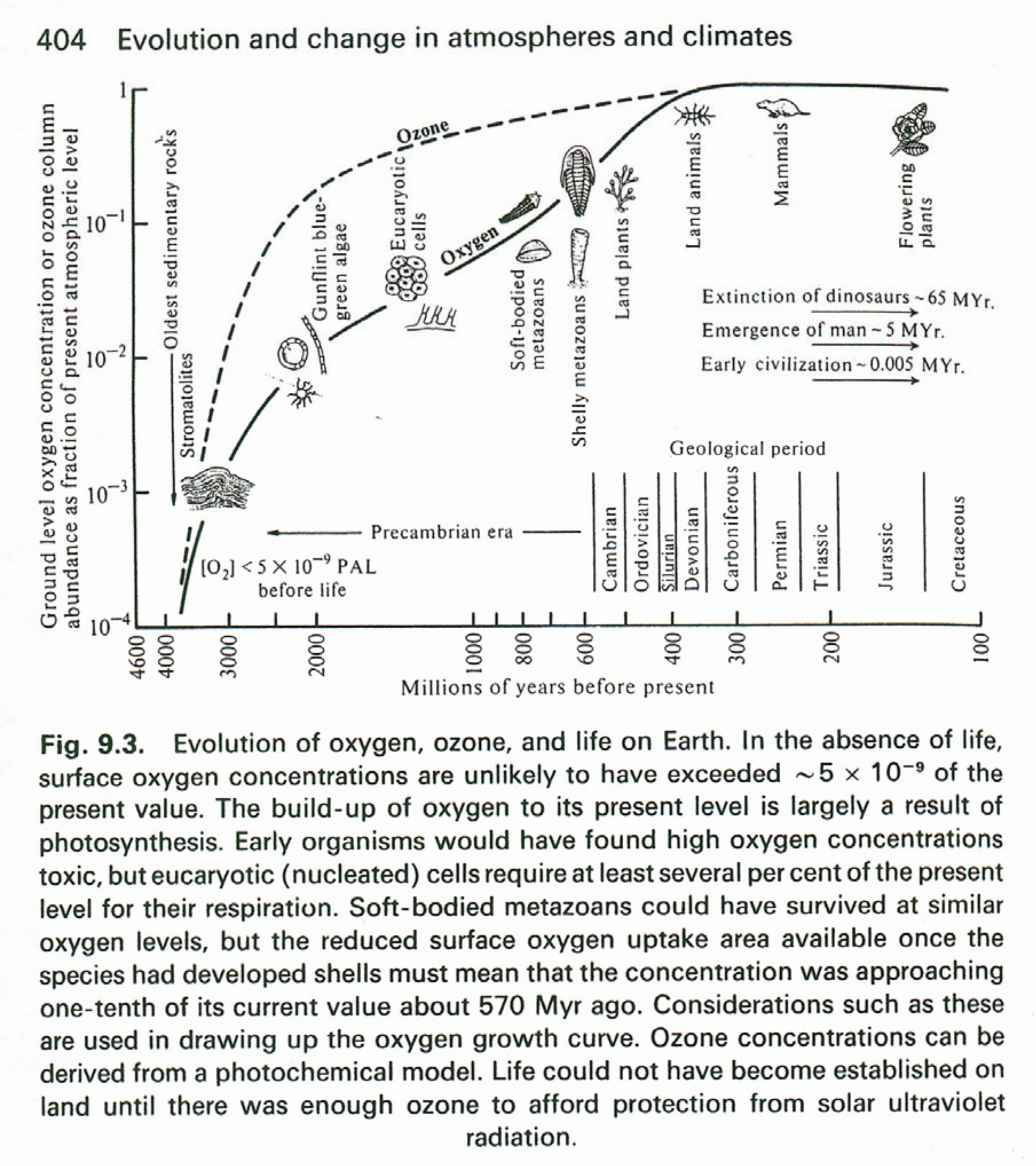


Fig. 9.3. Evolution of oxygen, ozone, and life on Earth. In the absence of life, surface oxygen concentrations are unlikely to have exceeded $\sim 5 \times 10^{-9}$ of the present value. The build-up of oxygen to its present level is largely a result of photosynthesis. Early organisms would have found high oxygen concentrations toxic, but eucaryotic (nucleated) cells require at least several per cent of the present level for their respiration. Soft-bodied metazoans could have survived at similar oxygen levels, but the reduced surface oxygen uptake area available once the species had developed shells must mean that the concentration was approaching one-tenth of its current value about 570 Myr ago. Considerations such as these are used in drawing up the oxygen growth curve. Ozone concentrations can be derived from a photochemical model. Life could not have become established on land until there was enough ozone to afford protection from solar ultraviolet radiation.

$O_2 + hv \rightarrow O + O$

$O + O_2 \rightarrow O_3$

Mehr in Detail später

Live on earth started in a reduced atmosphere

Photosynthesis:

$2H_2O + CO_2 + h\nu \rightarrow CH_2O + H_2O + O_2$ + energy

live in the sea, or in mudded areas because of lack of O_3-layer

gradual increase of O_2 level to 0.01 - 0.1 PAL

formation of O_3-layer makes live on the surface possible

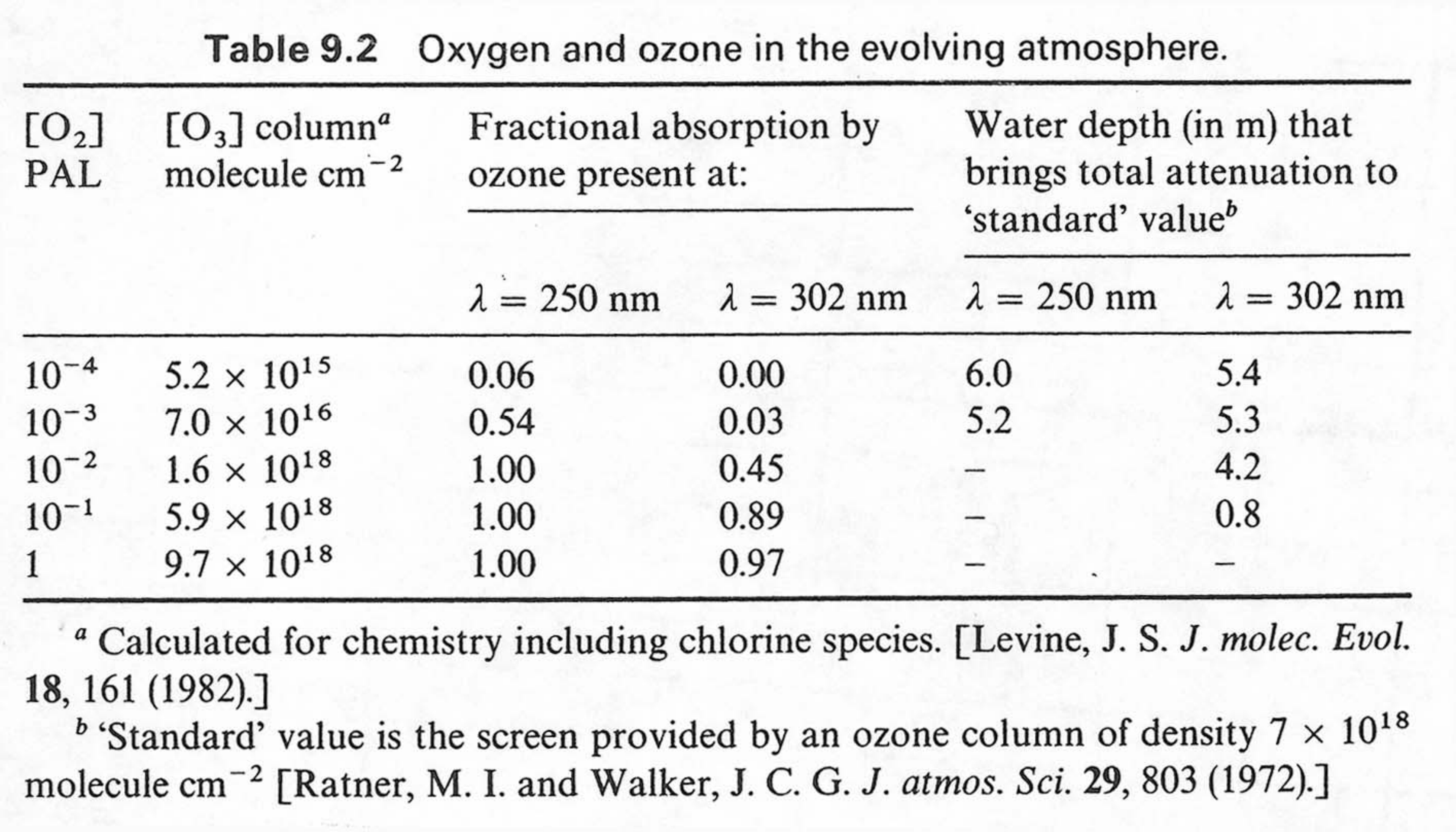


Table 9.2 Oxygen and ozone in the evolving atmosphere.

$[O_2]$ PAL	$[O_3]$ column[a] molecule cm^{-2}	Fractional absorption by ozone present at:		Water depth (in m) that brings total attenuation to 'standard' value[b]	
		$\lambda = 250$ nm	$\lambda = 302$ nm	$\lambda = 250$ nm	$\lambda = 302$ nm
10^{-4}	5.2×10^{15}	0.06	0.00	6.0	5.4
10^{-3}	7.0×10^{16}	0.54	0.03	5.2	5.3
10^{-2}	1.6×10^{18}	1.00	0.45	–	4.2
10^{-1}	5.9×10^{18}	1.00	0.89	–	0.8
1	9.7×10^{18}	1.00	0.97	–	–

[a] Calculated for chemistry including chlorine species. [Levine, J. S. *J. molec. Evol.* **18**, 161 (1982).]

[b] 'Standard' value is the screen provided by an ozone column of density 7×10^{18} molecule cm^{-2} [Ratner, M. I. and Walker, J. C. G. *J. atmos. Sci.* **29**, 803 (1972).]

Respiration:

$C_nH_mO_p + O_2 \rightarrow H_2O + CO_2 + \text{energy}$

(more energy than by photosynthesis)

Fermentation:

$C_nH_mO_p \rightarrow C_2H_5OH + CO_2 + \text{energy}$

Possible fluctuations in concentration levels

1) Higher O_2 levels in the past, upto 25 %

Proof. Current insects about 10 cm
In the past about 50 cm

Probability of forest-fires increases by 70 % with every percent increase in O_2-concentration, leading to decrease in O_2-levels

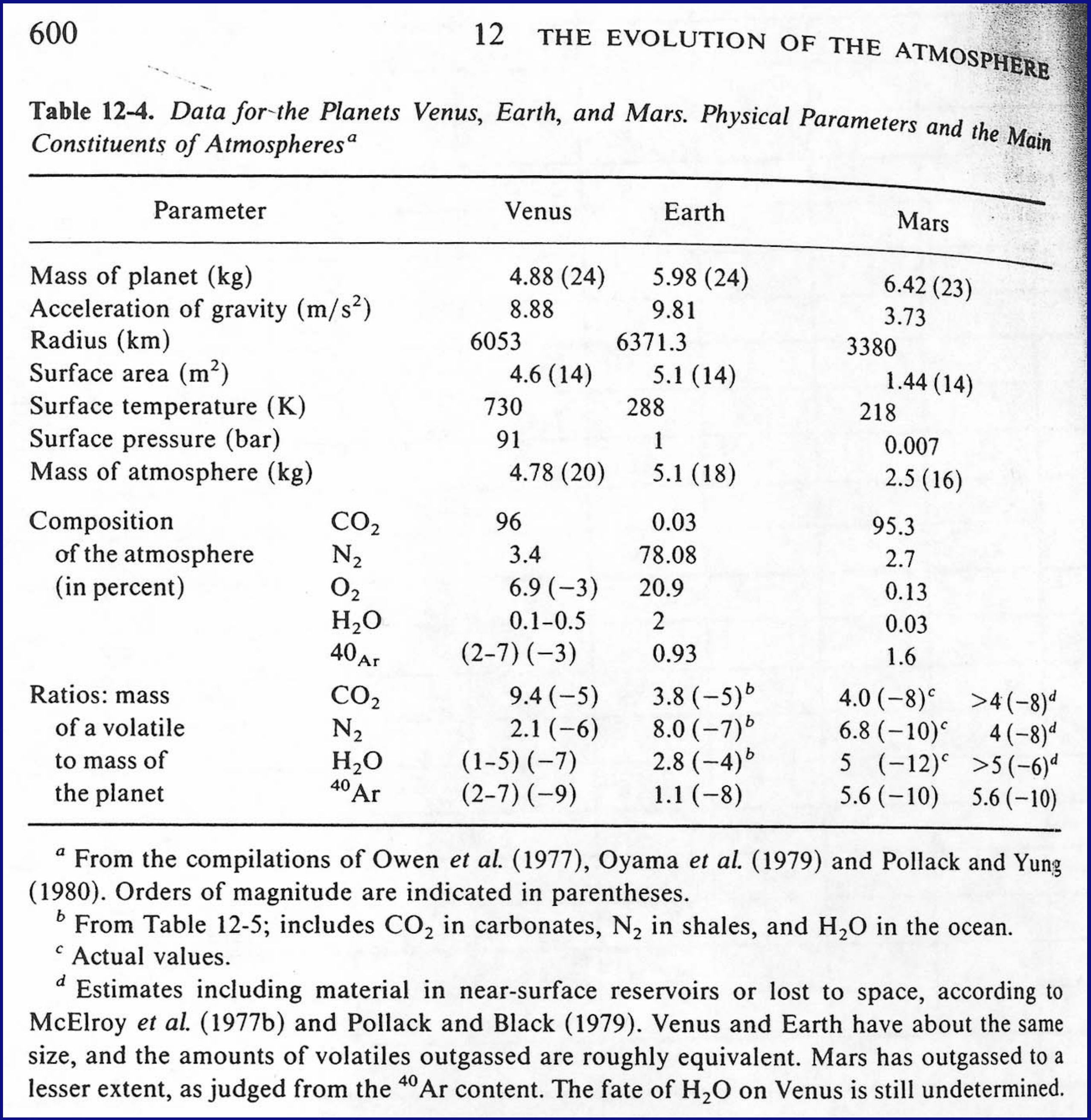


Table 12-4. *Data for the Planets Venus, Earth, and Mars. Physical Parameters and the Main Constituents of Atmospheres*[a]

Parameter		Venus	Earth	Mars	
Mass of planet (kg)		4.88 (24)	5.98 (24)	6.42 (23)	
Acceleration of gravity (m/s^2)		8.88	9.81	3.73	
Radius (km)		6053	6371.3	3380	
Surface area (m^2)		4.6 (14)	5.1 (14)	1.44 (14)	
Surface temperature (K)		730	288	218	
Surface pressure (bar)		91	1	0.007	
Mass of atmosphere (kg)		4.78 (20)	5.1 (18)	2.5 (16)	
Composition of the atmosphere (in percent)	CO_2	96	0.03	95.3	
	N_2	3.4	78.08	2.7	
	O_2	6.9 (−3)	20.9	0.13	
	H_2O	0.1–0.5	2	0.03	
	^{40}Ar	(2–7) (−3)	0.93	1.6	
Ratios: mass of a volatile to mass of the planet	CO_2	9.4 (−5)	3.8 (−5)[b]	4.0 (−8)[c]	>4 (−8)[d]
	N_2	2.1 (−6)	8.0 (−7)[b]	6.8 (−10)[c]	4 (−8)[d]
	H_2O	(1-5) (−7)	2.8 (−4)[b]	5 (−12)[c]	>5 (−6)[d]
	^{40}Ar	(2-7) (−9)	1.1 (−8)	5.6 (−10)	5.6 (−10)

[a] From the compilations of Owen *et al.* (1977), Oyama *et al.* (1979) and Pollack and Yung (1980). Orders of magnitude are indicated in parentheses.

[b] From Table 12-5; includes CO_2 in carbonates, N_2 in shales, and H_2O in the ocean.

[c] Actual values.

[d] Estimates including material in near-surface reservoirs or lost to space, according to McElroy *et al.* (1977b) and Pollack and Black (1979). Venus and Earth have about the same size, and the amounts of volatiles outgassed are roughly equivalent. Mars has outgassed to a lesser extent, as judged from the ^{40}Ar content. The fate of H_2O on Venus is still undetermined.

Io : a satellite of Jupiter. Active volcano’s, atmosphere with SO_2 and O-atoms

Titan : a satellite of Saturn. Possibly pools of liquid CH_4, < 91 K

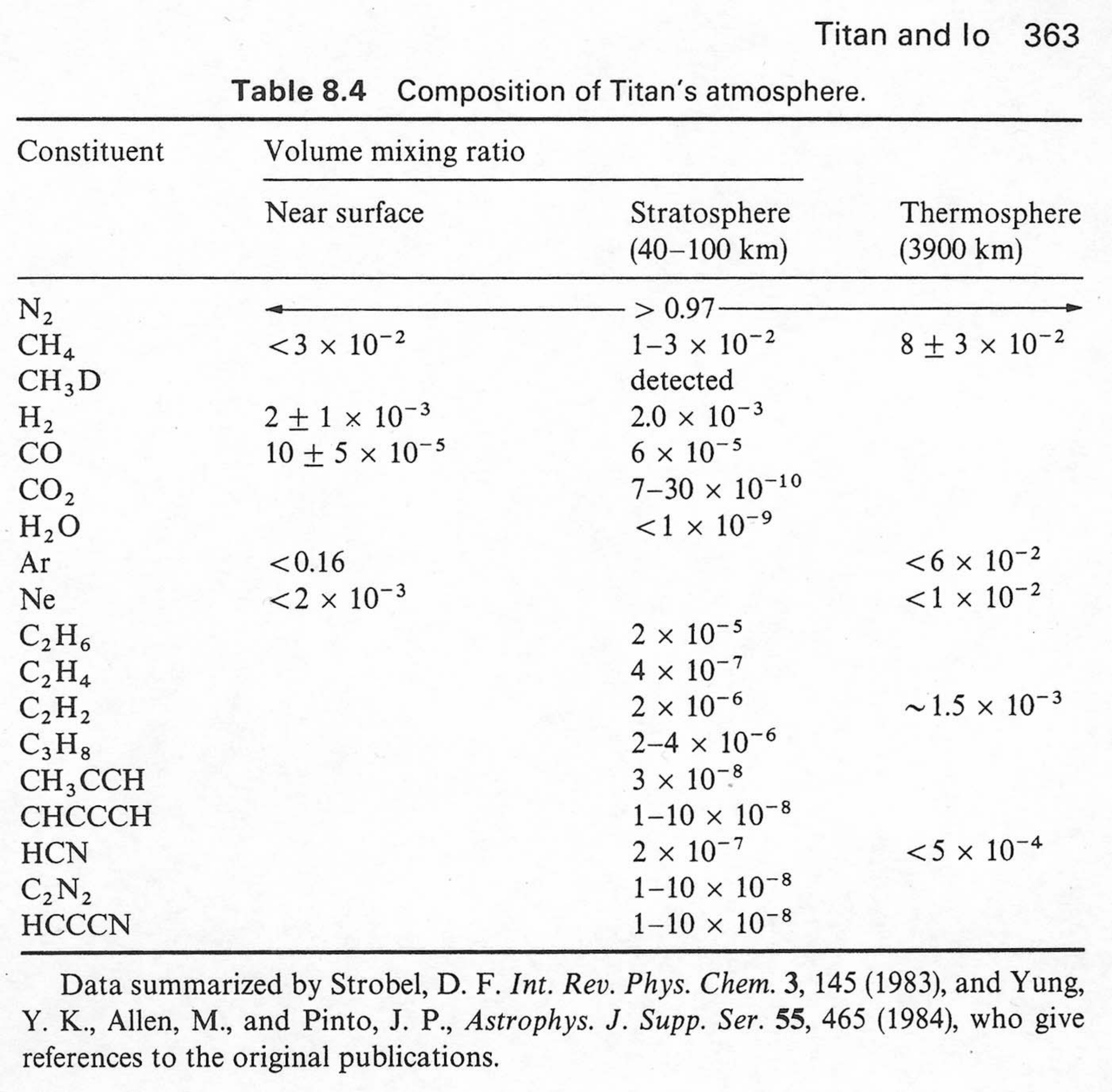


Table 8.4 Composition of Titan's atmosphere.

Constituent	Volume mixing ratio		
	Near surface	Stratosphere (40–100 km)	Thermosphere (3900 km)
N_2	← > 0.97 →		
CH_4	$< 3 \times 10^{-2}$	$1\text{–}3 \times 10^{-2}$	$8 \pm 3 \times 10^{-2}$
CH_3D		detected	
H_2	$2 \pm 1 \times 10^{-3}$	2.0×10^{-3}	
CO	$10 \pm 5 \times 10^{-5}$	6×10^{-5}	
CO_2		$7\text{–}30 \times 10^{-10}$	
H_2O		$< 1 \times 10^{-9}$	
Ar	< 0.16		$< 6 \times 10^{-2}$
Ne	$< 2 \times 10^{-3}$		$< 1 \times 10^{-2}$
C_2H_6		2×10^{-5}	
C_2H_4		4×10^{-7}	
C_2H_2		2×10^{-6}	$\sim 1.5 \times 10^{-3}$
C_3H_8		$2\text{–}4 \times 10^{-6}$	
CH_3CCH		3×10^{-8}	
CHCCCH		$1\text{–}10 \times 10^{-8}$	
HCN		2×10^{-7}	$< 5 \times 10^{-4}$
C_2N_2		$1\text{–}10 \times 10^{-8}$	
HCCCN		$1\text{–}10 \times 10^{-8}$	

Data summarized by Strobel, D. F. *Int. Rev. Phys. Chem.* **3**, 145 (1983), and Yung, Y. K., Allen, M., and Pinto, J. P., *Astrophys. J. Supp. Ser.* **55**, 465 (1984), who give references to the original publications.

The chemical composition of the atmosphere is far from equilibrium

		Present world	Equilibrium world
Air	CO_2	0.03	99
	N_2	78	0
	O_2	21	~ 0
	Ar	1	1
Ocean	H_2O	96	63
	NaCl	3.5	35
	$NaNO_3$	~ O	1.7

Live is the deviation from equilibrium, the living planet

Gaia hypothesis : **James Lovelock**

Homeostasis : **The eco-system creates the atmosphere, the environment, in which it feels well**

The system contains numerous (delicate) feed-back mechanisms to keep the balance

Capacity of control

Doom-scenario I

New micro-organisms appear:

They kill the plants/forests

CO_2 rises

T > 100 °C

H_2O-vapour to stratosphere

$H_2O + h\nu \rightarrow H_2 + O$

H_2 escapes to space

$3O + N_2 \rightarrow 2NO_3$

NO_3 desolves in the sea, before evaporation

Results in CO_2-atmosphere at high temperatures: Venus

Doom-scenario II

New micro-organisms appear:

They consume nearly all CO_2

CO_2 decreases

T decreases to ~ -10 / -15 °C

Atmosphere with some CO_2, some H_2O: Mars

Current composition of the earth atmosphere

N_2	78.09 %
O_2	20.95 %, very minor decrease by increase of CO_2
Ar	0.93 %
CO_2	0.0036 %, equals 360 ppm, pre-industrial 270 ppm
Ne	18.2 ppm
He	5.24 ppm
CH_4	1.8 ppm = 1800 ppb, pre-industrial 600 ppb
Kr	1140 ppb

Composition of the dry atmosphere, H_2O-vapour between 0.02-4 % in the troposphere

Units

ppm : parts per million : 10^{-6}
ppb : parts per billion : 10^{-9}
ppt : parts per trillion : 10^{-12}

Nearly always : volume ratio: ppm (ν)
Sometimes : mass ratio

Example : O_2: 20.95 % is volume ratio (ν)

Moleculair weight O_2 : 32
Averaged moleculair weight air : 29
O_2 mass-ratio : 20.95 x 32/29 = 23.1 % (m)

Also used, especially in air quality: mass/volume:
gr/m^3, or µgr/m^3 (10^{-6} gr)

ppm (ν) = RT/pMi x conc. in µgr/m^3

Mi is moleculair weight

So, µgr/m^3 is function from T and p
Often µgr/m^3 STP = standard temperature and pressure:
1013 hPa and 20 °C (293 K)

Atmospheric residence time

The earth + atmosphere is a (nearly) closed system
(only not for H_2, but the sun-wind contains protons~
no effective loss of H_2)

Definition: The mean residence time of a gasmolecule:
t = mass of gas in the atmosphere / emission per time-unit
= mass ... / sink per time unit

In case of equilibrium

Emission : Anthropogenic and/or biogenic and/or natural (geogenic)

Sink : dry deposition and/or wet deposition and/or chemical conversion

Example

Total mass of the atmosphere : $5.15\ 10^{18}$ kg

(total mass of the oceans:
$1.4\ 10^{21}$ kg, mass of the earth : $6.0\ 10^{24}$ kg)
N_2 . 78 % $3.9\ 10^{18}$ kg

N_2-emission . biogenic : 10^{12} kg/year
anthropogenic : $0.06\ 10^{12}$ kg/year

$t = 3.9\ 10^{6}$ year

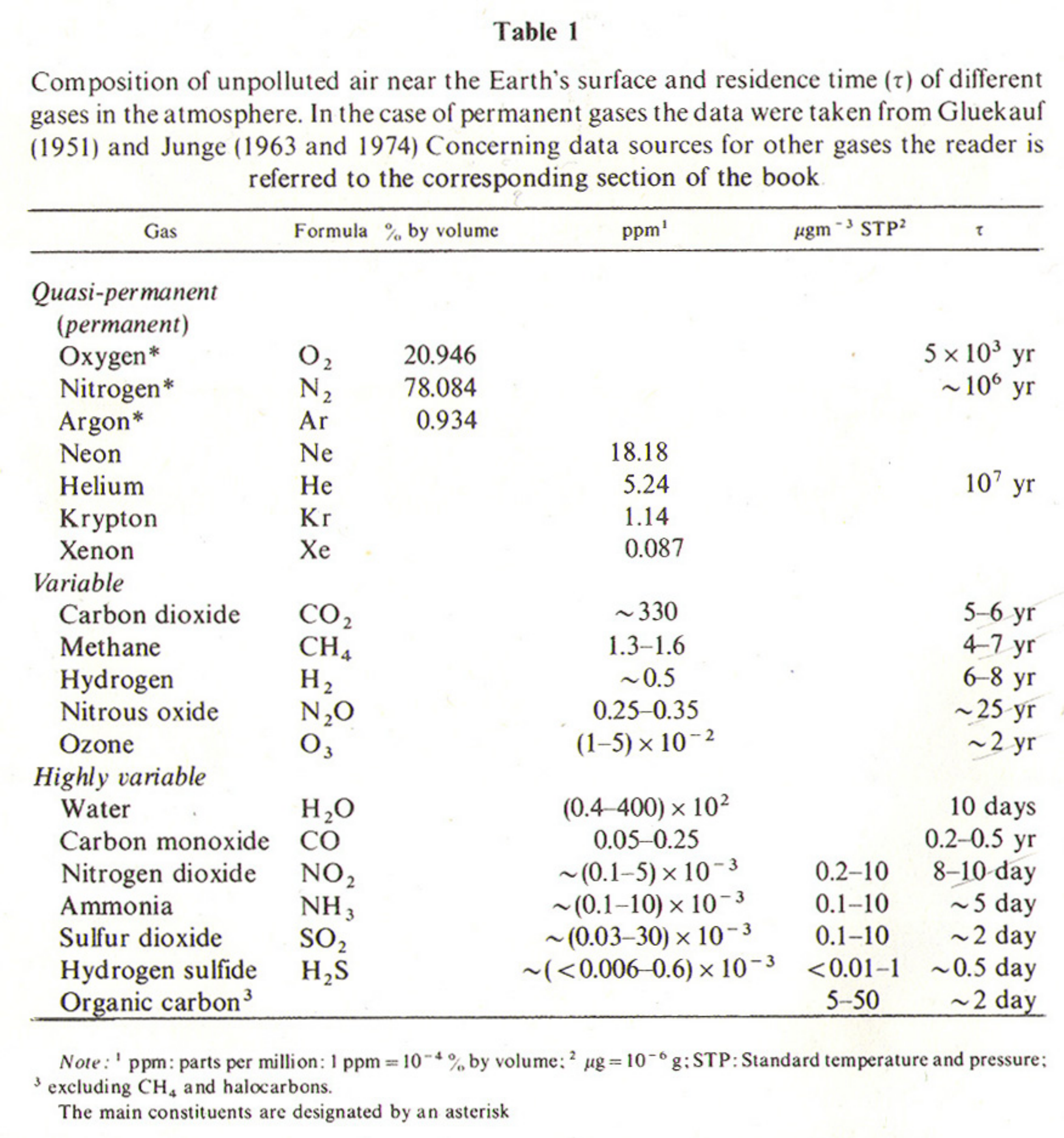


Table 1

Composition of unpolluted air near the Earth's surface and residence time (τ) of different gases in the atmosphere. In the case of permanent gases the data were taken from Gluekauf (1951) and Junge (1963 and 1974) Concerning data sources for other gases the reader is referred to the corresponding section of the book

Gas	Formula	% by volume	ppm[1]	μgm^{-3} STP[2]	τ
Quasi-permanent					
(permanent)					
Oxygen*	O_2	20.946			5×10^3 yr
Nitrogen*	N_2	78.084			$\sim 10^6$ yr
Argon*	Ar	0.934			
Neon	Ne		18.18		
Helium	He		5.24		10^7 yr
Krypton	Kr		1.14		
Xenon	Xe		0.087		
Variable					
Carbon dioxide	CO_2		~ 330		5–6 yr
Methane	CH_4		1.3–1.6		4–7 yr
Hydrogen	H_2		~ 0.5		6–8 yr
Nitrous oxide	N_2O		0.25–0.35		~ 25 yr
Ozone	O_3		$(1–5) \times 10^{-2}$		~ 2 yr
Highly variable					
Water	H_2O		$(0.4–400) \times 10^2$		10 days
Carbon monoxide	CO		0.05–0.25		0.2–0.5 yr
Nitrogen dioxide	NO_2		$\sim (0.1–5) \times 10^{-3}$	0.2–10	8–10 day
Ammonia	NH_3		$\sim (0.1–10) \times 10^{-3}$	0.1–10	~ 5 day
Sulfur dioxide	SO_2		$\sim (0.03–30) \times 10^{-3}$	0.1–10	~ 2 day
Hydrogen sulfide	H_2S		$\sim (< 0.006–0.6) \times 10^{-3}$	$< 0.01–1$	~ 0.5 day
Organic carbon[3]				5–50	~ 2 day

Note: [1] ppm: parts per million: 1 ppm = 10^{-4} % by volume; [2] $\mu g = 10^{-6}$ g; STP: Standard temperature and pressure; [3] excluding CH_4 and halocarbons.

The main constituents are designated by an asterisk

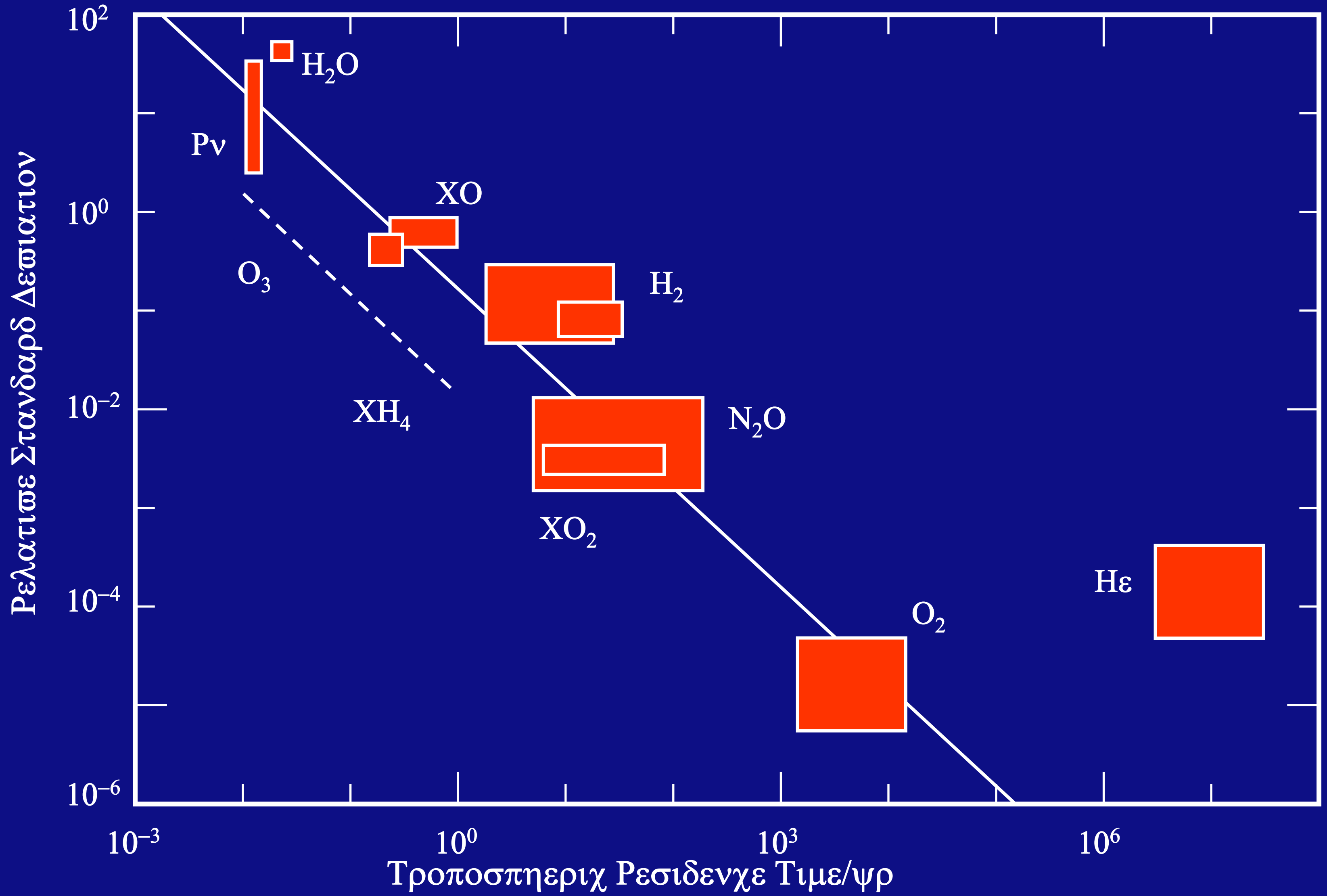
Junge's law

$$C = \bar{C} + C^{*} \text{ (fluctuation)}$$

$$C^{1} = \sqrt{\overline{C^{*2}}}$$

$$\frac{C^{1}}{\bar{C}} = a.T^{-b}$$

T in years; $a = 2.16.10^{-2}$; $b = 0.95$



Regel van Junge: Empirisch getrokken lijn

$C^1 / \overline{C} = a\ T^{-b}$ a: $2.16.10^{-2}$ gestippelde lijn: $C^1 / C\ .\ T = 0.14$

b: 0.95 Dus: grote spreiding

T in jaren

Atmospheric mixing time scales

Troposphere, zonal average ≈ 2 weeks

Troposphere, global ≈ 1-2 years

Troposphere + stratosphere, global ≈ 2-5 years

Small τ: large variation in concentration in time and place

Large τ: constant (not at sources/sinks)

Some general concepts concerning global circulation and transport / turbulent diffusion

Some general concepts concerning chemistry, photo-chemistry, radiation

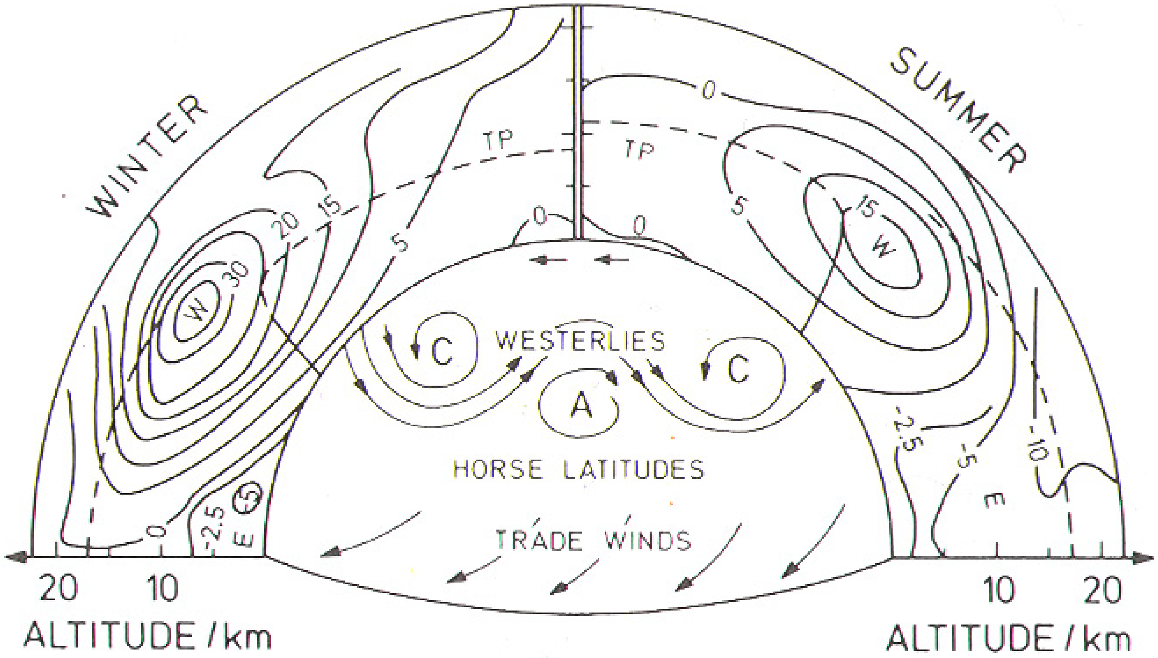


Fig. 1-6. Mean zonal circulation in the northern hemisphere, 0–20 km. Distribution of wind velocities (in units of m/s) was taken from Labitzke (1980). W, Mean winds from the west; E, mean winds from the east; the heavy lines indicate the approximate location of the polar front, the broken lines the tropopause. The maximum wind speed coincides approximately with the subtropical jet stream. The location of the polar jet fluctuates considerably and does not show up in the average. The center is to illustrate wind directions near the earth surface (trade winds and westerlies); cyclones (C) and anticyclones (A) imbedded in the westerlies are only sketched; the frontal systems associated with cyclones cannot be shown in this extremely simplified diagram.

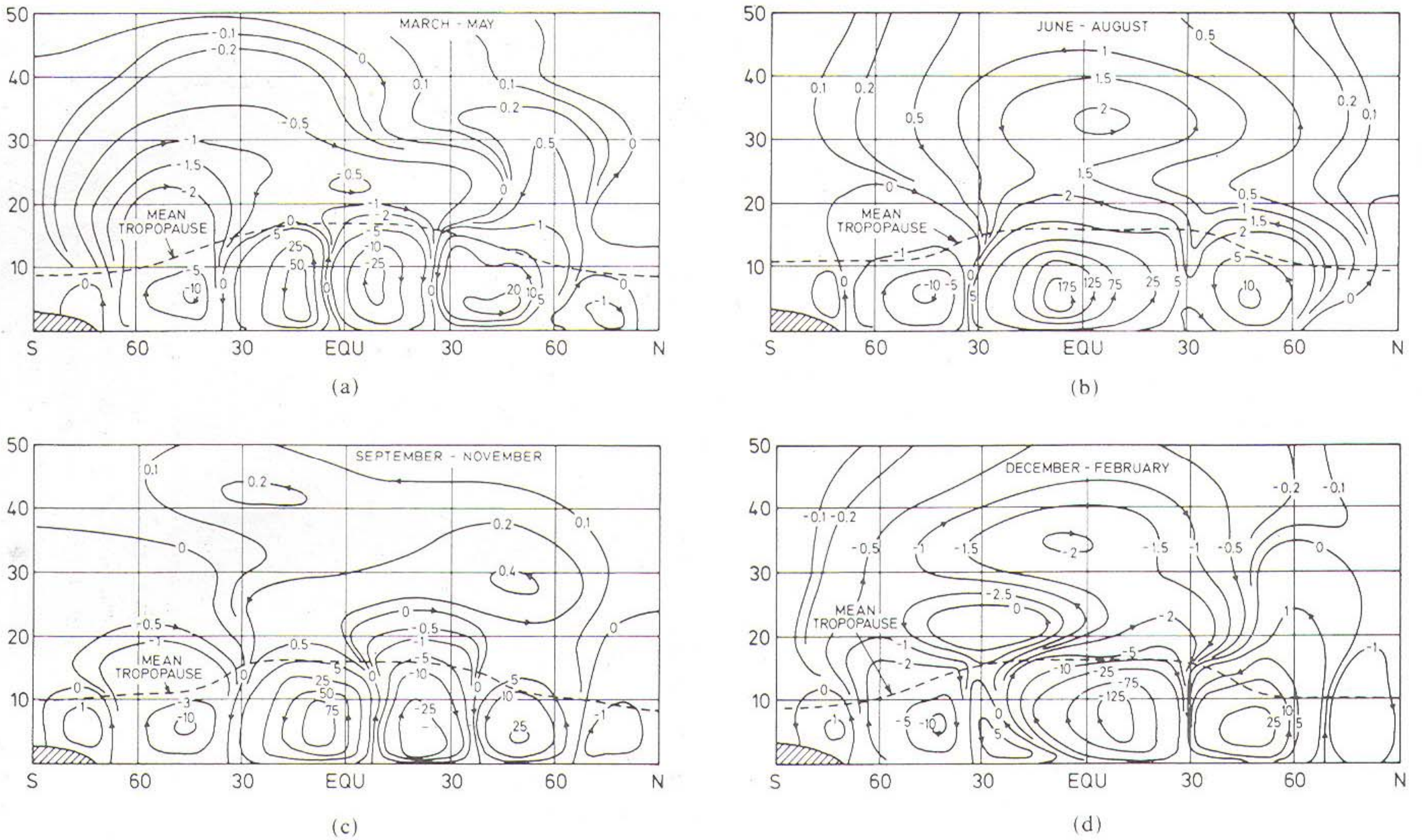


Fig. 1-7. Mean meridional circulation. [Adapted from Louis (1975); below 15 km from Newell *et al.* (1972).] (a) December–February. (b) March–May. (c) June–August. (d) September–November; mass stream lines in units of Tg/s.

Turbulent diffusion / Eddy diffusion is essential to describe the concentration patterns

Kz ~ 1-10 m^2/s

Ky ~ 2.10^{+6} m^2/s

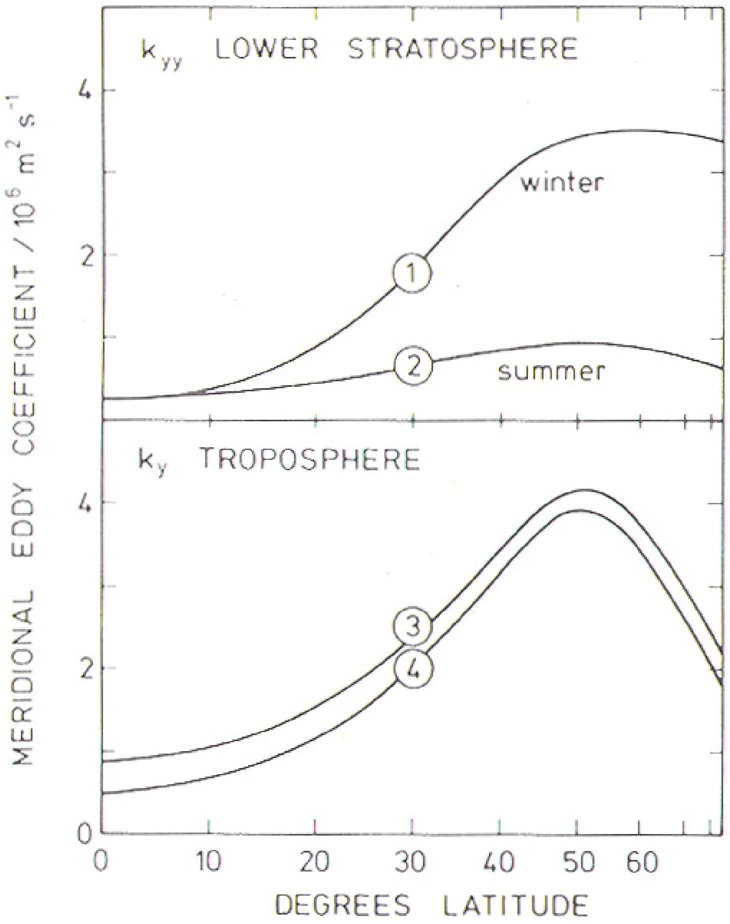


Fig. 1-8. Eddy diffusion coefficients in the northern hemisphere. Upper frame: Lower stratosphere (100 mbar, about 16 km altitude); curve 1 for December-January, curve 2 for June-August, approximated from Luther (1975) and Hidalgo and Crutzen (1977). Lower frame: One-dimensional K_y values for the troposphere after Czeplak and Junge (1974); curve 3 based on wind variance data of Flohn (1961) and Newell *et al.* (1966); curve 4 based on data of Newell *et al.* (1972), annual average.

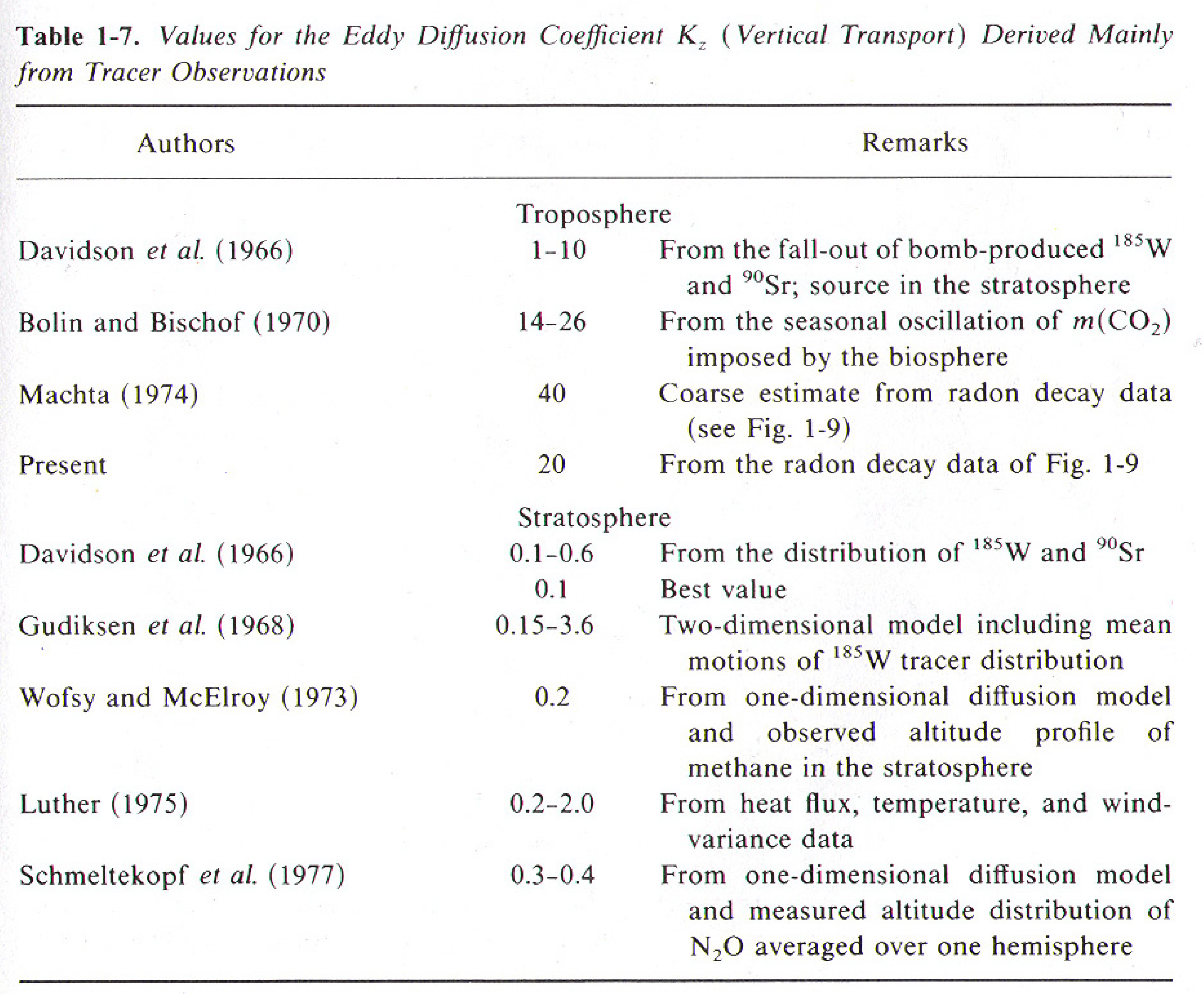


Table 1-7. *Values for the Eddy Diffusion Coefficient K_z (Vertical Transport) Derived Mainly from Tracer Observations*

Authors		Remarks
	Troposphere	
Davidson *et al.* (1966)	1–10	From the fall-out of bomb-produced ^{185}W and ^{90}Sr; source in the stratosphere
Bolin and Bischof (1970)	14–26	From the seasonal oscillation of $m(CO_2)$ imposed by the biosphere
Machta (1974)	40	Coarse estimate from radon decay data (see Fig. 1-9)
Present	20	From the radon decay data of Fig. 1-9
	Stratosphere	
Davidson *et al.* (1966)	0.1–0.6	From the distribution of ^{185}W and ^{90}Sr
	0.1	Best value
Gudiksen *et al.* (1968)	0.15–3.6	Two-dimensional model including mean motions of ^{185}W tracer distribution
Wofsy and McElroy (1973)	0.2	From one-dimensional diffusion model and observed altitude profile of methane in the stratosphere
Luther (1975)	0.2–2.0	From heat flux, temperature, and wind-variance data
Schmeltekopf *et al.* (1977)	0.3–0.4	From one-dimensional diffusion model and measured altitude distribution of N_2O averaged over one hemisphere

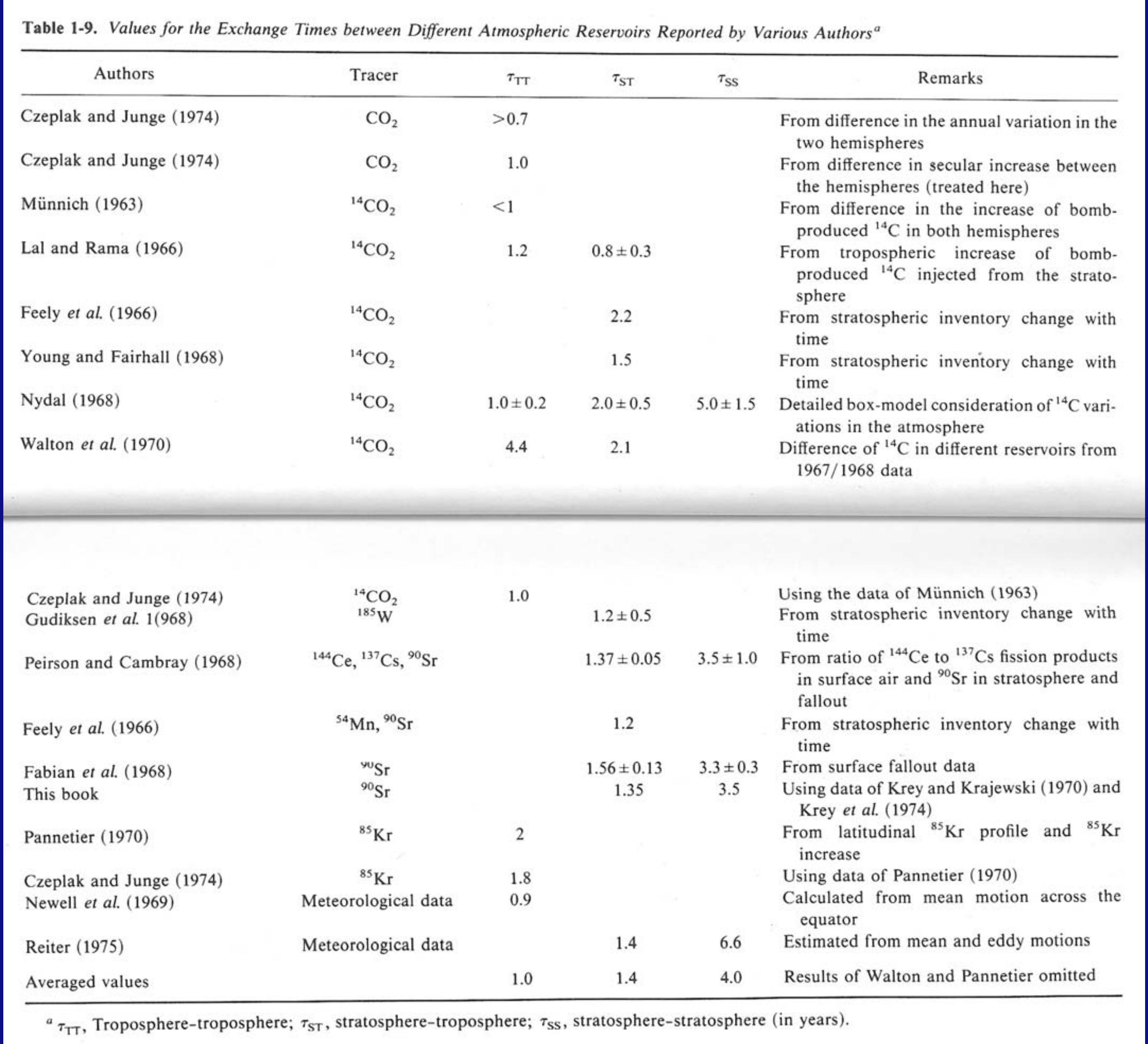


Table 1-9. *Values for the Exchange Times between Different Atmospheric Reservoirs Reported by Various Authors*[a]

Authors	Tracer	τ_{TT}	τ_{ST}	τ_{SS}	Remarks
Czeplak and Junge (1974)	CO_2	>0.7			From difference in the annual variation in the two hemispheres
Czeplak and Junge (1974)	CO_2	1.0			From difference in secular increase between the hemispheres (treated here)
Münnich (1963)	$^{14}CO_2$	<1			From difference in the increase of bomb-produced ^{14}C in both hemispheres
Lal and Rama (1966)	$^{14}CO_2$	1.2	0.8 ± 0.3		From tropospheric increase of bomb-produced ^{14}C injected from the stratosphere
Feely *et al.* (1966)	$^{14}CO_2$		2.2		From stratospheric inventory change with time
Young and Fairhall (1968)	$^{14}CO_2$		1.5		From stratospheric inventory change with time
Nydal (1968)	$^{14}CO_2$	1.0 ± 0.2	2.0 ± 0.5	5.0 ± 1.5	Detailed box-model consideration of ^{14}C variations in the atmosphere
Walton *et al.* (1970)	$^{14}CO_2$	4.4	2.1		Difference of ^{14}C in different reservoirs from 1967/1968 data
Czeplak and Junge (1974)	$^{14}CO_2$	1.0			Using the data of Münnich (1963)
Gudiksen *et al.* 1(968)	^{185}W		1.2 ± 0.5		From stratospheric inventory change with time
Peirson and Cambray (1968)	^{144}Ce, ^{137}Cs, ^{90}Sr		1.37 ± 0.05	3.5 ± 1.0	From ratio of ^{144}Ce to ^{137}Cs fission products in surface air and ^{90}Sr in stratosphere and fallout
Feely *et al.* (1966)	^{54}Mn, ^{90}Sr		1.2		From stratospheric inventory change with time
Fabian *et al.* (1968)	^{90}Sr		1.56 ± 0.13	3.3 ± 0.3	From surface fallout data
This book	^{90}Sr		1.35	3.5	Using data of Krey and Krajewski (1970) and Krey *et al.* (1974)
Pannetier (1970)	^{85}Kr	2			From latitudinal ^{85}Kr profile and ^{85}Kr increase
Czeplak and Junge (1974)	^{85}Kr	1.8			Using data of Pannetier (1970)
Newell *et al.* (1969)	Meteorological data	0.9			Calculated from mean motion across the equator
Reiter (1975)	Meteorological data		1.4	6.6	Estimated from mean and eddy motions
Averaged values		1.0	1.4	4.0	Results of Walton and Pannetier omitted

[a] τ_{TT}, Troposphere-troposphere; τ_{ST}, stratosphere-troposphere; τ_{SS}, stratosphere-stratosphere (in years).

Chemical reactions occur by adding energy to the system: By – elevated – temperature or by radiation.

In the atmosphere the strongest driving force is radiation, sunlight, so photo-chemistry. Thermal reactions are less important.

Some aspects: Mass-conservation. Stoichiometry

Example: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (only at $T > 400$ °C)

This is the overall reaction

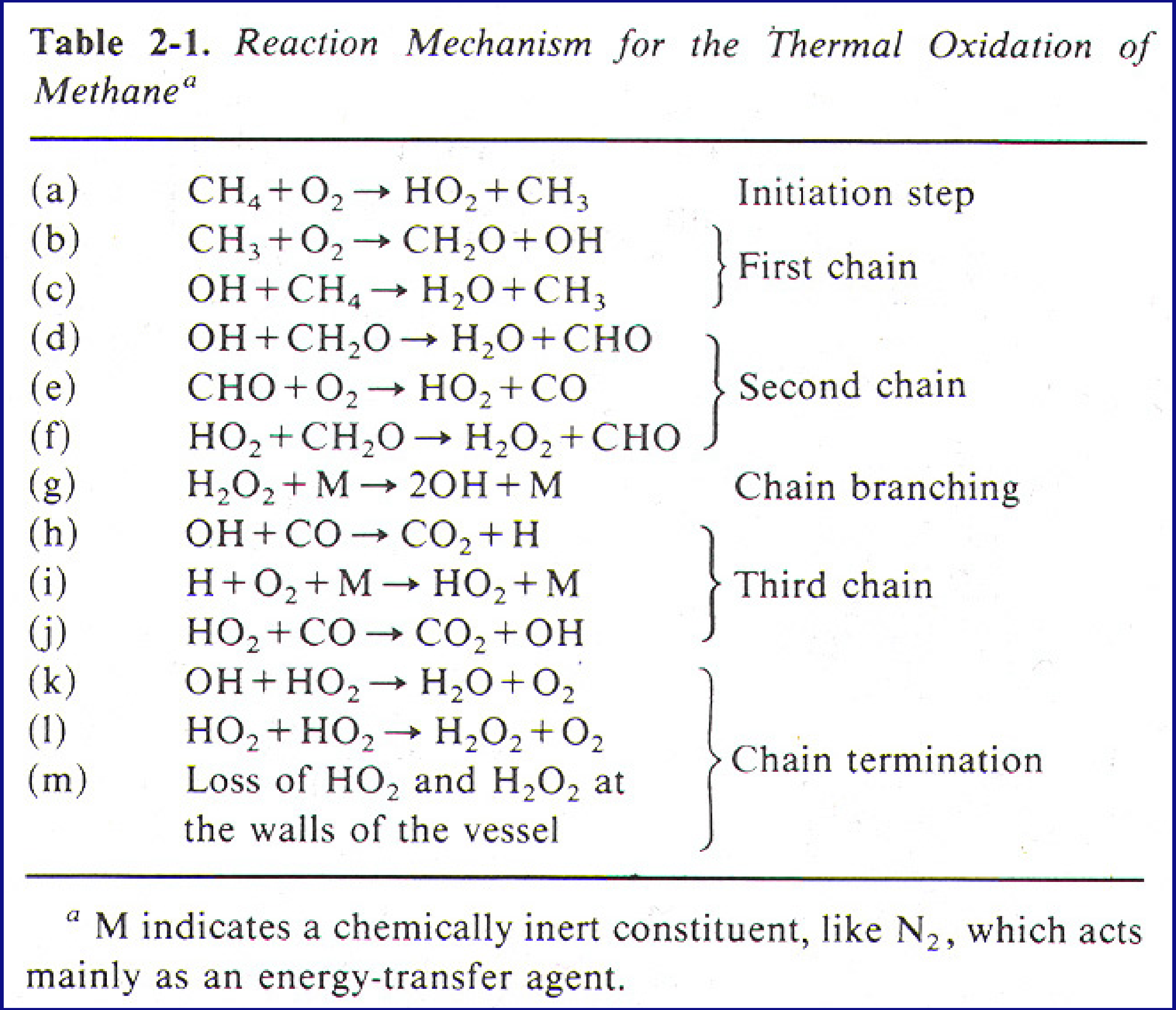


Table 2-1. *Reaction Mechanism for the Thermal Oxidation of Methane*[a]

(a)	$CH_4 + O_2 \rightarrow HO_2 + CH_3$	Initiation step
(b)	$CH_3 + O_2 \rightarrow CH_2O + OH$	First chain
(c)	$OH + CH_4 \rightarrow H_2O + CH_3$	
(d)	$OH + CH_2O \rightarrow H_2O + CHO$	Second chain
(e)	$CHO + O_2 \rightarrow HO_2 + CO$	
(f)	$HO_2 + CH_2O \rightarrow H_2O_2 + CHO$	
(g)	$H_2O_2 + M \rightarrow 2OH + M$	Chain branching
(h)	$OH + CO \rightarrow CO_2 + H$	Third chain
(i)	$H + O_2 + M \rightarrow HO_2 + M$	
(j)	$HO_2 + CO \rightarrow CO_2 + OH$	
(k)	$OH + HO_2 \rightarrow H_2O + O_2$	Chain termination
(l)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	
(m)	Loss of HO_2 and H_2O_2 at the walls of the vessel	

[a] M indicates a chemically inert constituent, like N_2, which acts mainly as an energy-transfer agent.

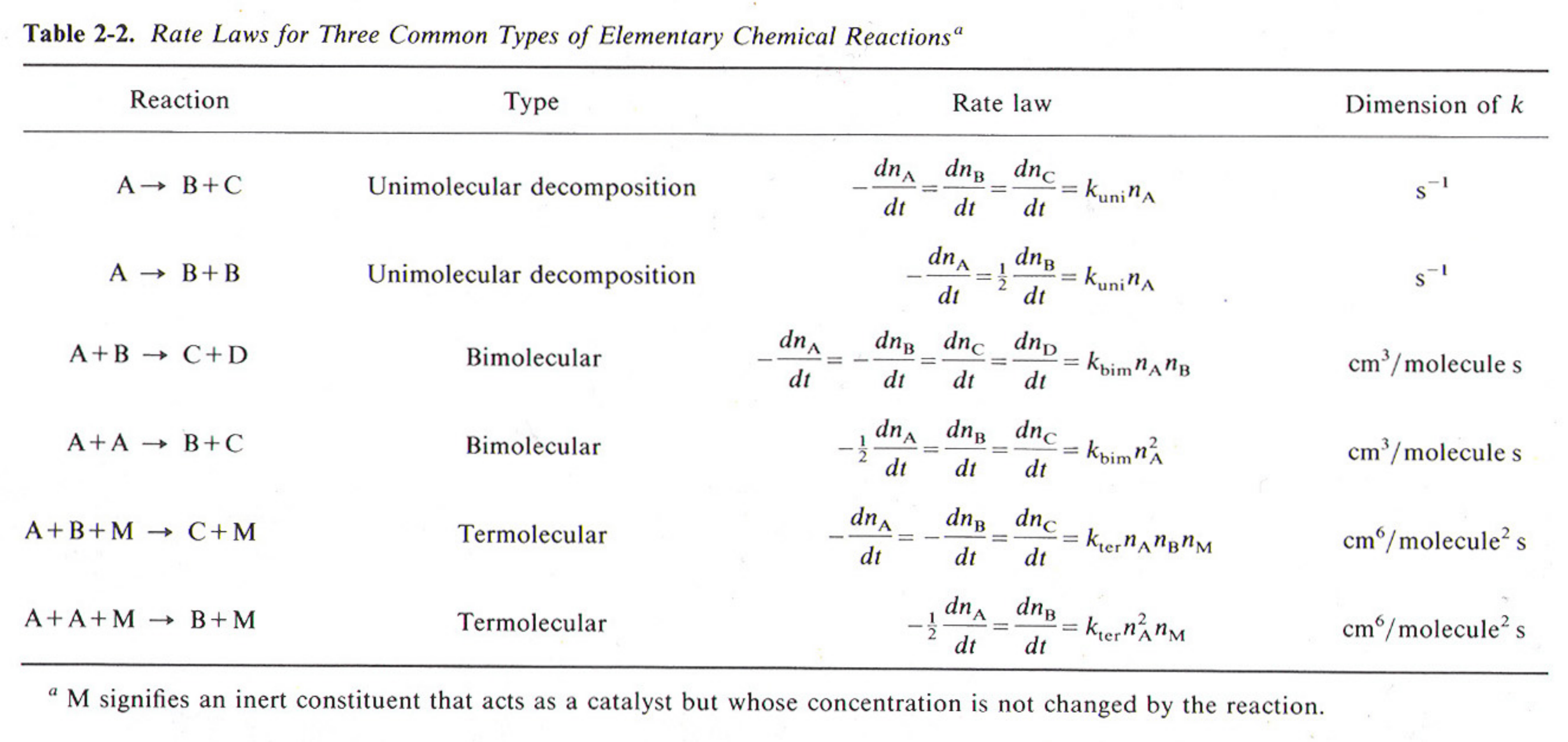
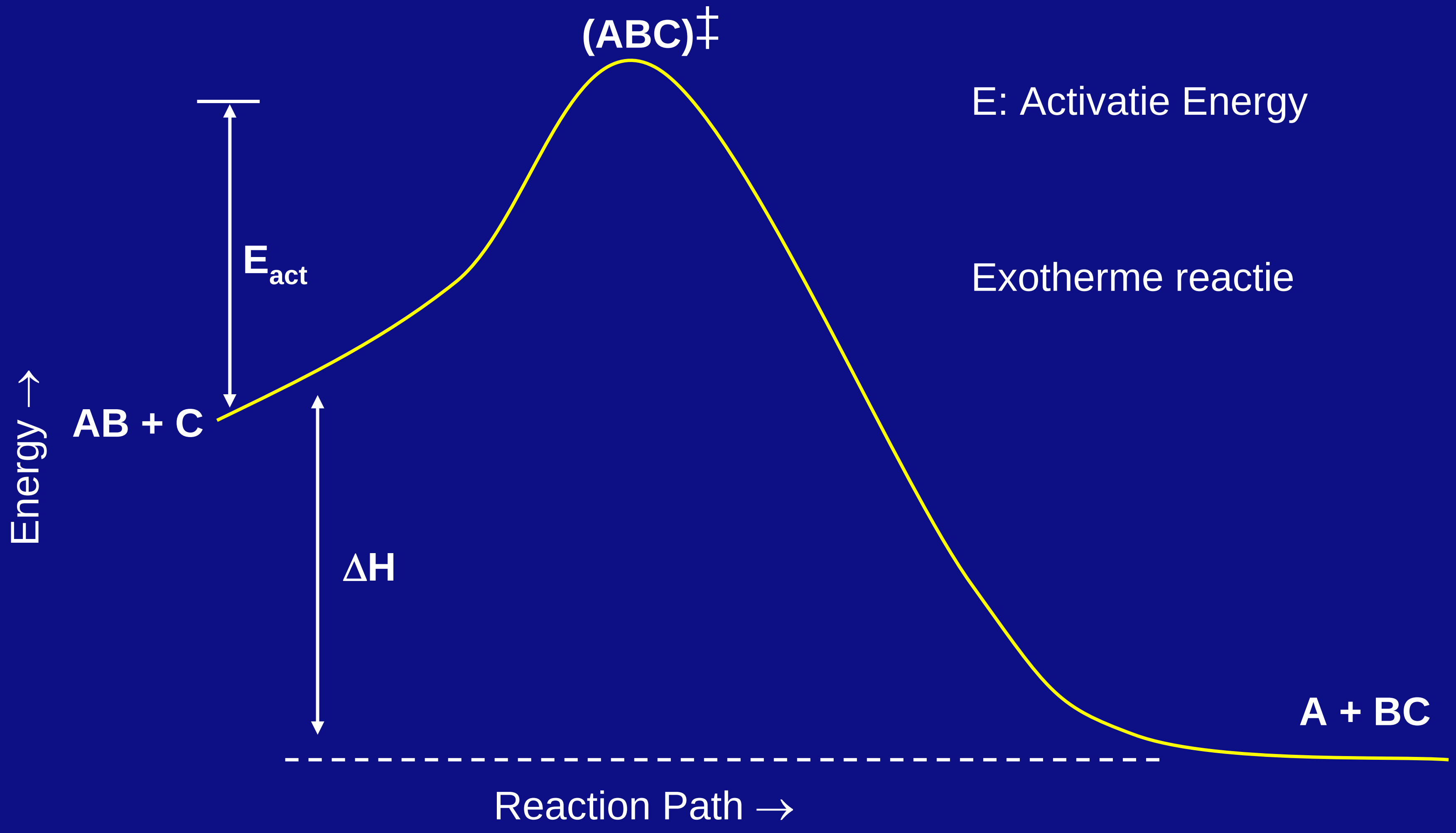


Table 2-2. *Rate Laws for Three Common Types of Elementary Chemical Reactions*[a]

Reaction	Type	Rate law	Dimension of *k*
$A \rightarrow B + C$	Unimolecular decomposition	$-\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt} = k_{uni} n_A$	s^{-1}
$A \rightarrow B + B$	Unimolecular decomposition	$-\frac{dn_A}{dt} = \frac{1}{2}\frac{dn_B}{dt} = k_{uni} n_A$	s^{-1}
$A + B \rightarrow C + D$	Bimolecular	$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \frac{dn_C}{dt} = \frac{dn_D}{dt} = k_{bim} n_A n_B$	$cm^3/molecule\ s$
$A + A \rightarrow B + C$	Bimolecular	$-\frac{1}{2}\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt} = k_{bim} n_A^2$	$cm^3/molecule\ s$
$A + B + M \rightarrow C + M$	Termolecular	$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \frac{dn_C}{dt} = k_{ter} n_A n_B n_M$	$cm^6/molecule^2\ s$
$A + A + M \rightarrow B + M$	Termolecular	$-\frac{1}{2}\frac{dn_A}{dt} = \frac{dn_B}{dt} = k_{ter} n_A^2 n_M$	$cm^6/molecule^2\ s$

[a] M signifies an inert constituent that acts as a catalyst but whose concentration is not changed by the reaction.



E: Activatie Energy

Exotherme reactie

Depiction of the transition state for a bimolecular reaction

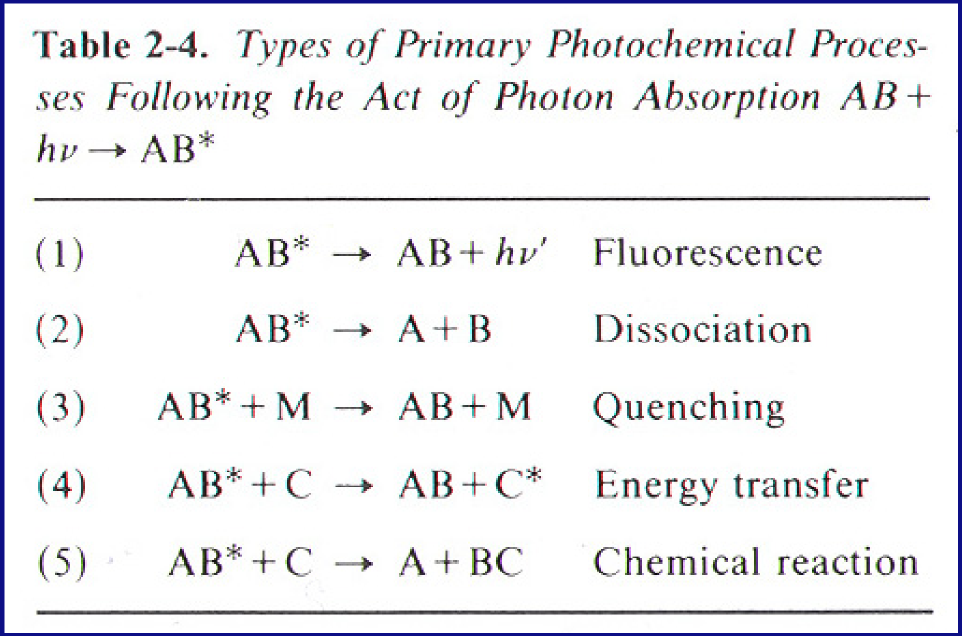


Table 2-4. *Types of Primary Photochemical Processes Following the Act of Photon Absorption* $AB + h\nu \rightarrow AB^*$

(1)	$AB^* \rightarrow AB + h\nu'$	Fluorescence
(2)	$AB^* \rightarrow A + B$	Dissociation
(3)	$AB^* + M \rightarrow AB + M$	Quenching
(4)	$AB^* + C \rightarrow AB + C^*$	Energy transfer
(5)	$AB^* + C \rightarrow A + BC$	Chemical reaction

$AB + h\nu \rightarrow A + B$ (dissociation)

$$\frac{dn_{ab}}{dt} = n_{ab} \, . \, j_i$$

j_i = photo-dissociation constant

$$j_i = \int_{\Delta\lambda} \varnothing_i \, (\lambda) \, \sigma_{ab} \, (\lambda) \, I \, (\lambda) \, d \, \lambda$$

$\varnothing_i \, (\lambda)$: Quantum yield

$$= \frac{\text{product molecules formed/cm}^3\text{ s}}{\text{photons absorbed/cm}^3\text{ s}}$$

$\sigma_{ab}(\lambda)$: Absorption cross-section

$I(\lambda)$: Local photo flux

$I_{total} = I_{direct}$ (taking into account absorption)

$+ I_{diffuse}$

$+ I_{reflected}$ (at earth surface and clouds)

Attenuation of solar radiation in the atmosphere

UV-A	**100 - 280 nm**
UV-B	**280 - 315 nm**
UV-C	**315 - 400 nm**
Visible light	**400 - 800 nm**
Infra-red	**> 800 nm**

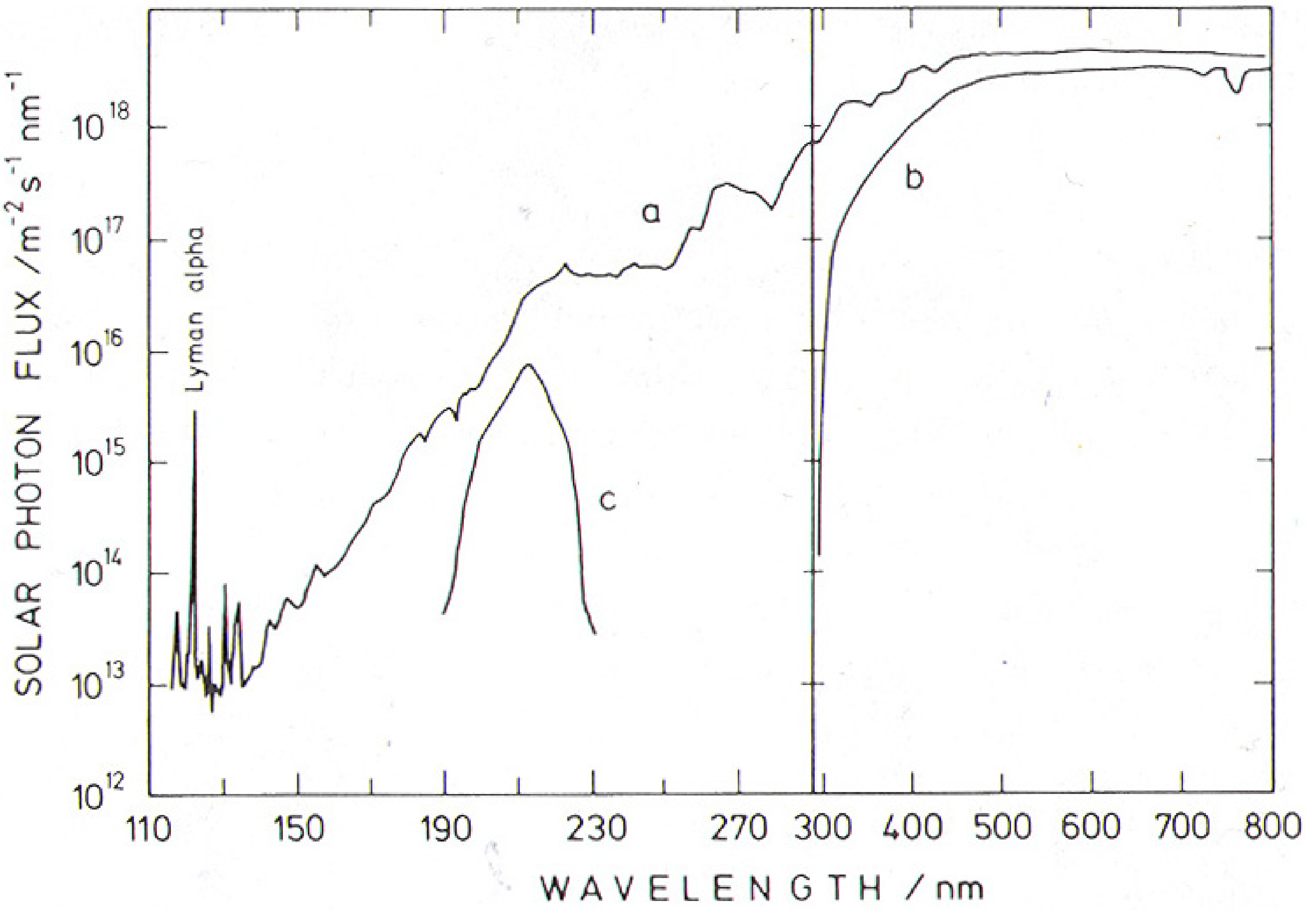


Fig. 2-5. The solar flux spectrum in the 120–800 nm wavelength region (a) outside the earth atmosphere, (b) at sea level, and (c) at about 30 km altitude to show the atmospheric window in the 185–215 nm wavelength region.

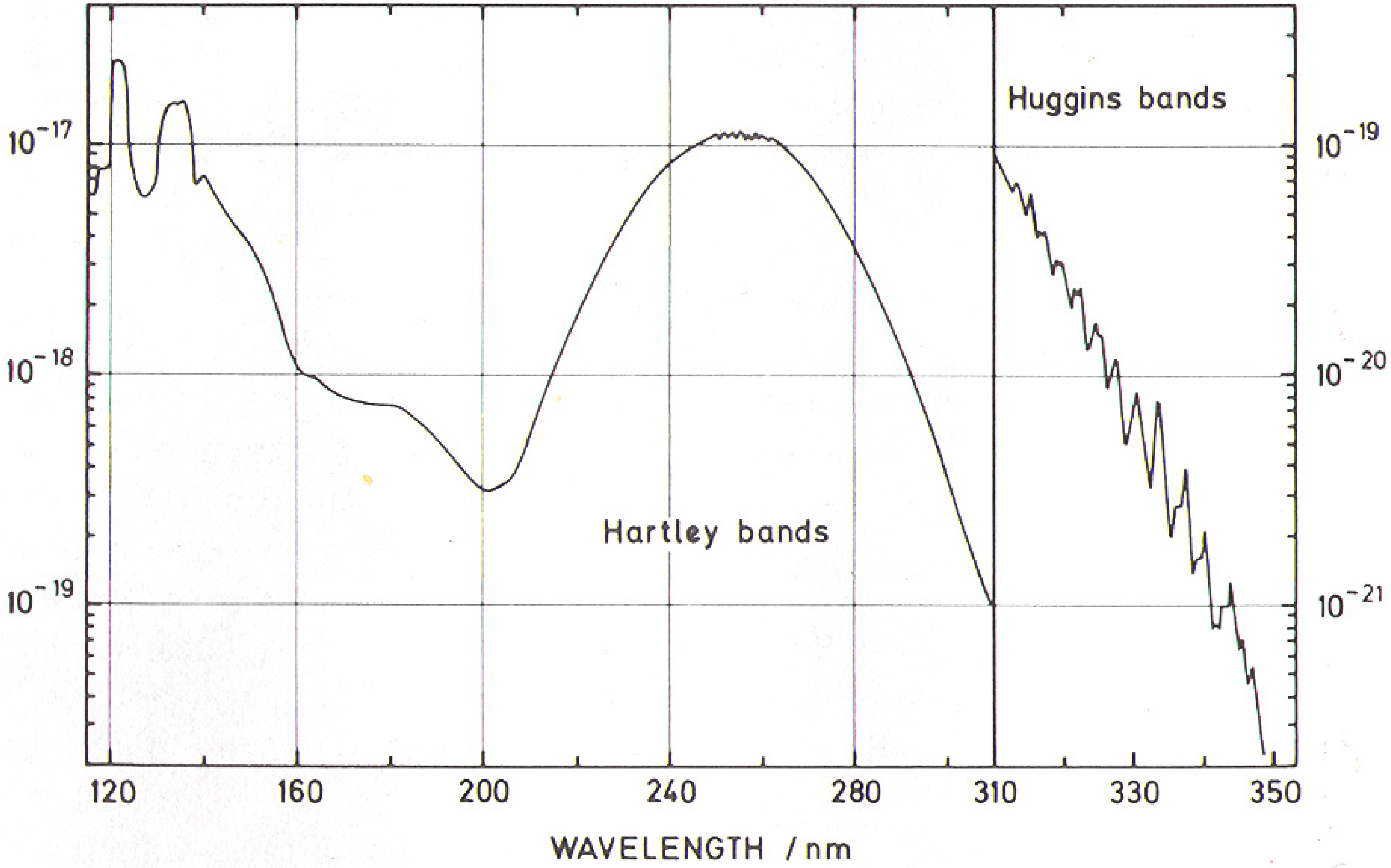


Fig. 2-8. Absorption spectrum of ozone in the wavelength region 115–350 nm, with cross sections given in units of cm^2/molecule. Data used are from Inn and Tanaka (1953), Tanaka *et al.* (1953), and Griggs (1968).

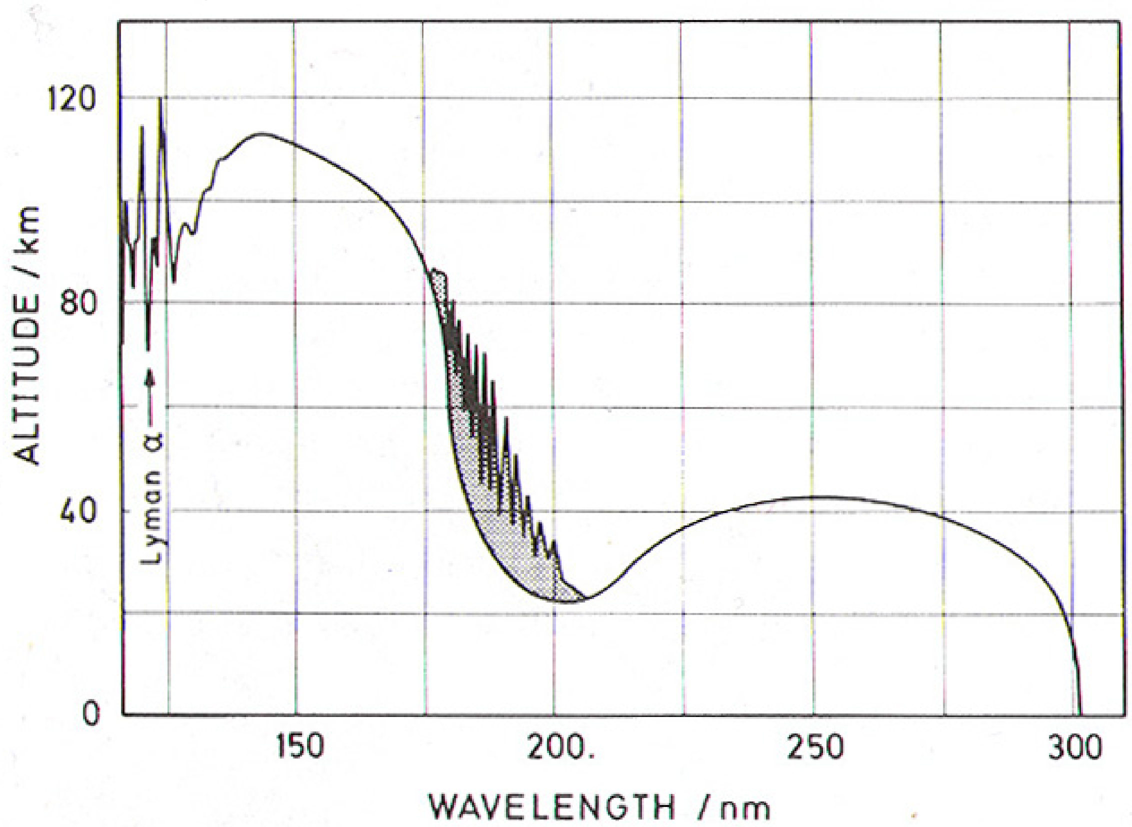


Fig. 2-9. Altitude at which incoming solar radiation from an overhead sun is attenuated to one-tenth the initial intensity.

Stratospheric chemistry and other trace gases

First, some observations

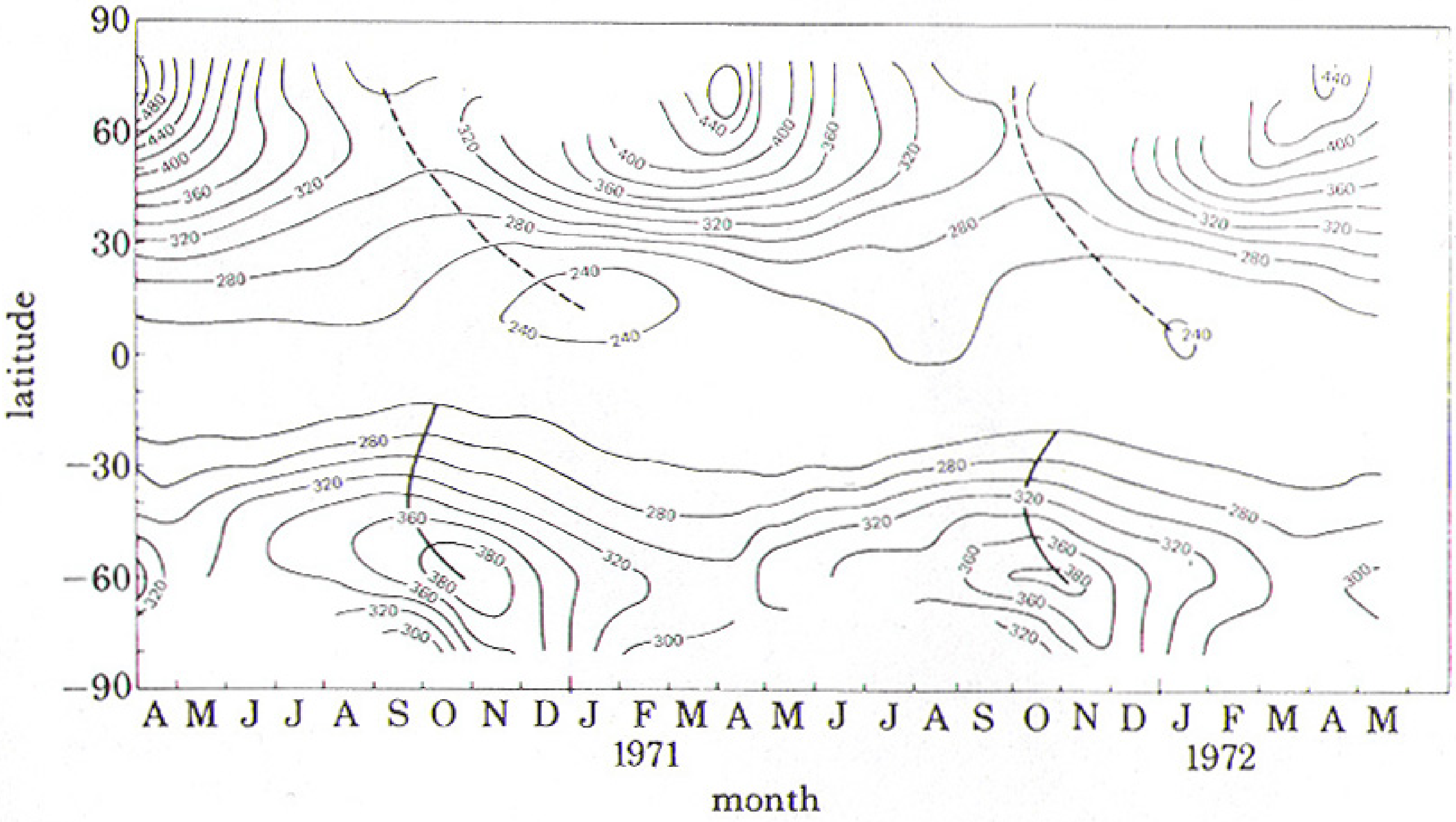


Fig. 3-1. Total ozone versus time and latitude as derived from 10° zonal means of *Nimbus* 4 satellite data. [From Hilsenrath *et al.* (1979), with permission.]

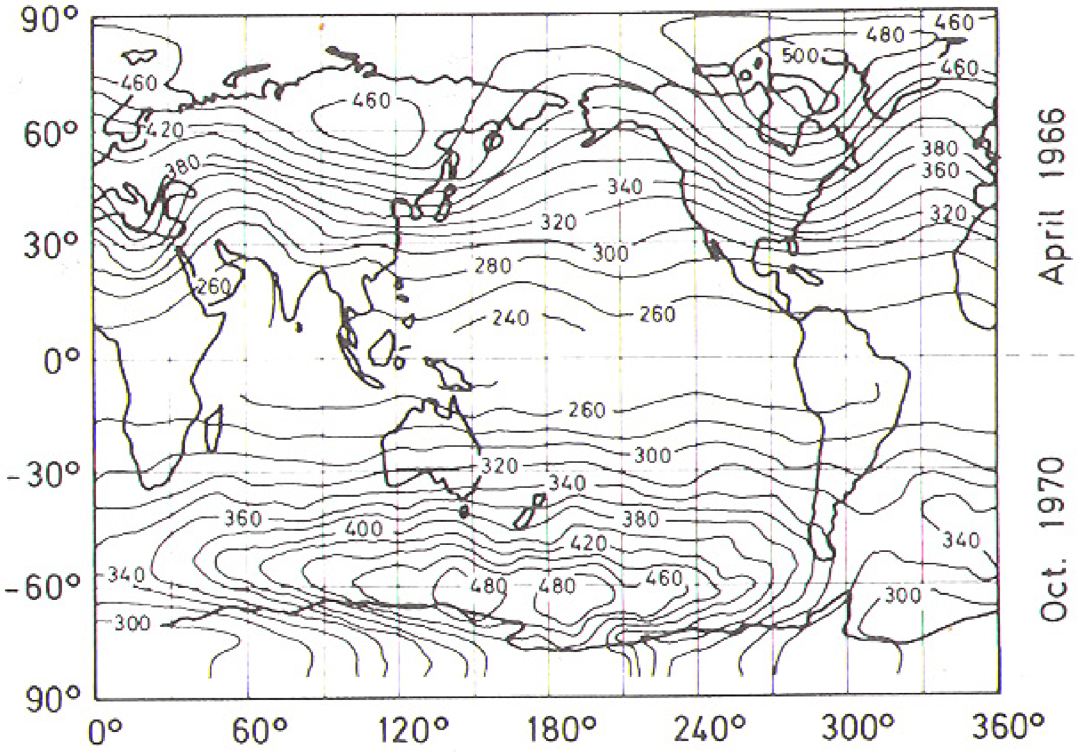


Fig. 3-2. Total ozone averaged versus latitude and longitude. [From Dütsch (1980), with permission.]

At 55 ° N	January	360 DU
	March	400 DU
	May	370 DU
	July	360 DU
	September	310 DU
	November	320 DU

DU = Dobson Unit = equivalent column height at standard pressure and temperature, in units of 10^{-2} mm

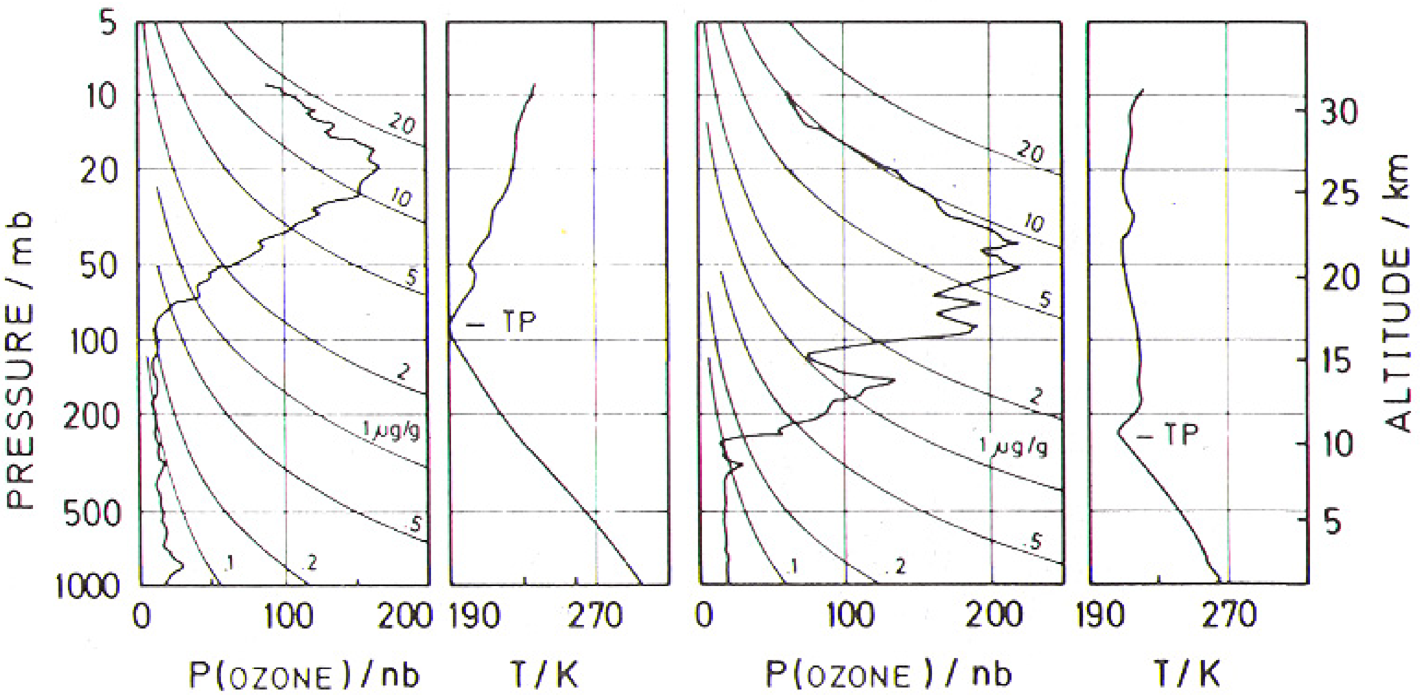


Fig. 3-3. Balloon soundings of ozone (in units of partial pressure). Left: Low latitude, Right: High latitude. Vertical temperature profiles are included to indicate the tropopause levels. [Adapted from Hering and Borden (1967).]

Formation of stratosphere O_3

$$O_2 + h\nu \rightarrow O + O \qquad j_a$$

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

$$O_3 + h\nu \rightarrow O_2 + O \qquad j_c$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad k_d$$

Role of stratospheric O_3:

- Absorption $\lambda < 300$ nm
- Temperature increase in the stratosphere

III. Stratospheric chemistry

Most of atmospheric chemistry is photo-chemistry

Solar spectrum

Photo-dissociation of O_2

$O_2 + hV \rightarrow O + O(`D)$ λ 180-240 nm

	50 km	30 km	15 km
$J(O_2)\ [s^{-1}]$	10^{-9}	5.10^{-11}	10^{-14}

Photo-dissociation of O_3

$O_3 + hV \rightarrow O_2 + O(`D)$ 200-300 nm

	50 km	30 km	15 km
$J(O_3)\ [s^{-1}]$	8.10^{-3}	10^{-3}	7.10^{-4}

Remark: $O(`D) + H_2O \rightarrow OH$

n_1 : conc. O

n_2 : conc. O_2

n_3 : conc. O_3

n_m : conc. $(N_2 + O_2)$

$$\frac{dn_1}{dt} = 2\, j_a \;\; n_2 - k_b \;\; n_1 \;\; n_2 \;\; n_m \\ + j_c \;\; n_3 - k_d \;\; n_1 \;\; n_3$$

$$\frac{dn_2}{dt} = -\, j_a \;\; n_2 - k_b \;\; n_1 \;\; n_2 \;\; n_m \\ + j_c \;\; n_3 \; + \; 2k_d \;\; n_1 \;\; n_3$$

$$\frac{dn_3}{dt} = k_d \;\; n_1 \;\; n_2 \;\; n_m \; + \; j_c \;\; n_3 \\ - k_d \;\; n_1 \;\; n_3$$

In addition:

$$n_2\,(O_2) >> n_1\,(O) + n_3\,(O_3)$$

$$\Rightarrow \frac{dn_2}{dt} = 0$$

n_1 (O) in equilibrium in 10-20 sec

$$\Rightarrow \frac{dn_1}{dt} = 0$$

As result:

$$n_3\,(O_3) = \left(\frac{B}{A}\right)^{1/2} \cdot \frac{1 - \exp.\,[-2\,(AB)^{1/2}\,t]}{1 + \exp.\,[-2\,(AB)^{1/2}\,t]}$$

$$A = 2\,k_d\,j_c\,/\,k_b\;\;n_2\;\;n_m$$
$$B = 2\,j_a\,n_2$$

In equilibrium:

Theory of Chapman (1932)

From the 4 reactions follows:

$$\text{conc. } O_3 = \text{conc. } O_2 \left(\frac{K_b \cdot j_a \cdot \text{conc } (N_2 + O_2)}{K_d \cdot j_c} \right)^{0.5}$$

(for equilibrium, long time scales)

Qualitative correct, but factor 2 too high compared to measurements

Possible explanation of the overestimation of stratospheric ozone by Chapman Theory:

- **Dynamics, transport. However, this should not influence the total budget**
- **Chemistry, missing loss-processes**

Remark: This explanation should hold for the natural, undisturbed stratospheric ozone layer!

O_3 “residence time”

50 km	**5 - 20 hours**
30 km	**≈ 1 week**
20 km	**1 - 3 years**

Other stratospheric trace gases

N_2O, H_2O, CH_4, (CH_3Cl etc.)
Origin: the troposphere

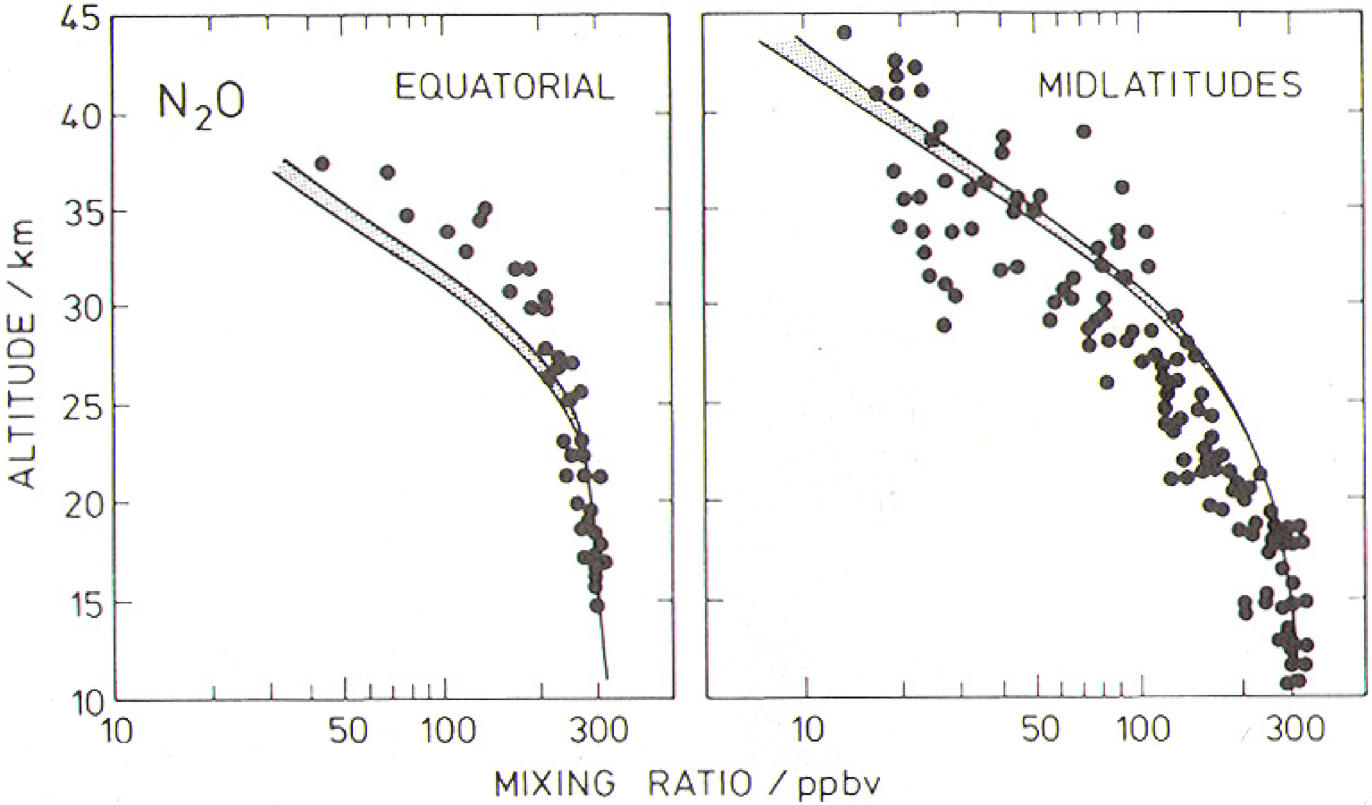


Fig. 3-6. Vertical profiles of the N_2O mixing ratio at low and high latitudes. From measurements of Heidt *et al.* (1980), Tyson *et al.* (1978), Vedder *et al.* (1978, 1981), Fabian *et al.* (1979b, 1981), Goldan *et al.* (1980, 1981). The solid lines were calculated by Gidel *et al.* (1983) with a two-dimensional model.

N_2O (ca. 90 % of biogenic origin)

$N_2O + hV \rightarrow N_2 + O\,('D)$ $\lambda \approx 200$ nm

$O\,('D) + N_2O \rightarrow N_2 + O_2$

$\rightarrow 2NO$

↑

from O_3-photo-dissociation

Followed by:

$NO + O_3 \rightarrow NO_2 + O$

$NO_2 + hV \rightarrow NO + O$

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

$(NO + NO_2 = \text{constant})$

$O + NO_2 \rightarrow NO + O_2$

$(O + O_3 \rightarrow 2O_2)$

Leading to:

$O_3 + hV \rightarrow O + O_2$

$O + NO_2 \rightarrow O_2 + NO$

$NO + O_3 \rightarrow NO_2 + O_2$

Netto: $O_3 + O_3 \rightarrow 2O_2$

With NO_x as catalyst

Paul Crutzen: 1970

“The influence of nitrogen oxides on the atmospheric ozone content”

Quart. J.R.Met.Soc. (1970), 320-325

Impact of NO and NO_2, but also of:

OH

HO_2

No explanation where NO/NO_2 comes from,

mentiones “photodissociation” of N_2O

But main source is $N_2O + O \rightarrow 2NO$

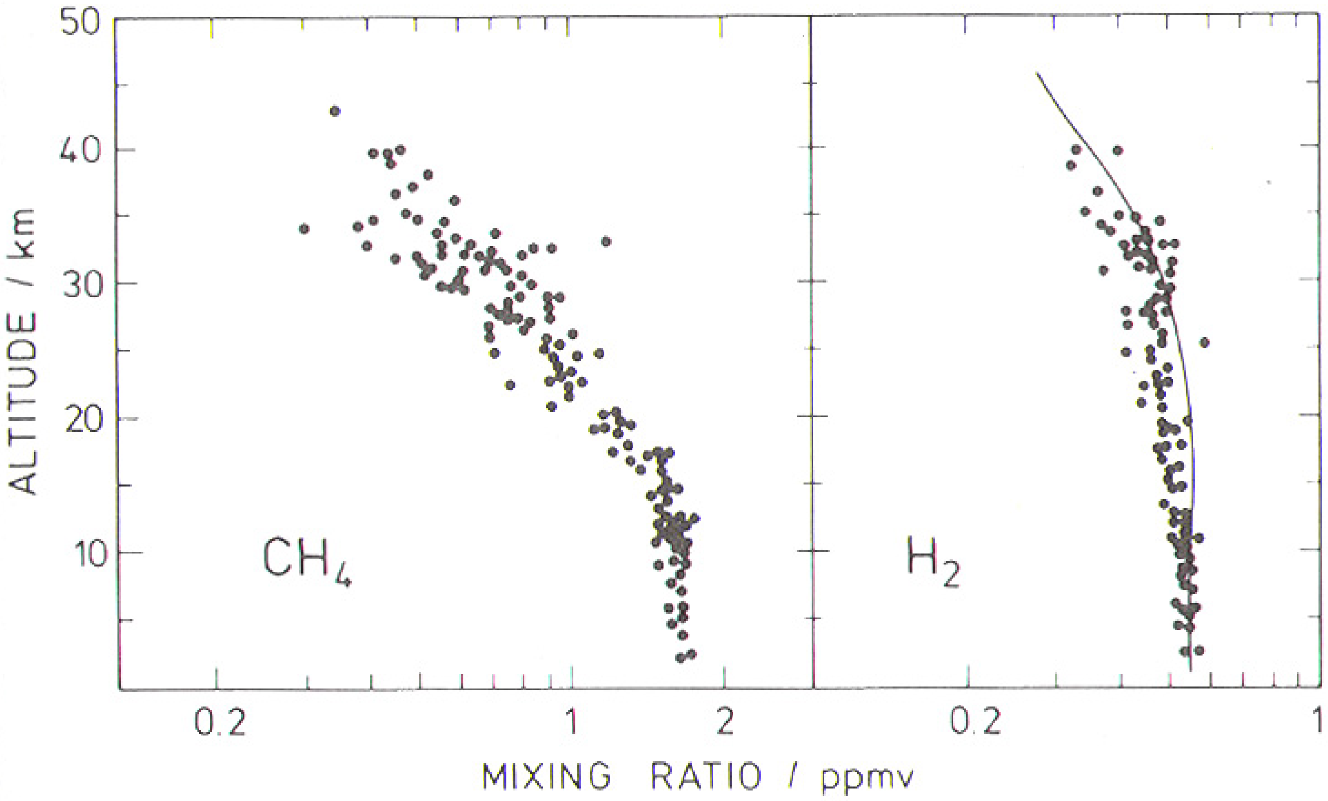


Fig. 3-10. Vertical distribution of methane and hydrogen in the stratosphere at midlatitudes (40–60° N). [From observations of Bush *et al.* (1978), Ehhalt and Heidt (1973), Ehhalt *et al.* (1974, 1975), Pollock *et al.* (1980), Heidt and Ehhalt (1980), Fabian *et al.* (1979, 1981b), and Volz *et al.* (1981b).]

H_2O troposphere: 0.2 - 4%

stratosphere: 2 - 7 ppm

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

CH_4 in the stratosphere

$CH_4 + OH \rightarrow H_2O + CH_3$ (lower stratosphere)

$CH_4 + O(^1D) \rightarrow OH + CH_3$ (higher stratosphere)

$CH_4 + Cl \rightarrow HCl + CH_3$

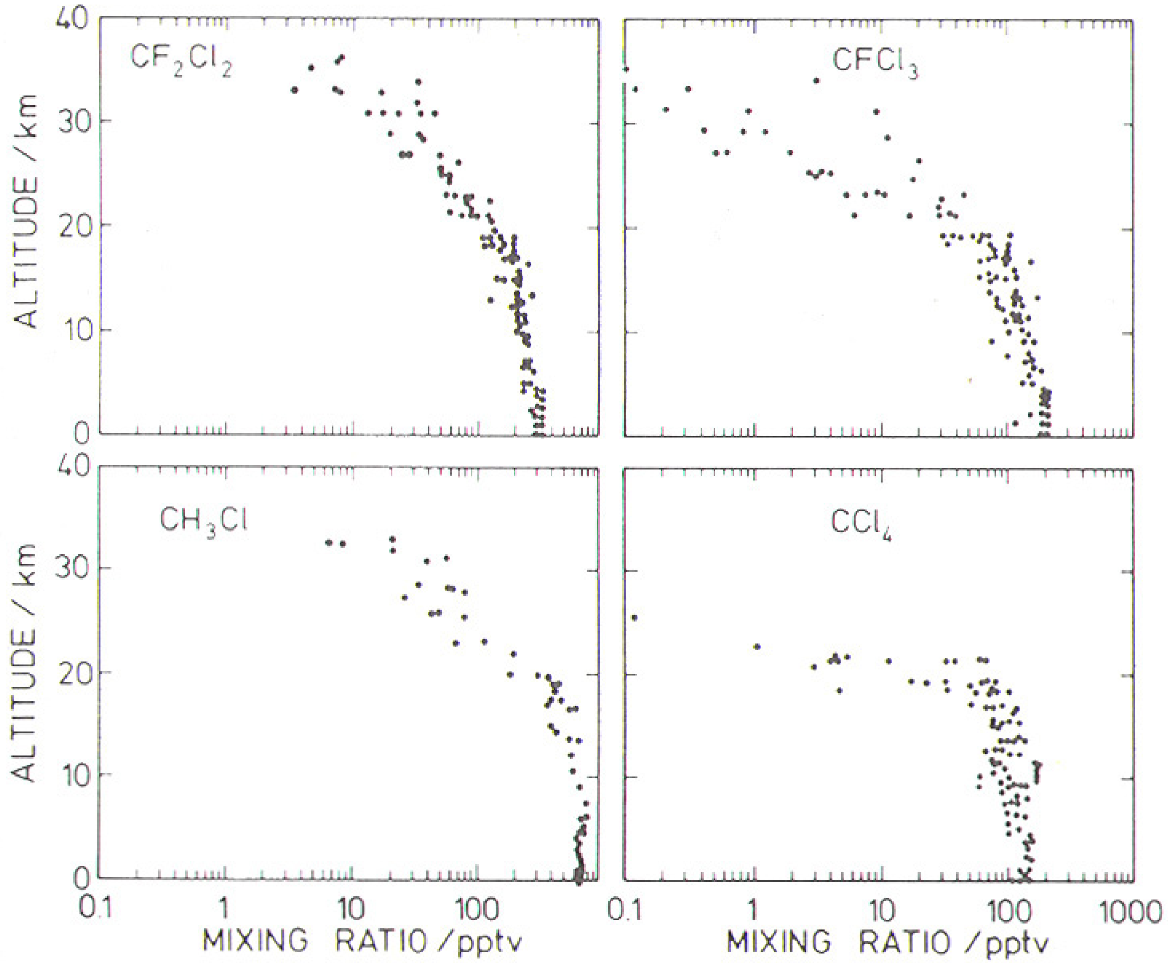


Fig. 3-11. Vertical distribution of CF$_2$Cl$_2$, CFCl$_3$, CH$_3$Cl, and CCl$_4$ in the stratosphere. [Data compiled by Fabian (1986) from Lovelock (1974a), Heidt *et al.* (1975), Schmeltekopf *et al.* (1975), Krey *et al.* (1977), Robinson *et al.* (1977), Seiler *et al.* (1978b), Tyson *et al.* (1978), Vedder *et al.* (1978, 1981), Fabian *et al.* (1979), Goldan *et al.* (1980), Penkett *et al.* (1980a), Rasmussen *et al.* (1980), Fabian *et al.* (1981a), Leifer *et al.* (1981), Schmidt *et al.* (1981), Rasmussen *et al.* (1982a), and Borchers *et al.* (1983).]

Stratospheric chlorine

Methylchloride:	CH_3Cl **(biogenic)**
F_{11}**:**	$CFCl_3$ **(antropogenic)**
F_{12}**:**	CF_2Cl_2 **(antropogenic)**
Carbontetrachloride:	CCl_4 **(antropogenic)**
Methylchloroform:	CH_3CCl_3 **(antropogenic)**

Example: $CFCl_3 + hV \rightarrow Cl + CFCl_2$ λ **170-190 nm**

$CFCl_2 + O_2 \rightarrow COFCl + ClO$

Followed by:

$$\begin{array}{lcl} \mathrm{Cl} + \mathrm{O}_3 & \rightarrow & \mathrm{ClO} + \mathrm{O}_2 \\ \mathrm{O} + \mathrm{ClO} & \rightarrow & \mathrm{Cl} + \mathrm{O}_2 \\ \mathrm{O}_3 + h\mathrm{V} & \rightarrow & \mathrm{O} + \mathrm{O}_2 \\ \hline \end{array}$$

Netto: $\mathrm{O}_3 + \mathrm{O}_3 \rightarrow 2\mathrm{O}_2$

With Cl as catalyst

Molina and Rowland: 1974

“Stratospheric sink for chlorofluormethanes: chlorine atom-catalysed destruction of ozone”
Nature, vol.249, June 28, 1974, 810-812

Loss reactions for Cl

$Cl + CH_4 \rightarrow HCl + CH_3$

$Cl + HO_2 \rightarrow HCl + O_2$

$Cl + H_2 \rightarrow HCl + H$

CH_4 most important reaction

$OH + HCl \rightarrow H_2O + Cl$: slow

Important:
Binding Cl in less reactive compounds

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + NO_2 \rightarrow ClONO_2$

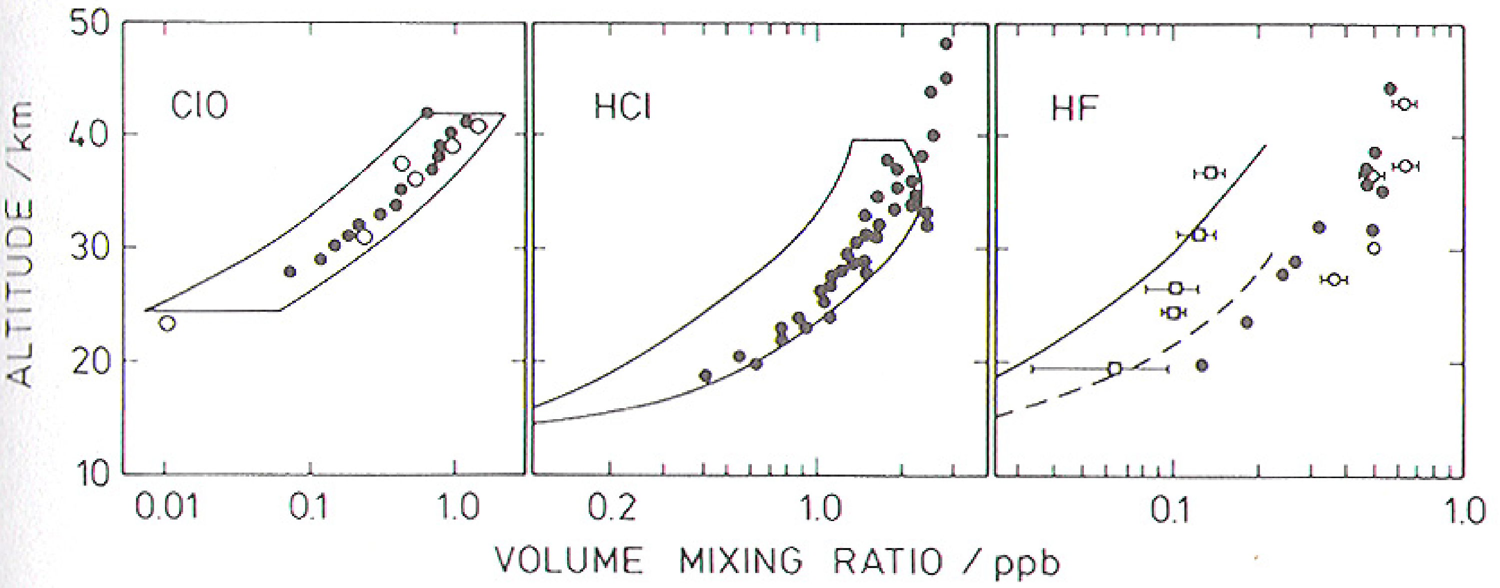


Fig. 3-12. Vertical distribution of ClO, HCl, and HF in the stratosphere. Left: Filled circles give the averages of eight altitude profiles for ClO measured in 1976–1979 by *in situ* resonance fluorescence; the envelope indicates the range of values (Weinstock *et al.*, 1981); two additional high-mixing-ratio profiles are not included. The open circles are from balloon-borne infrared remote measurements by Waters *et al.* (1981) and Menzies (1983). Center: The envelope encompasses observational data for HCl obtained by balloon-borne infrared measurement techniques (Farmer *et al.*, 1980; Buijs, 1980; Raper *et al.*, 1977; Eyre and Roscoe, 1977; Williams *et al.*, 1976; Zander, 1981); filled circles represent more recent preliminary data cited in WMO (1985). Right: Balloon-borne infrared remote measurements of HF [——— Farmer *et al.* (1980), - - - Buijs (1980), ○ Zander (1975, 1981), ● preliminary data cited in WMO (1985); and observations of HF by *in situ* filter collections (Mroz *et al.*, 1977).

Photo-dissociation in the stratosphere

N_2O, $CFCl_3$, CF_2Cl_2, CCl_4 (all $\lambda > 175$ nm)

No photo-dissociation of CH_4, NH_3

Components without H-atoms: photo-dissociation

Components with H-atom: reaction with OH and O ('D)

Photo-dissociation in the troposphere

NO_2	λ	175 - 240 nm
		240 - 307 nm
CH_2O	λ	< 300 nm

Stratospheric ozone budget

$$\begin{array}{lcl} X + O_3 & \rightarrow & XO + O_2 \\ XO + O_{2n+1} & \rightarrow & X + (n+1)\ O_2 \\ \hline \end{array}$$

Netto: $O_3 + O_{2n+1} \rightarrow (n+2)\ O_2$

n: 0 or 1

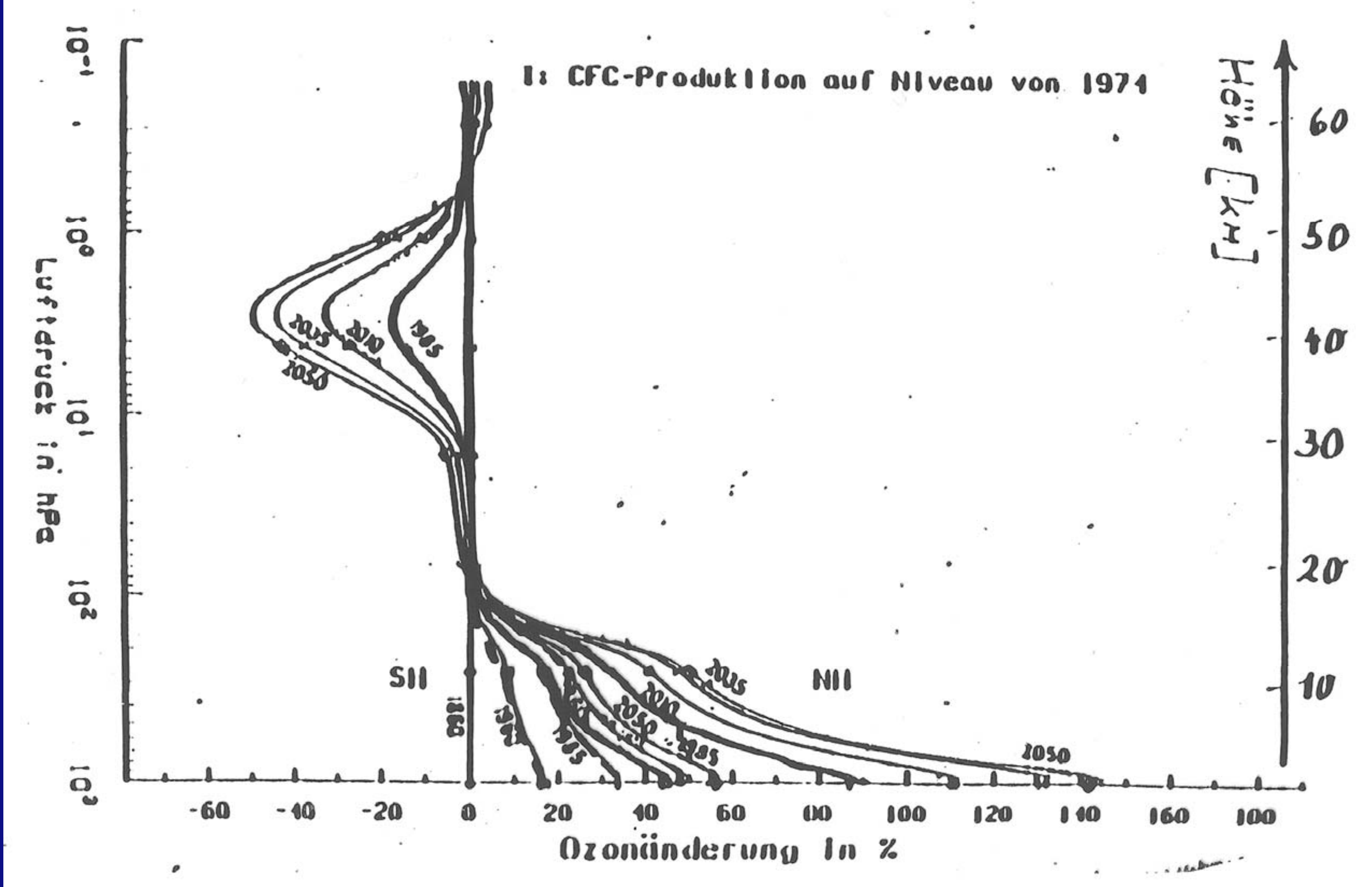
X: H, OH, NO, Cl, O

Model calculations, Crutzen & Schmailzel, 1983

Stratosphere, 2-D model

$$\begin{array}{lclll} O + O_3 & \rightarrow & 2O_2 & 20\% & \\ NO + O_3 & \rightarrow & NO_2 + O_2 & 30\% & \\ H + O_3 & \rightarrow & OH + O_2 & 30\% & \\ Cl + O_3 & \rightarrow & ClO + O_2 & 20\% & \leftarrow \text{anthropogenic} \end{array}$$

Also: $ClO + NO_2 \rightarrow ClONO_2$


I: CFC-Produktion auf Niveau von 1974
Höhe [km]
60
50
40
30
20
10
Luftdruck in hPa
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
2025
2010
1985
2050
SH
NH
2025
2010
2050
1985
2050
-60
-40
-20
0
20
40
60
80
100
120
140
160
180
Ozonänderung in %

CFC-11 : $CFCl_3$	:	last number	amount of F
		fore-last number	amount of H+1
		first number	amount of C-1

CF C-22 : HCF_2Cl

F_{11}: DuPont, 1932, for cooling

Production	$F_{11} + F_{12}$
1960	150.10^3 ton/year
1974	800
1982	600
1986	750

← spray-can war

Concentrations

	1975	1986	1991
F_{11}	0.1 ppb	0.23	0.30
F_{12}	0.1-0.2 ppb	0.40	0.50

Residence time

Estimates	F_{11}	F_{12}
Sze & Wu (1974)	10 year	10-20 years
Singh (1979)	40	70
Crutzen (1987)	75-100	75-100
Elkins (1993)	55	140

- **British Antartic Survey; 1982**
- **TOMS instrument NASA**

Ozone hole: fully unexpected

Normal chemistry can not explain this

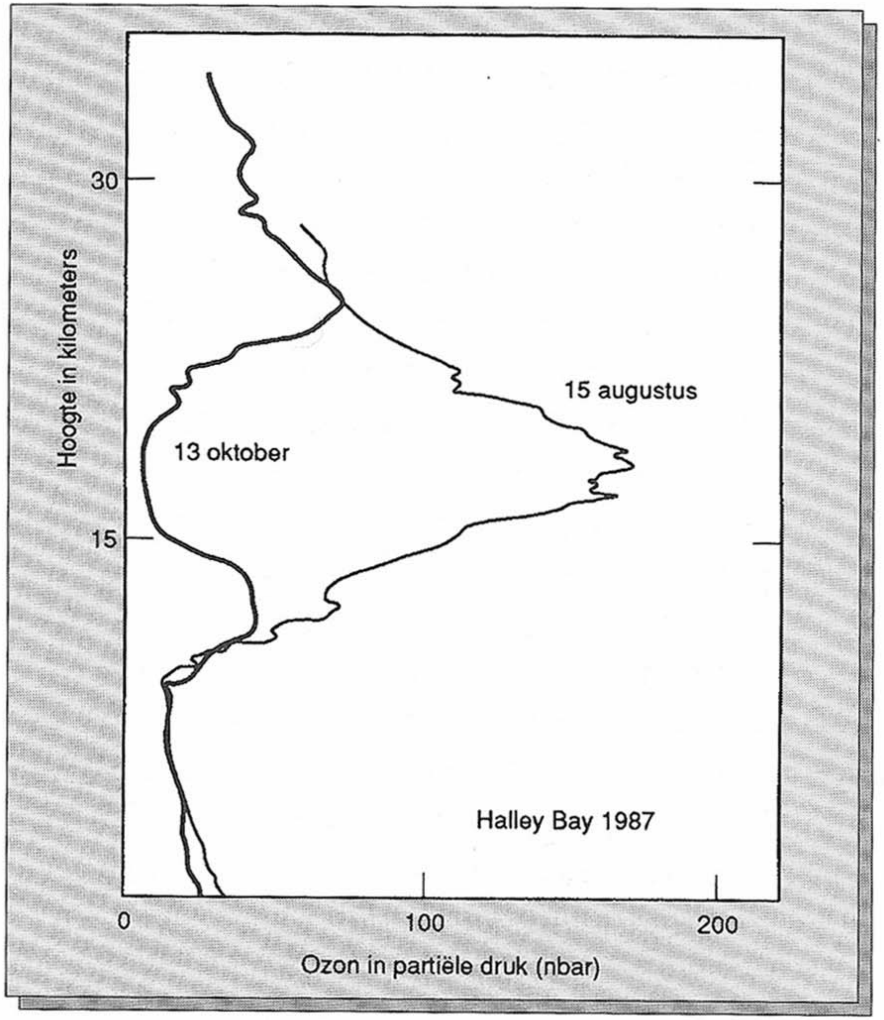
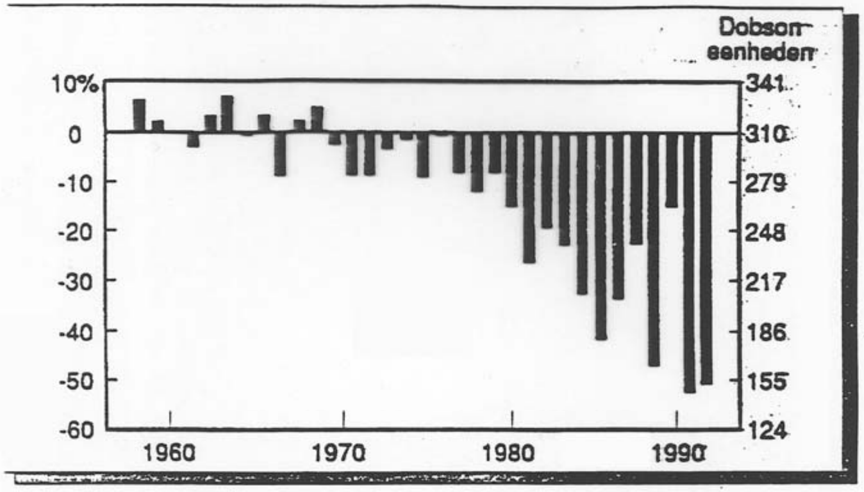
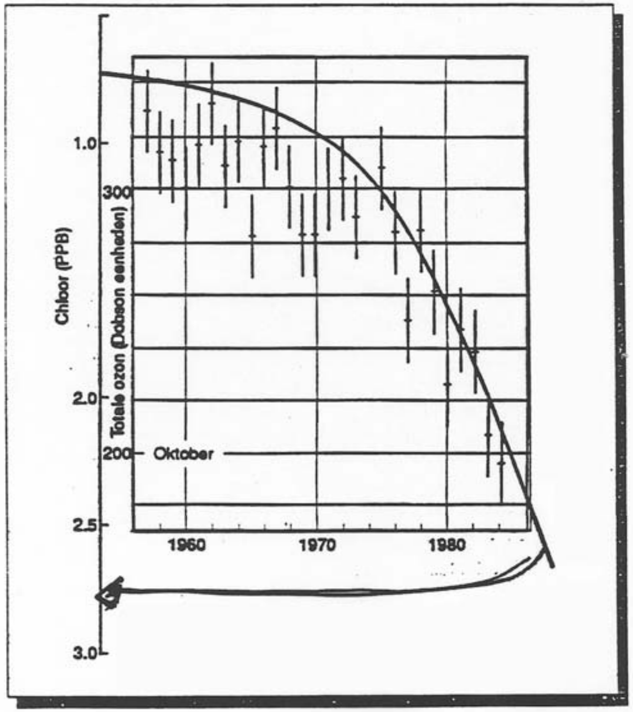


Fig. 9 Het ozongat
(Bron: 'Menschliche Einflüsse auf die Chemie der globalen Atmosphäre', Paul J. Crutzen, 1989)





‘Om het behoud van de ozonlaag’
John Gribbin, DuPoc, Wageningen, 1992

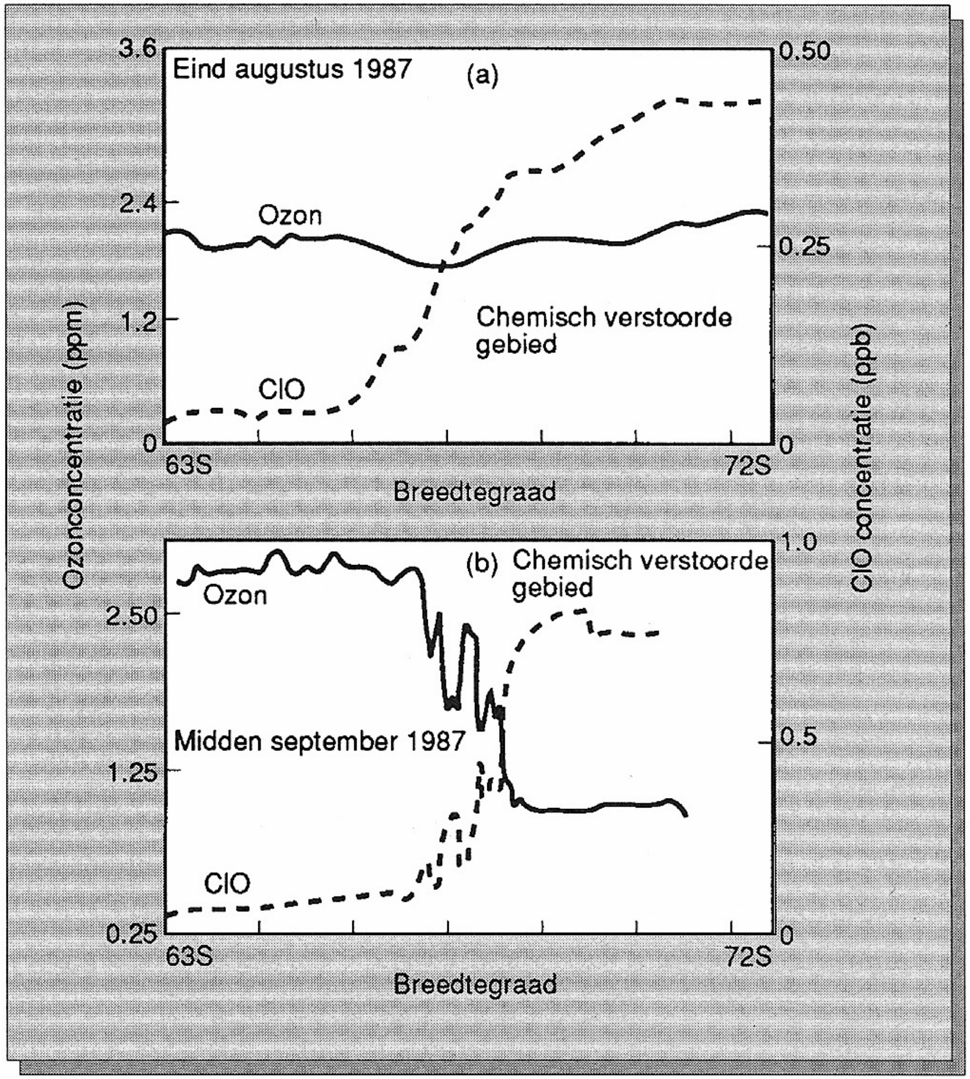


Fig. 10 De samenhang tussen ozon en ClO. ‘het rokende pistool’
(Bron: ‘Menschliche Einflüsse auf die Chemie der globalen Atmosphäre’, Paul J. Crutzen, 1989)

Situation

Polar night: polar vortex ≈ 60 ºS

temperature: < -83 ºC

$HNO_3 + H_2O \rightarrow$ polar stratospheric clouds, PSC's

In the polar night, at the surface of PSC's:

$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$

$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

Inactive Cl becomes potential active Cl

At sunrise

$Cl_2 + hV$ → $2Cl$

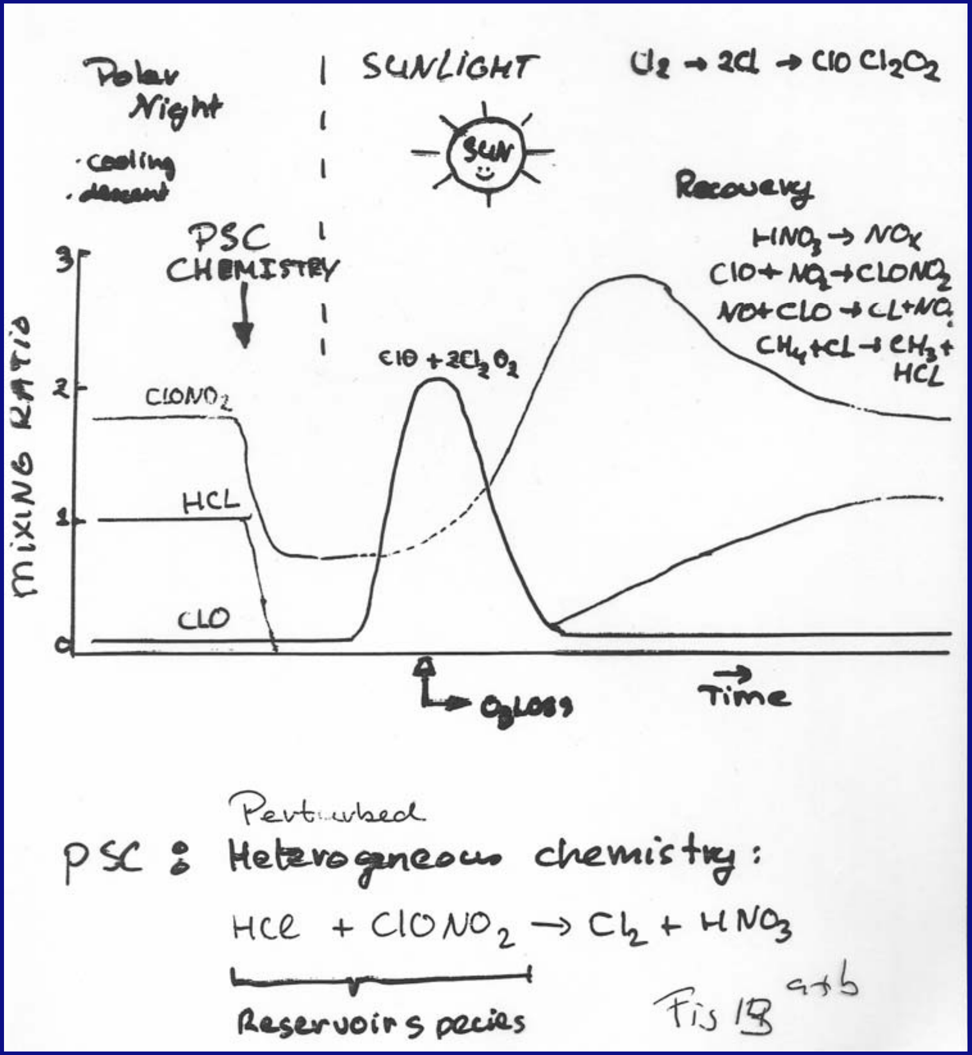
$HOCl + hV$ → $OH + Cl$

O_3 increase after October:

breaking of polar vortex → mixing

T > - 83 °C, no polar clouds

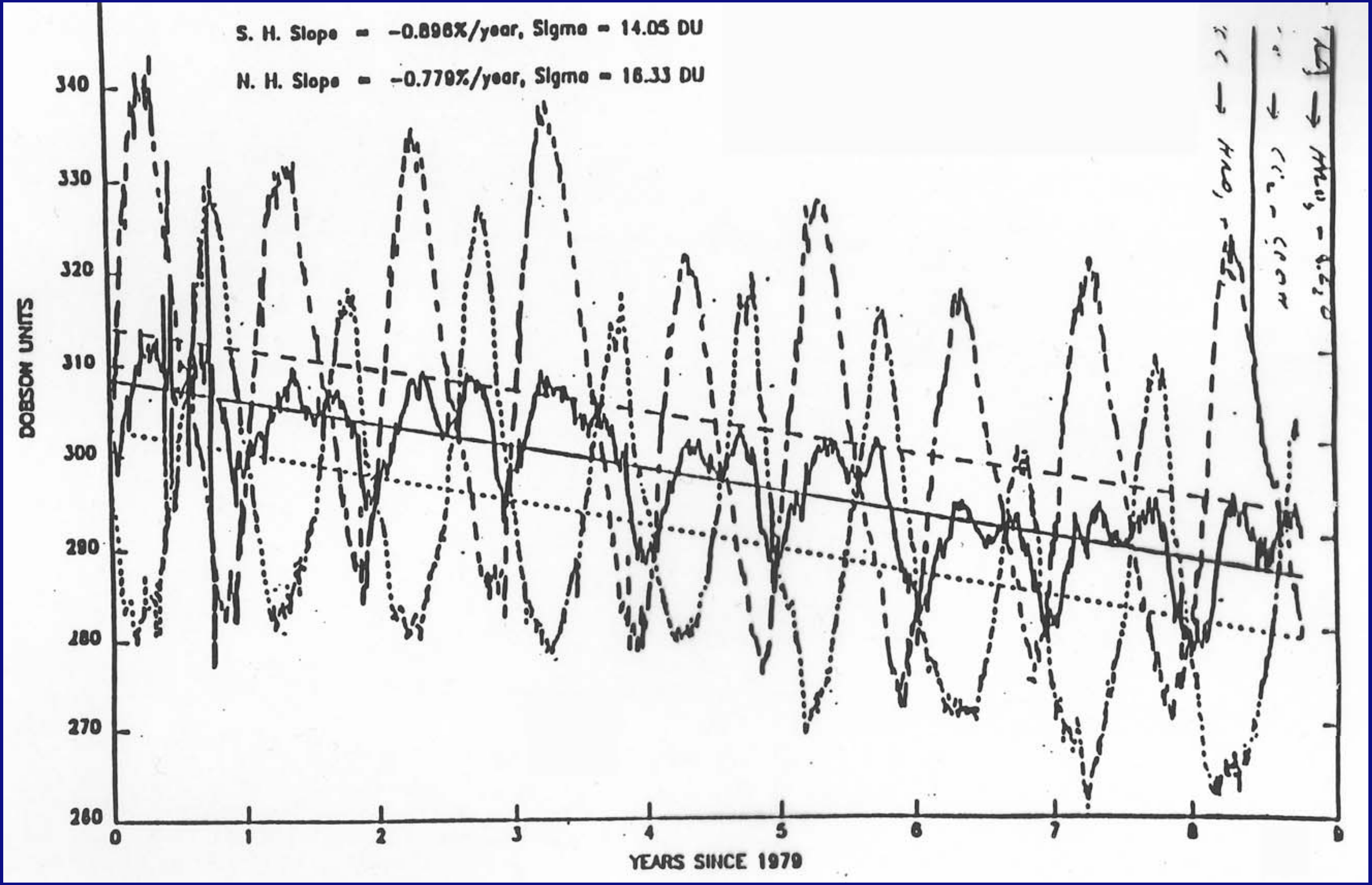
PSC: Polar Stratospheric Clouds
Key Role



PSC: Perturbed Heterogeneous chemistry:

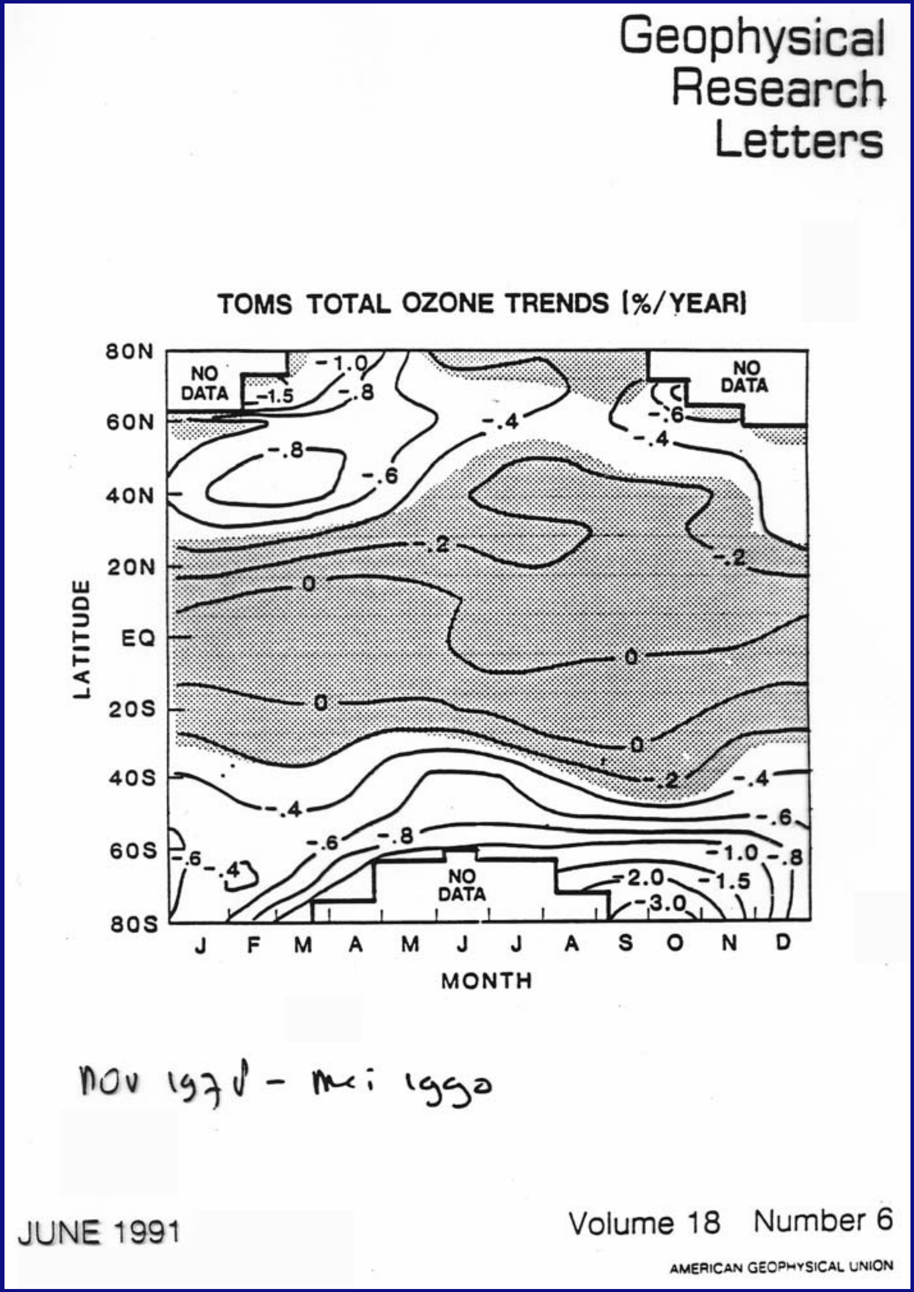
$$\underbrace{HCl + ClONO_2}_{\text{Reservoir species}} \rightarrow Cl_2 + HNO_3$$

Fig 18 a+b


S. H. Slope = -0.898%/year, Sigma = 14.05 DU
N. H. Slope = -0.779%/year, Sigma = 16.33 DU
DOBSON UNITS
340
330
320
310
300
290
280
270
260
0
1
2
3
4
5
6
7
8
9
YEARS SINCE 1979

Stratospheric ozone worldwide

- **Seasonal variation ≈ 50 DU**
- **Solar cycle ≈ 6 DU**
- **Quasi-biennal oscillations ≈ 8 DU**
- **Vulcano’s ≈ …**



Geophysical
Research
Letters

TOMS TOTAL OZONE TRENDS (%/YEAR)

nov 1978 - mei 1990

JUNE 1991

Volume 18 Number 6

AMERICAN GEOPHYSICAL UNION

Increase of UV-B leads to:

- **Increase in melonomia, skin cancer**
- **1% less O_3 leads to 4 % more skin cancer**
- **Eye-problems**
- **Damage to protection-system at the skin-surface**
- **Damage to plancton**

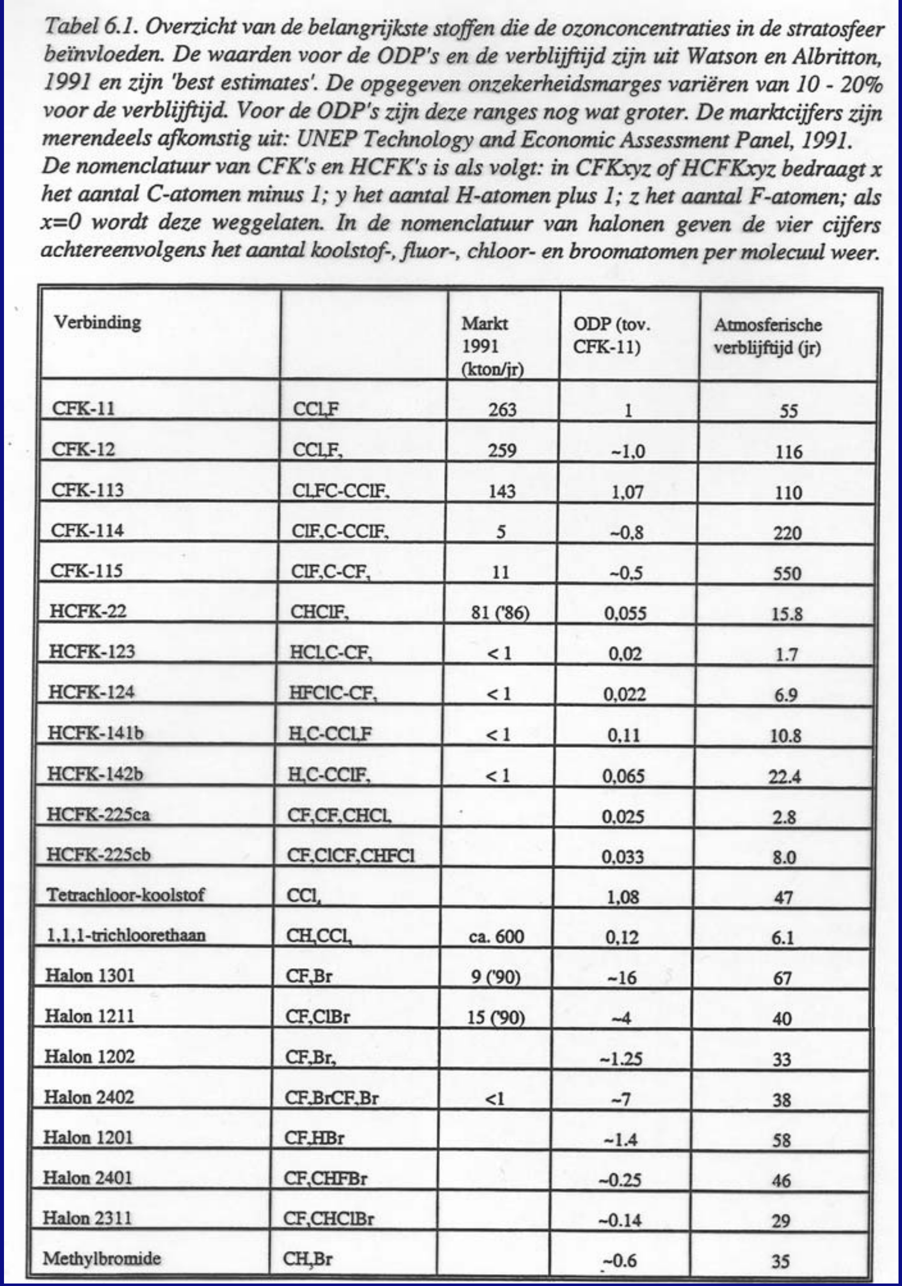
1) **Ozone depletion potential-ODP**

mean O_3-depletion due to kg. of species X, divided by:
mean O_3-depletion due to kg. CFC-11

2) **Global warming potential-GWP**

increase radiative forcing due to kg of species X, divided by:
increase radiative forcing due to kg.CO_2 (or CFC-11)

3) **Atmospheric residence time**



Tabel 6.1. Overzicht van de belangrijkste stoffen die de ozonconcentraties in de stratosfeer beïnvloeden. De waarden voor de ODP's en de verblijftijd zijn uit Watson en Albritton, 1991 en zijn 'best estimates'. De opgegeven onzekerheidsmarges variëren van 10 - 20% voor de verblijftijd. Voor de ODP's zijn deze ranges nog wat groter. De marktcijfers zijn merendeels afkomstig uit: UNEP Technology and Economic Assessment Panel, 1991. De nomenclatuur van CFK's en HCFK's is als volgt: in CFKxyz of HCFKxyz bedraagt x het aantal C-atomen minus 1; y het aantal H-atomen plus 1; z het aantal F-atomen; als x=0 wordt deze weggelaten. In de nomenclatuur van halonen geven de vier cijfers achtereenvolgens het aantal koolstof-, fluor-, chloor- en broomatomen per molecuul weer.

Verbinding		Markt 1991 (kton/jr)	ODP (tov. CFK-11)	Atmosferische verblijftijd (jr)
CFK-11	CCl_3F	263	1	55
CFK-12	CCl_2F_2	259	~1,0	116
CFK-113	$Cl_2FC\text{-}CClF_2$	143	1,07	110
CFK-114	$ClF_2C\text{-}CClF_2$	5	~0,8	220
CFK-115	$ClF_2C\text{-}CF_3$	11	~0,5	550
HCFK-22	$CHClF_2$	81 ('86)	0,055	15.8
HCFK-123	$HCl_2C\text{-}CF_3$	< 1	0,02	1.7
HCFK-124	$HFClC\text{-}CF_3$	< 1	0,022	6.9
HCFK-141b	$H_3C\text{-}CCl_2F$	< 1	0,11	10.8
HCFK-142b	$H_3C\text{-}CClF_2$	< 1	0,065	22.4
HCFK-225ca	$CF_3CF_2CHCl_2$		0,025	2.8
HCFK-225cb	CF_2ClCF_2CHFCl		0,033	8.0
Tetrachloor-koolstof	CCl_4		1,08	47
1,1,1-trichloorethaan	CH_3CCl_3	ca. 600	0,12	6.1
Halon 1301	CF_3Br	9 ('90)	~16	67
Halon 1211	CF_2ClBr	15 ('90)	~4	40
Halon 1202	CF_2Br_2		~1.25	33
Halon 2402	CF_2BrCF_2Br	<1	~7	38
Halon 1201	CF_2HBr		~1.4	58
Halon 2401	CF_3CHFBr		~0.25	46
Halon 2311	$CF_3CHClBr$		~0.14	29
Methylbromide	CH_3Br		~0.6	35

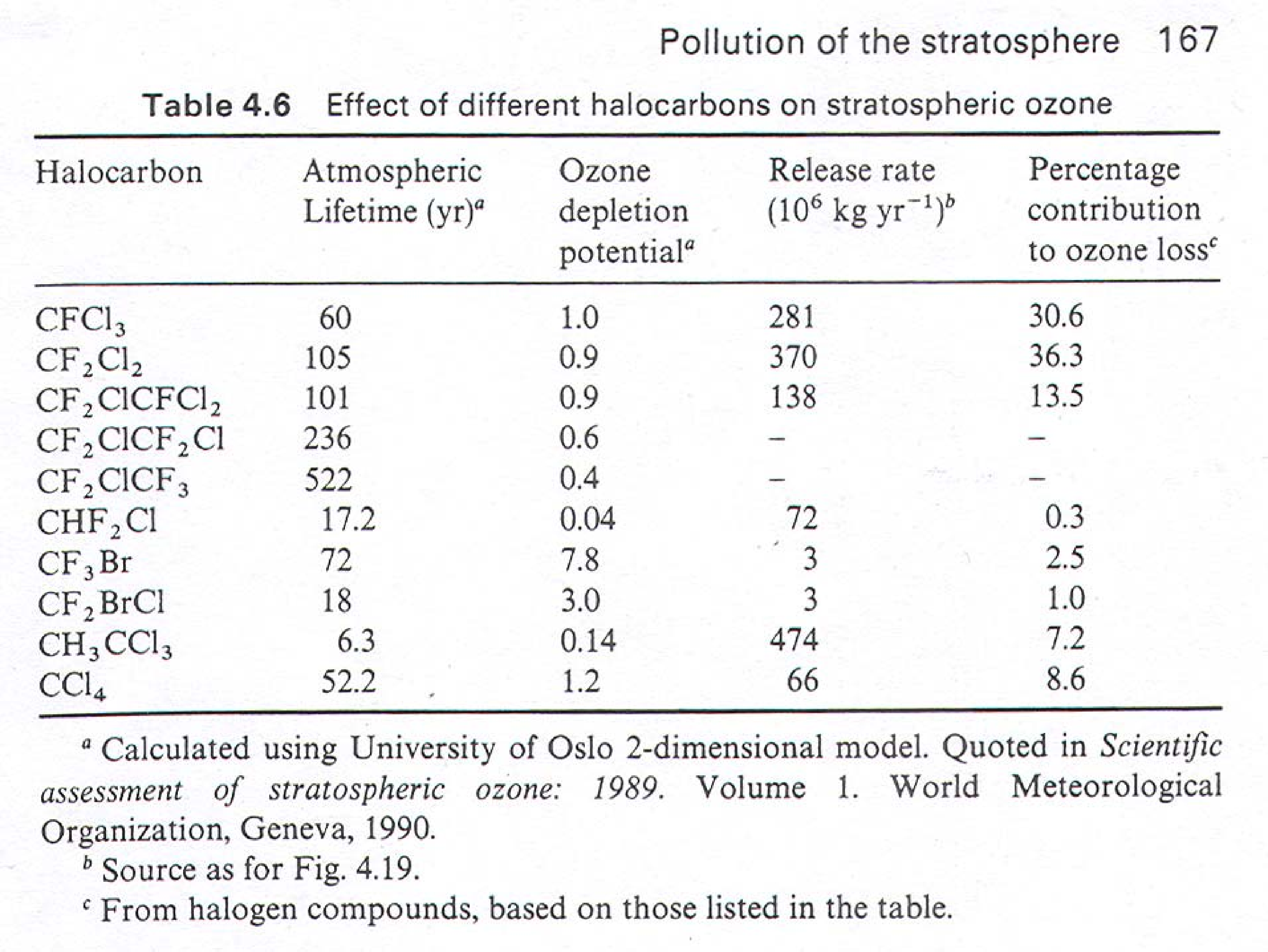


Table 4.6 Effect of different halocarbons on stratospheric ozone

Halocarbon	Atmospheric Lifetime (yr)[a]	Ozone depletion potential[a]	Release rate (10^6 kg yr^{-1})[b]	Percentage contribution to ozone loss[c]
$CFCl_3$	60	1.0	281	30.6
CF_2Cl_2	105	0.9	370	36.3
$CF_2ClCFCl_2$	101	0.9	138	13.5
CF_2ClCF_2Cl	236	0.6	–	–
CF_2ClCF_3	522	0.4	–	–
CHF_2Cl	17.2	0.04	72	0.3
CF_3Br	72	7.8	3	2.5
CF_2BrCl	18	3.0	3	1.0
CH_3CCl_3	6.3	0.14	474	7.2
CCl_4	52.2	1.2	66	8.6

[a] Calculated using University of Oslo 2-dimensional model. Quoted in *Scientific assessment of stratospheric ozone: 1989.* Volume 1. World Meteorological Organization, Geneva, 1990.

[b] Source as for Fig. 4.19.

[c] From halogen compounds, based on those listed in the table.

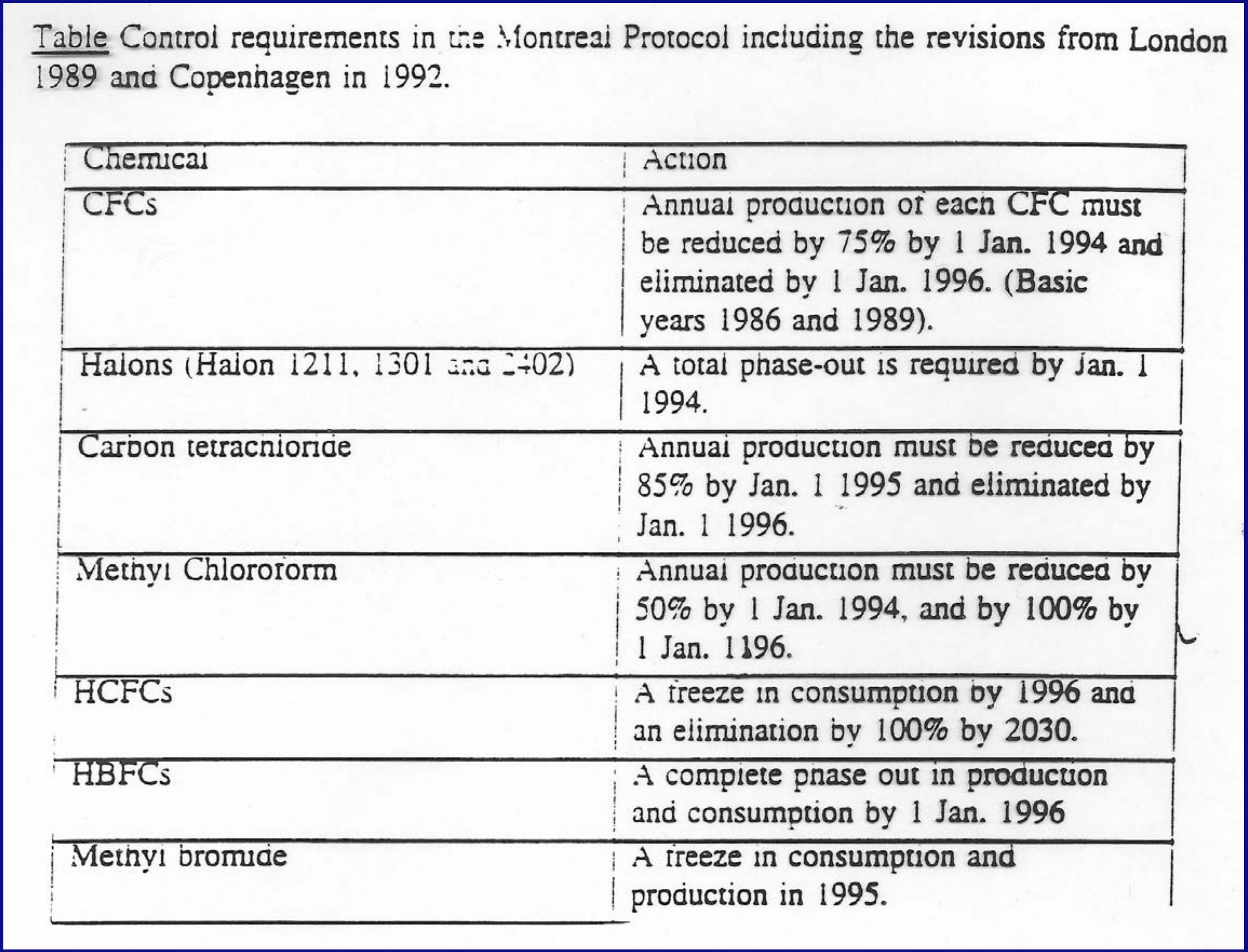
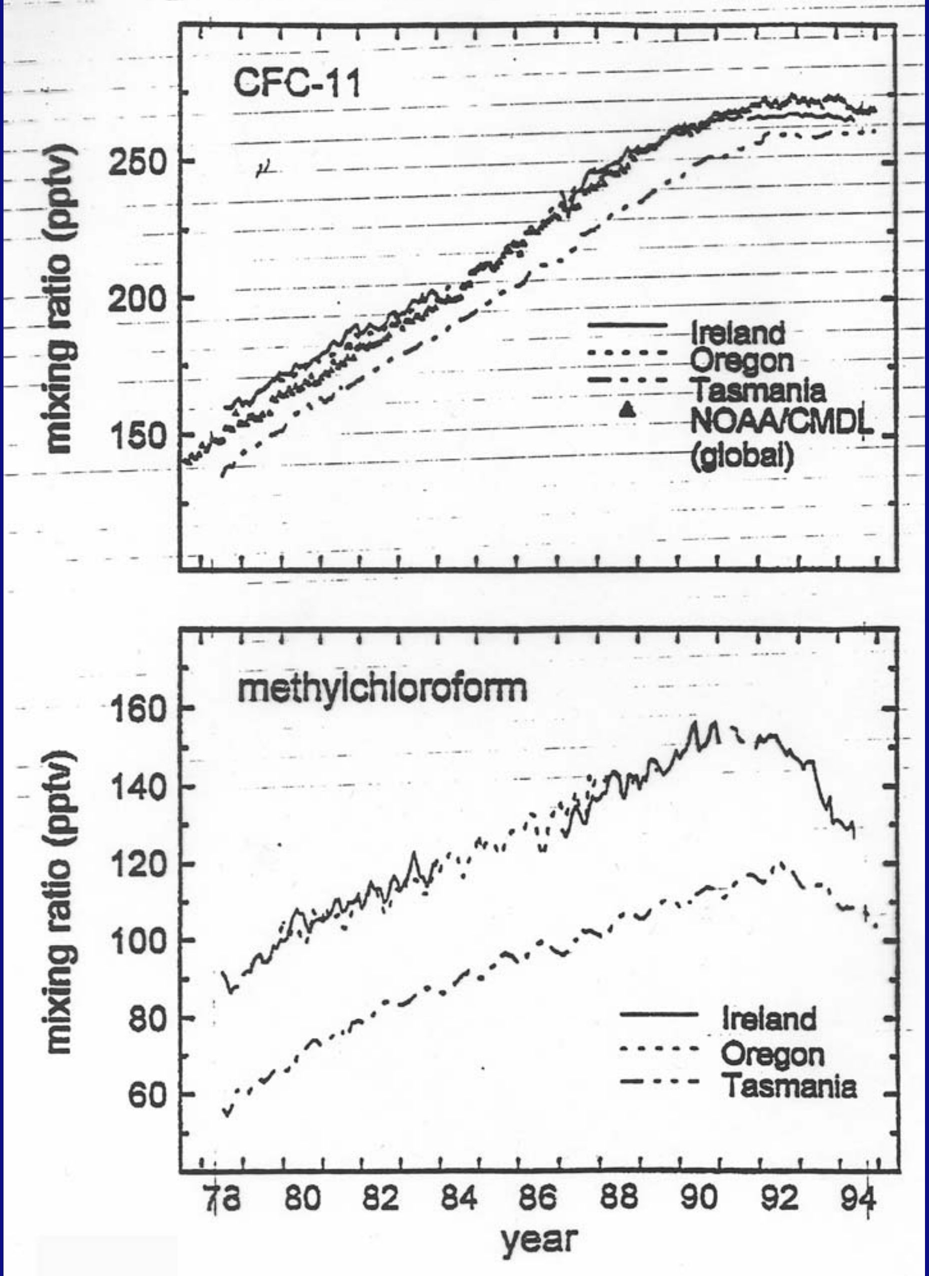


Table Control requirements in the Montreal Protocol including the revisions from London 1989 and Copenhagen in 1992.

Chemical	Action
CFCs	Annual production of each CFC must be reduced by 75% by 1 Jan. 1994 and eliminated by 1 Jan. 1996. (Basic years 1986 and 1989).
Halons (Halon 1211, 1301 and 2402)	A total phase-out is required by Jan. 1 1994.
Carbon tetrachloride	Annual production must be reduced by 85% by Jan. 1 1995 and eliminated by Jan. 1 1996.
Methyl Chloroform	Annual production must be reduced by 50% by 1 Jan. 1994, and by 100% by 1 Jan. 1196.
HCFCs	A freeze in consumption by 1996 and an elimination by 100% by 2030.
HBFCs	A complete phase out in production and consumption by 1 Jan. 1996
Methyl bromide	A freeze in consumption and production in 1995.


CFC-11
mixing ratio (pptv)
250
200
150
Ireland
Oregon
Tasmania
▲ NOAA/CMDL (global)
methylchloroform
mixing ratio (pptv)
160
140
120
100
80
60
Ireland
Oregon
Tasmania
78
80
82
84
86
88
90
92
94
year

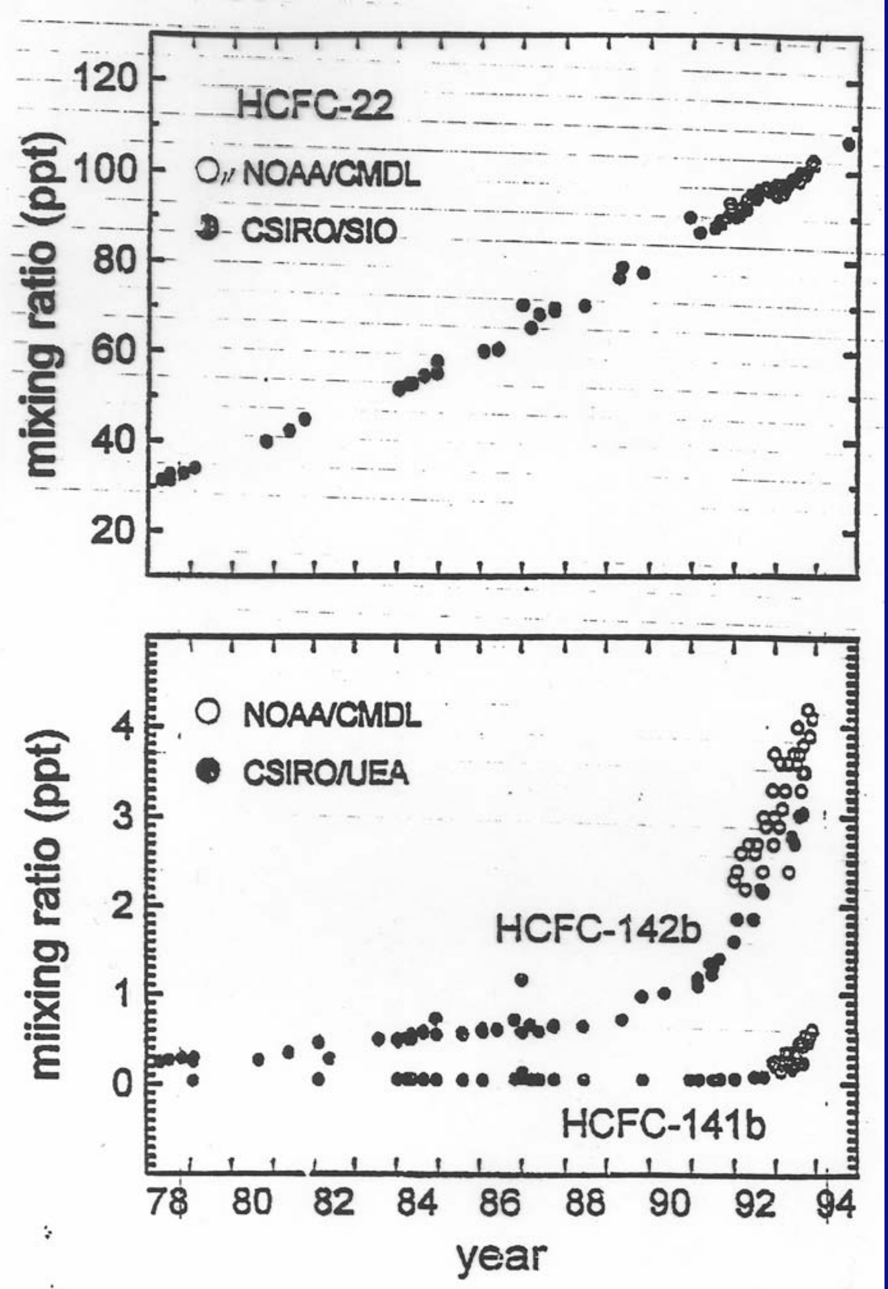

120
100
80
60
40
20
mixing ratio (ppt)
HCFC-22
○ NOAA/CMDL
● CSIRO/SIO
4
3
2
1
0
miixing ratio (ppt)
○ NOAA/CMDL
● CSIRO/UEA
HCFC-142b
HCFC-141b
78
80
82
84
86
88
90
92
94
year

Fig 15a

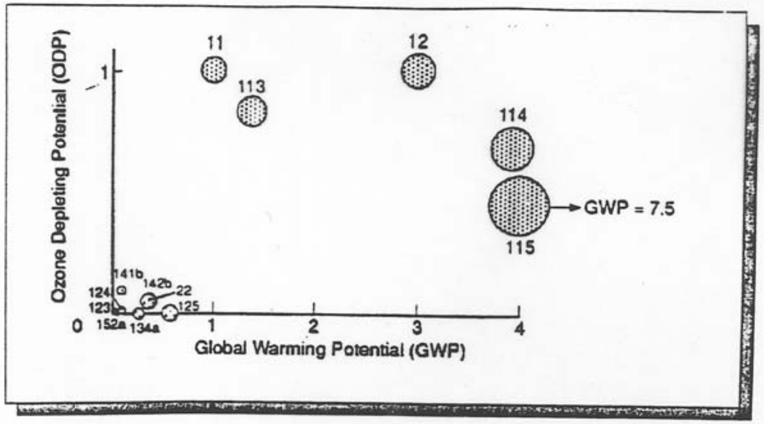


Fig. 15 Ozone Depletion Potential en Global Warming Potential van verschillende CFK' (beide t.o.v. CFK-11).
(Bron: WMO Globale Ozone Research and Monitoring Project - Report No. 20 "Scientific Assessment of Stratospheric Ozone: 1989)

Fig 15b

Cl-verandering t.o.v. 1985

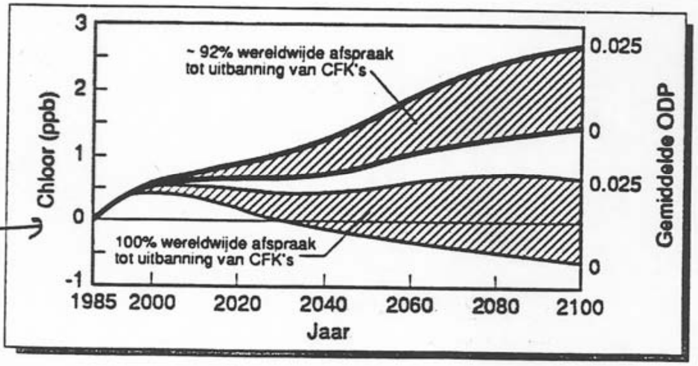


Fig. 16 Effecten van naleving van afspraken voor CFK's emissiereductie. De bandbreedte wordt veroorzaakt door substitutie met verschillende alternatieve CFK's.
(Bron: Future concentrations of stratospheric chlorine and bromine, EPA page 400/I-88/005, J.S. Hoffman en M.J. Gibbs, 1988)

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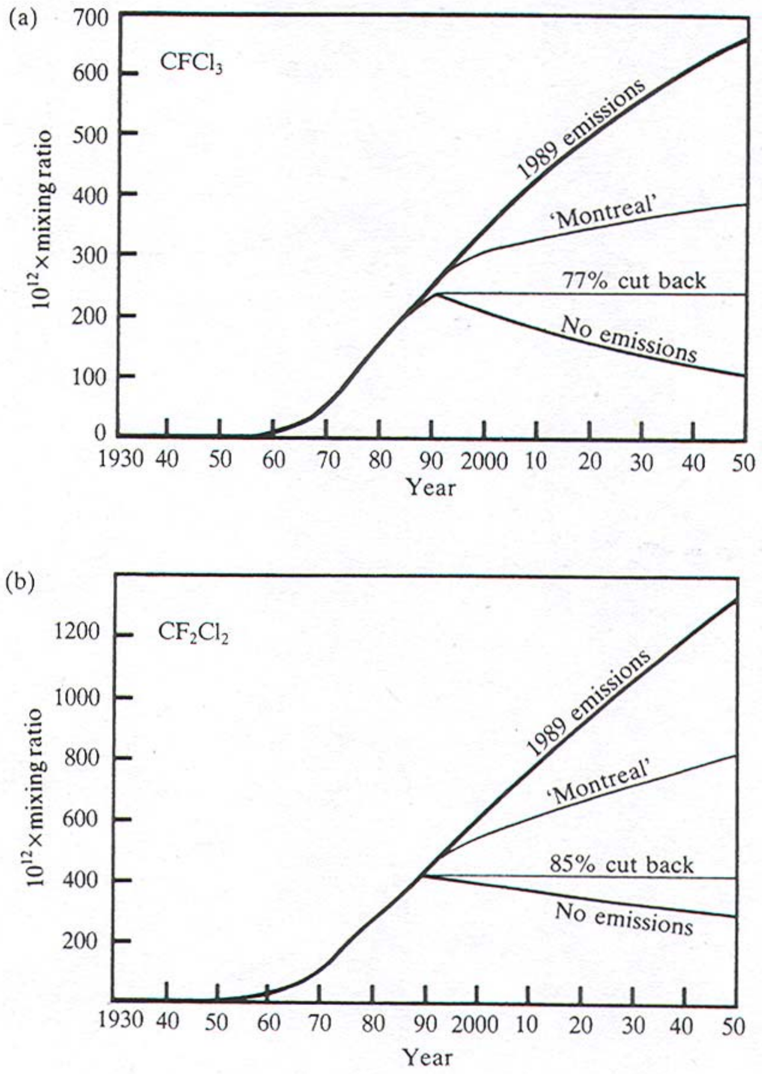
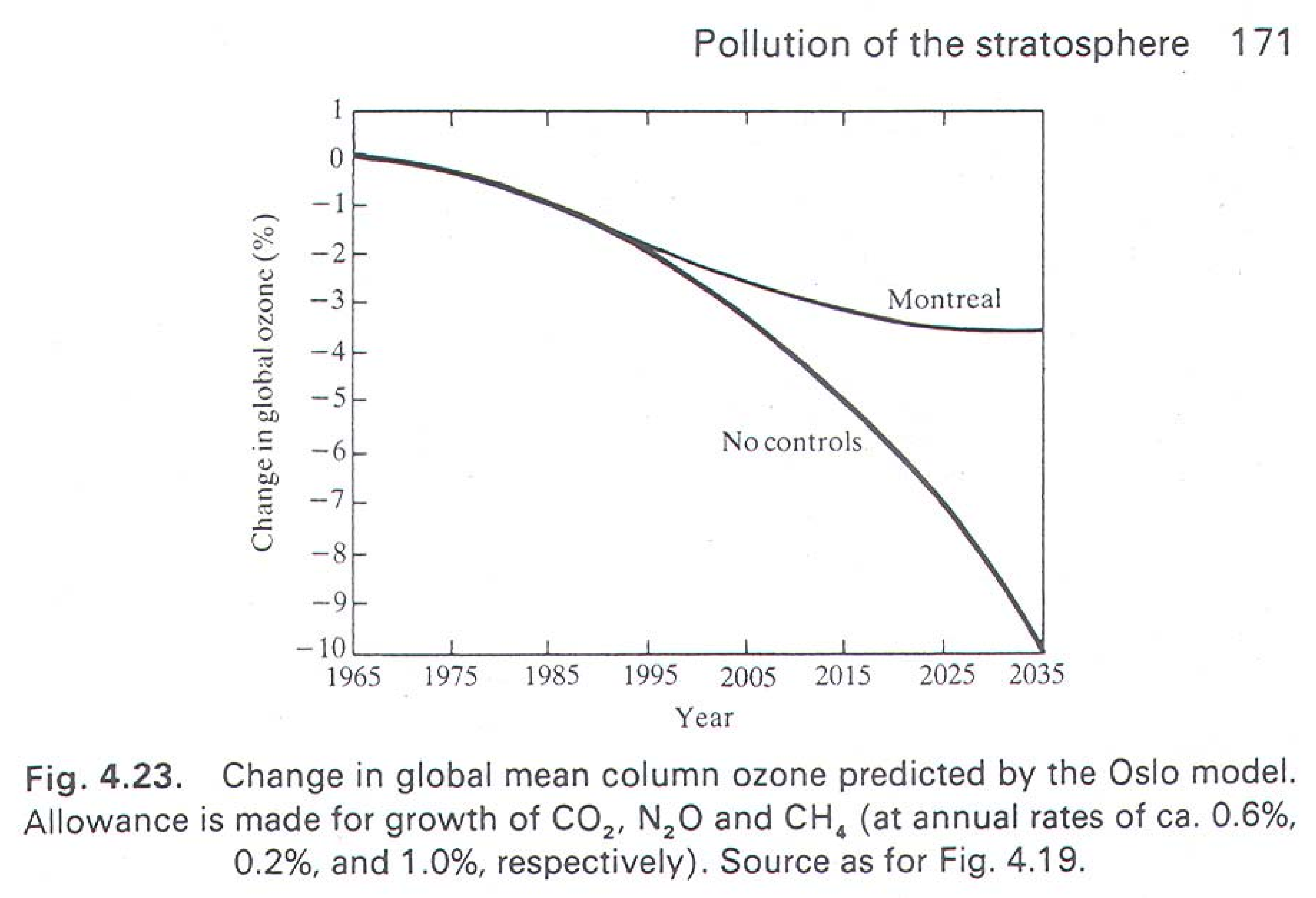


Fig. 4.21. Model predictions of the average concentrations of CFC11 and CFC12 in the atmosphere resulting from four different emission scenarios. Source: as for Fig. 4.19.



Pollution of the stratosphere 171

Fig. 4.23. Change in global mean column ozone predicted by the Oslo model. Allowance is made for growth of CO_2, N_2O and CH_4 (at annual rates of ca. 0.6%, 0.2%, and 1.0%, respectively). Source as for Fig. 4.19.

Koplung Klima-änderung und Stratosphärische O_3-Schicht

Erhöhte CO_2 usw.:

- **Erhöhte Temperatur in der Troposphäre**
- **So, Abkühlung in der Stratosphäre**
- **Mehr Polar Stratospheric Clouds**

J. Austin et al.

“Possibility of an Artic ozone hole in a double-CO_2 climate”,

Nature, vol. 360, Nov. 19, 1992, 221-225

Tropospheric chemistry

- **Gasphase chemistry: tropospheric ozone and related components**
- **Heterogeneous chemistry: Aerosol physics and chemistry**
- **Dry and wet deposition**
- **Chemical Transport Modelling - CTM**
- **Emissions**

Tropospheric ozone

- 90 % of all ozone is in the stratosphere, only about 10 % is in the troposphere
- Ozone concentration in the troposphere increases with height above the surface
- Basic question in 1970: What is the origin of ozone in the troposphere and at groundlevel??

  Diffusion from the stratosphere (Junge)

  Produced by anthropogenic emissions (Crutzen)

Current insight: In the Northern hemisphere:

Total troposphere: 50 % of the ozone from stratosphere
50 % anthropogenic

At ground level : 90-95 % anthropogenic

Ozone and summersmog

Los Angeles, 1945, Haagen-Smit

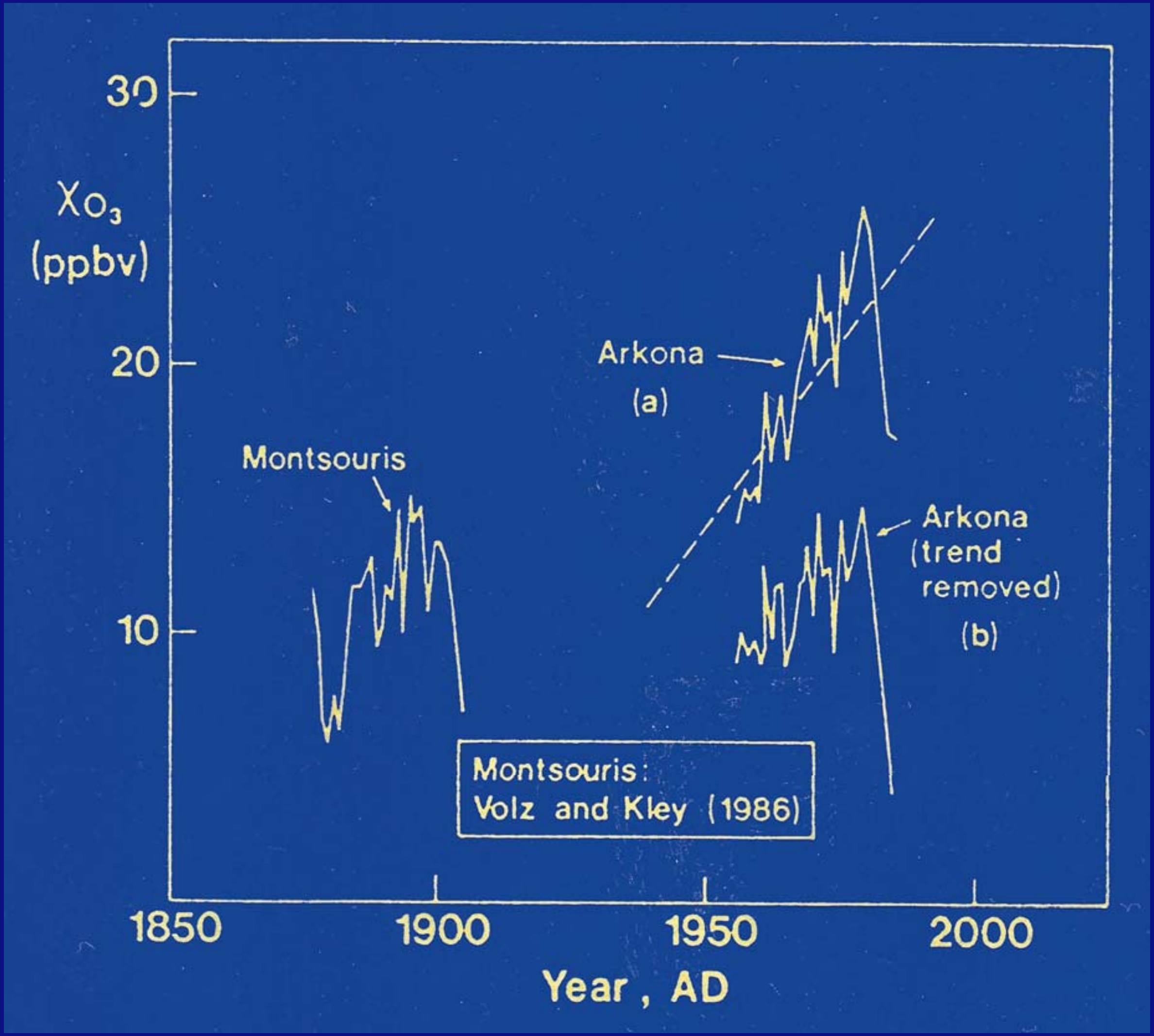
Photochemical smog : (smoke + fog = smog) in summer

Wintersmog : London ‘fog’ 1940-1950: SO_2 and Sulfate-aerosols

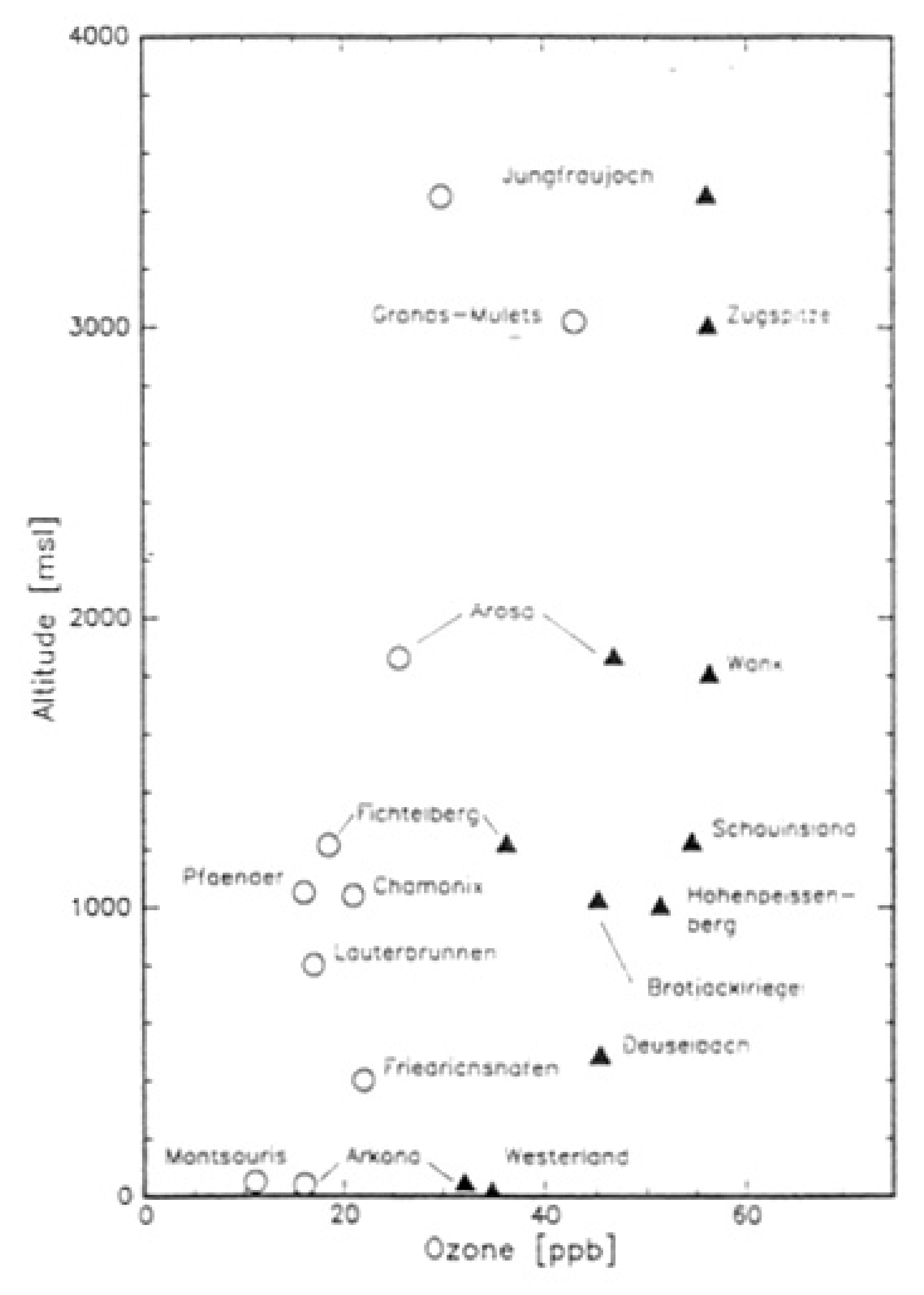
Summersmog : LA: NOx and Reactive Hydro-carbons

Effects : Eye-irritation, breathing problems (asmatics)
Forest
Plants (tomato’s, tabacco)

Surface-near ozone at Montsouris 1876-1905 (Volz et al., 1986) compared to the Arkona series



Observations



IV. Tropospheric chemistry

Stratospheric chemistry: mostly gasphase

Tropospheric chemistry: gasphase, aquous phase, aerosols

Formation of tropospheric ozone

$$\begin{array}{lcll}
NO_2 + hV & \rightarrow & NO + O & \lambda < 410\ \mathrm{nm} \\
O + O_2 + M & \rightarrow & O_3 + M & \\
O_3 + NO & \rightarrow & NO_2 + O_2 & \\
\hline
NO_2 + O_2 & \rightleftarrows & NO + O_3 &
\end{array}$$

Photo-stationairy state

Increase of tropospheric ozone: shift in photo-stationairy state:

$NO_2 + O_2 \rightleftarrows NO + O_3$

Reactive hydrocarbons:

$RH + OH + O_2 \rightarrow RO_2 + H_2O$

$RO_2 + NO \rightarrow RO + NO_2$

R: CH_3, C_2H_5 etc. etc.

$RO + O_2 \rightarrow$ Aldehydes + HO_2

$H_2O + NO \rightarrow NO_2 + OH$

Example

$CH_4 + OH \rightarrow H_2O + CH_3$

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\uparrow$

stable product

$CO + OH \rightarrow CO_2 + H$

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

$HO_2 + NO \rightarrow NO_2 + OH$

Netto:

$$CH_4 + 8\,O_2 \rightarrow CO + 4\,O_3 + 2\,OH + H_2O$$

$$CO + 2\,O_2 \rightarrow CO_2 + O_3$$

Also:

$$\begin{aligned} P\,(O_3) = {} & k_1\ [NO]\ [RO_2] \\ & + k_2\ [NO]\ [HO_2] \end{aligned}$$

Reactive Hydrocarbons: RH's transform NO in NO_2 without a loss of O_3, so leads to increase in O_3 concentration

Different RH's have a different Photochemical Ozone Creation Potential: POCP

	Initial NO-NO_2	Total, including products
Ethene	2	4
Propene	2	7
1-Butene	2	10
Ethane	2	6
Propane	3	8

RH : Reactive Hydrocarbons

VOC : Volatile Organic Compounds

NMVOC : Non Methane VOC

Alkanes : Saturated Compounds

Examples : Ethane C_2H_6 atmospheric life-time : 80 days

Propane C_3H_8 15 days

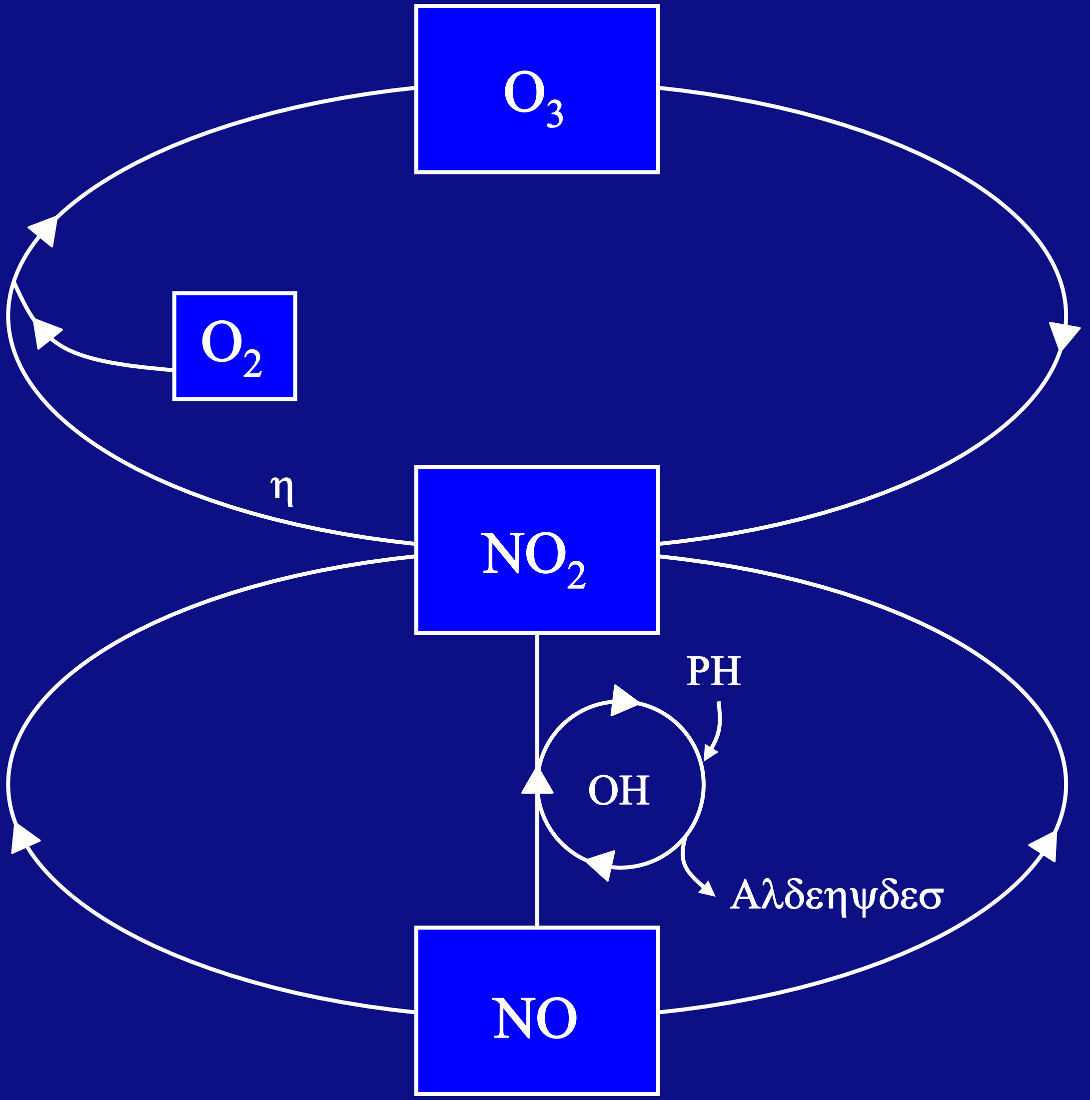
Alkenes : Unsaturated Compounds

Examples : Ethene C_2H_4 2 days

Propene C_3H_6 15 hours

Isoprene C_5H_8 5 hours (biogenic)

Alkynes	**:**	**Example:**	**Acethylene C_2H_2**	**30 days**
Aromatics	**:**	**Example:**	**Benzene C_6H_6**	**20 days (carciogenic)**
Tolueen	**:**		**$C_6H_5CH_3$**	**3.6 days**
Terpenes	**:**		**$C_{10}H_{16}$**	**2 hours (biogenic)**
Aldehydes and ketones	**:**	**Example:**	**Formaldehyde HCHO**	**1.6 days**
Alcohols	**:**	**Example:**	**Methanol: CH_3OH**	**20 days**



O_3

O_2

η

NO_2

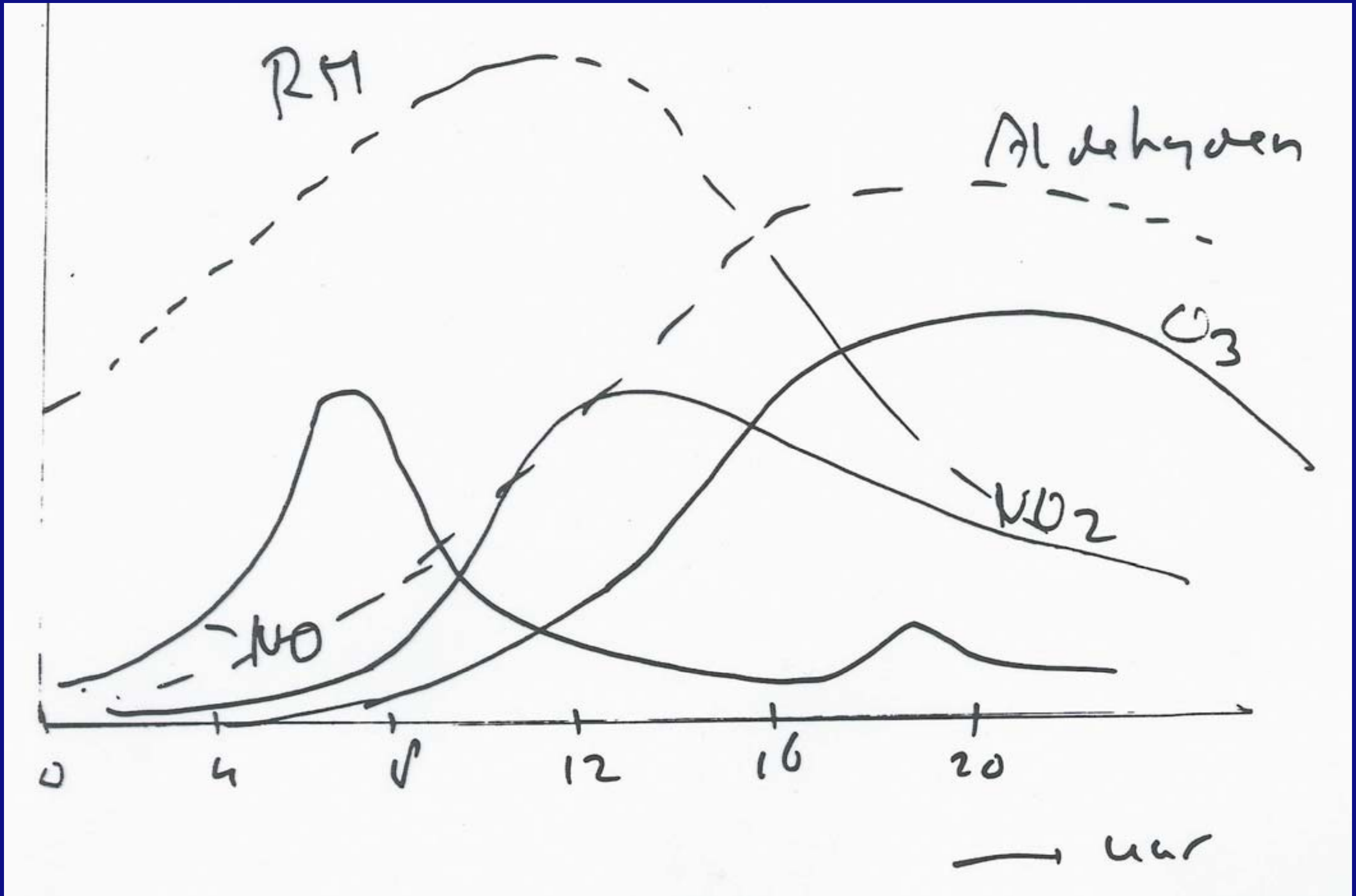
PH

OH

Αλδεηψδεσ

NO

Meting in L.A.



$NO \rightarrow NO_2 \rightarrow O_3$

$RH \rightarrow$ Aldehyden

Policy for tropospheric O_3

RH versus NO_x abatement,

Non-lineair: $NO + O_3 \rightleftarrows NO_2 + O_2$

lowering of NO leads to increase in O_3

high RH/NO_x-ratio: NO_x-strategy

low RH/NO_x-ratio: RH-strategy

Biogenic RH-emissions

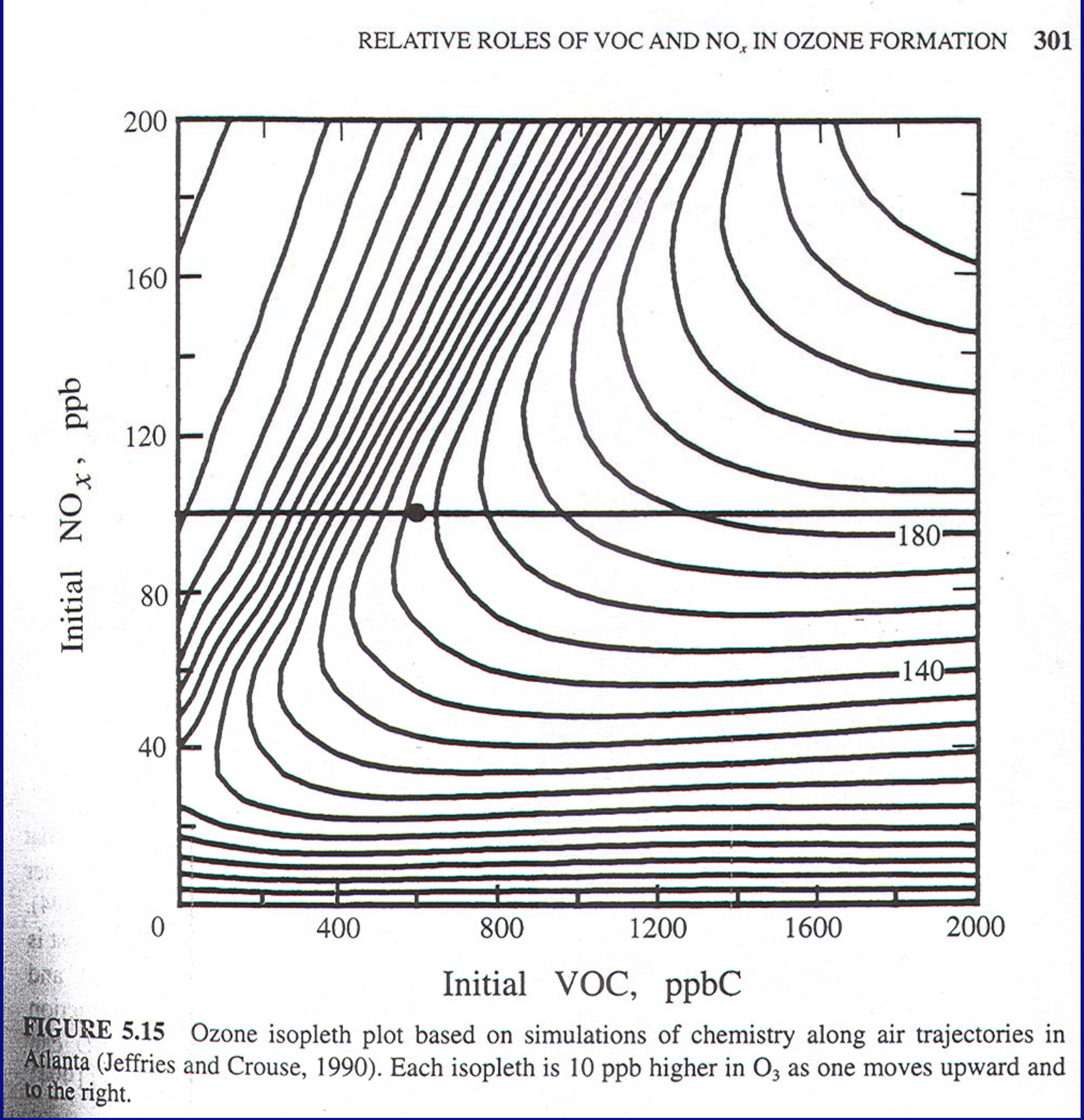


FIGURE 5.15 Ozone isopleth plot based on simulations of chemistry along air trajectories in Atlanta (Jeffries and Crouse, 1990). Each isopleth is 10 ppb higher in O_3 as one moves upward and to the right.

Normal reactions in Northern Hemisphere, for NOx < 50 ppt

$RH + OH + O_2 \rightarrow RO_2 + H_2O$

$RO_2 + NO \rightarrow RO + NO_2$

$RO + O_2 \rightarrow$ aldehydes

$HO_2 + NO \rightarrow NO_2 + OH$

For NOx < 50 ppt

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$O_3 + HO_2 \rightarrow 2O_2 + OH$

$O_3 + OH \rightarrow O_2 + HO_2$

Leads to decrease on O_3-concentration

The formation of the OH-radical, the hydroxyl-radical

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

$$O\ ('D) + H_2O \rightarrow 2\ OH$$

In free troposphere (> 2/3 km)

reaction OH with CH_4, CO most important

In the polluted boundary layers

reaction OH with NO_2 and HCHO most important

residence time OH ≈ 0.3 - 25 sec

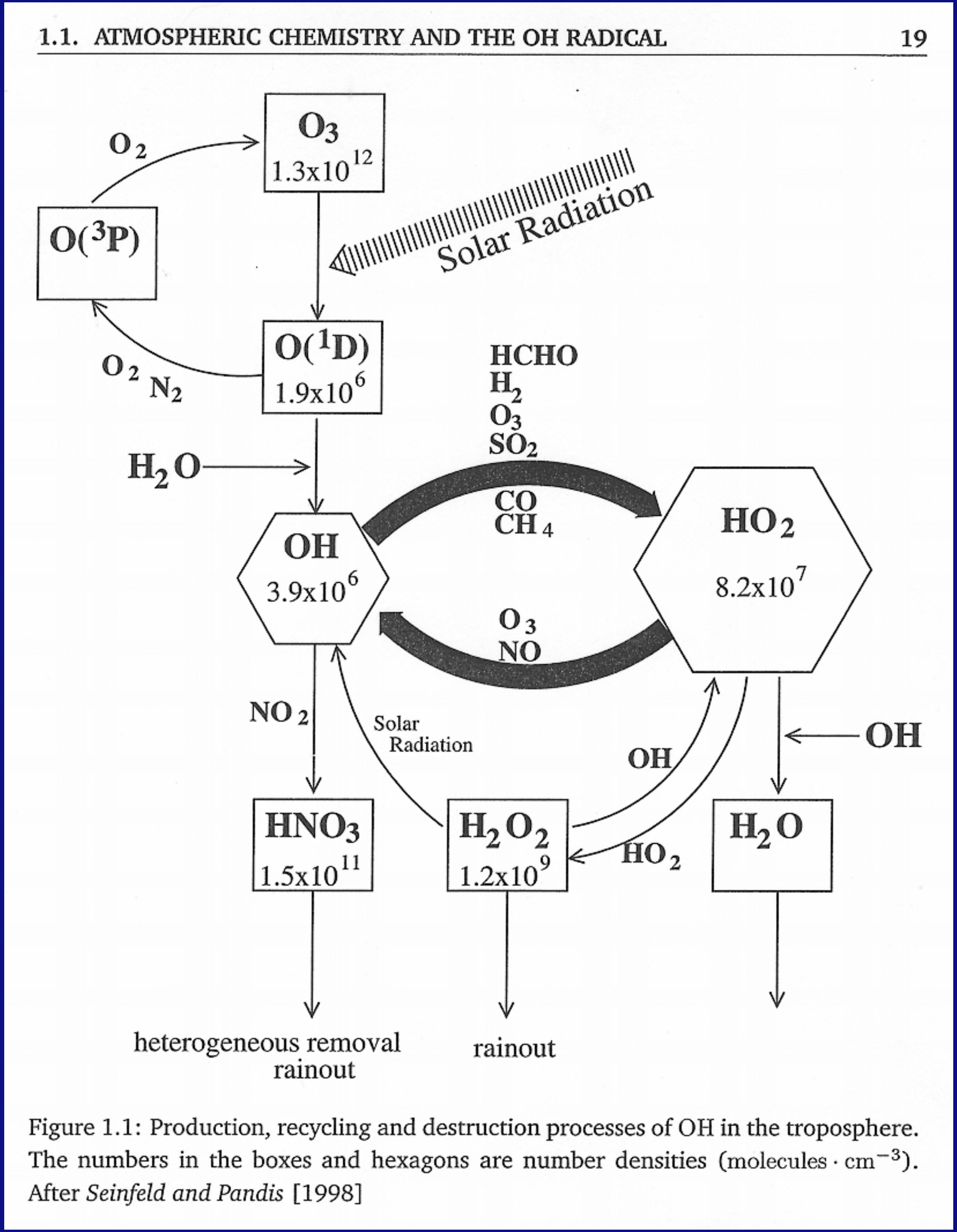
mean concentration: 5.10^5 molecules/cm^3

OH-radical 'discovered' by Levy, 1971

OH reactes with CH_4, CO, with NO_2, HCHO, H_2, O_3, NH_3, SO_2, RH

OH is the cleansing agent of the atmosphere, and determines the atmospheric life time of species

OH does not react with N_2, O_2, H_2O, CO_2



1.1. ATMOSPHERIC CHEMISTRY AND THE OH RADICAL 19

Figure 1.1: Production, recycling and destruction processes of OH in the troposphere. The numbers in the boxes and hexagons are number densities (molecules · cm^{-3}). After *Seinfeld and Pandis* [1998]

Trends in the OH-concentration

Increase in O_3	Increase in OH
Increase in hv	Increase in OH
Increase in H_2O	Increase in OH
Increase in CH_4	Decrease in OH
Increase in CO	Decrease in OH

But: increase in CH_4, CO leads to increase in O_3 also …

Guy Brasseur and Ron Prinn: “Is the ‘cleansing capacity’ of the atmosphere changing?”
IGBP Newsletter 43, 2002.
Conclusion: Relatively constant since 1850, may be about 20 % less.

Global CH_4-budget

Emission sources in Tg/ year

Animals	100-220
Rice-paddies	280
Swamp	130-260
Termites	150
Biomass-burning	30-100
Natural gas leakage	20
Coal mines	40
Total ~	500

Loss term

CH_4 + OH	~ 400 Tg/ year
CH_4-flux to the stratosphere	~ 60
Total	~ 460
Concentration CH_4	~ 1800 ppb Northern Hemisphere ~ 1700 ppb Southern Hemisphere
Atmospheric life-time	~ 8 years

Biogenic: Anaerob : $2\ H_2 + CO_2 \rightarrow CH_4 + O_2$

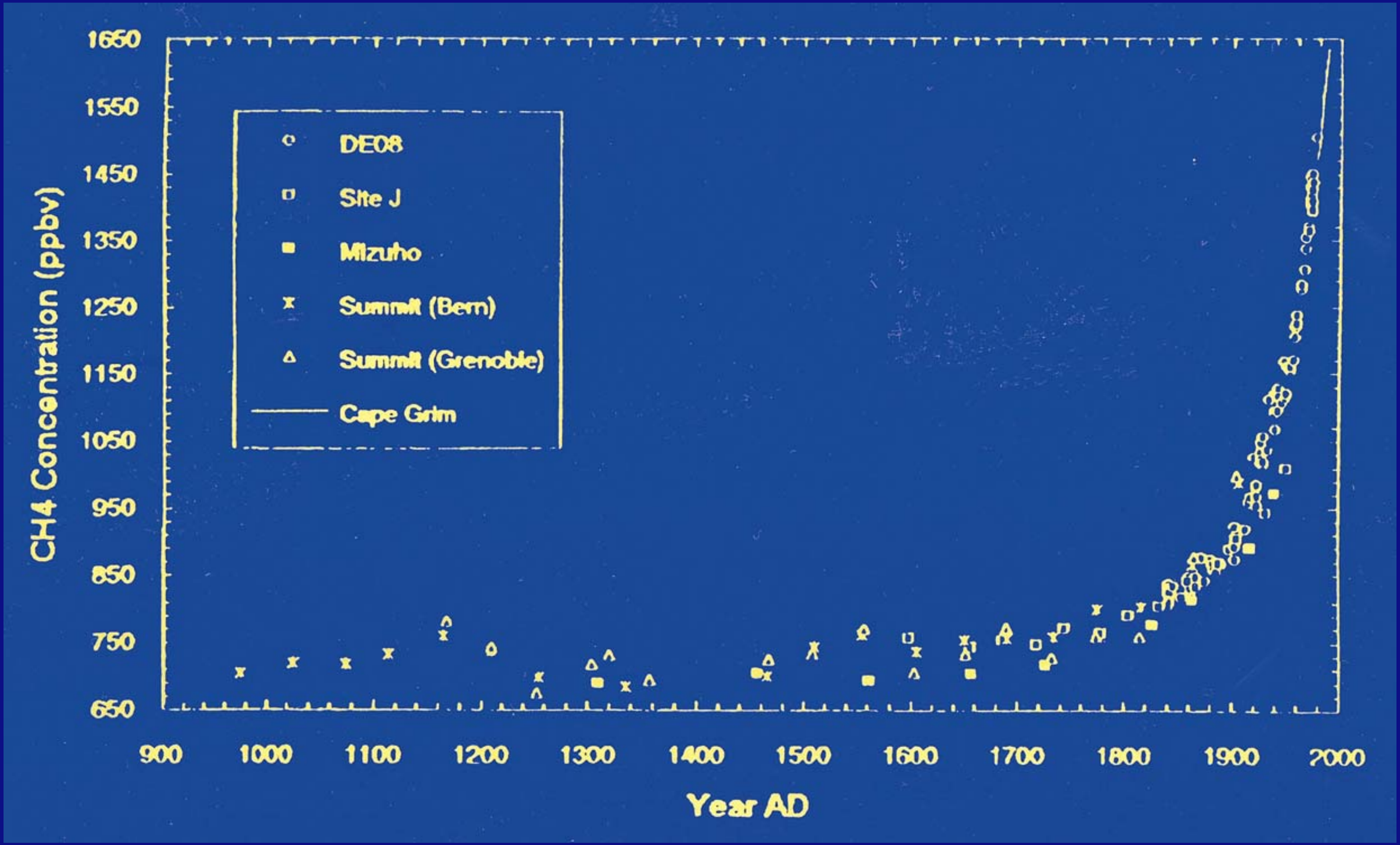
Aerob : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Biogenic/Anthropogenic distinction by

14^C production by cosmic radiation t ~ 5700 year

So, 14^C content biogenic emissions = 14^C content trees

14^C content fossil fuel = 0


CH4 Concentration (ppbv)
1650
1550
1450
1350
1250
1150
1050
950
850
750
650
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
Year AD
DE08
Site J
Mizuho
Summit (Bern)
Summit (Grenoble)
Cape Grim

Trend increase CH_4-concentration

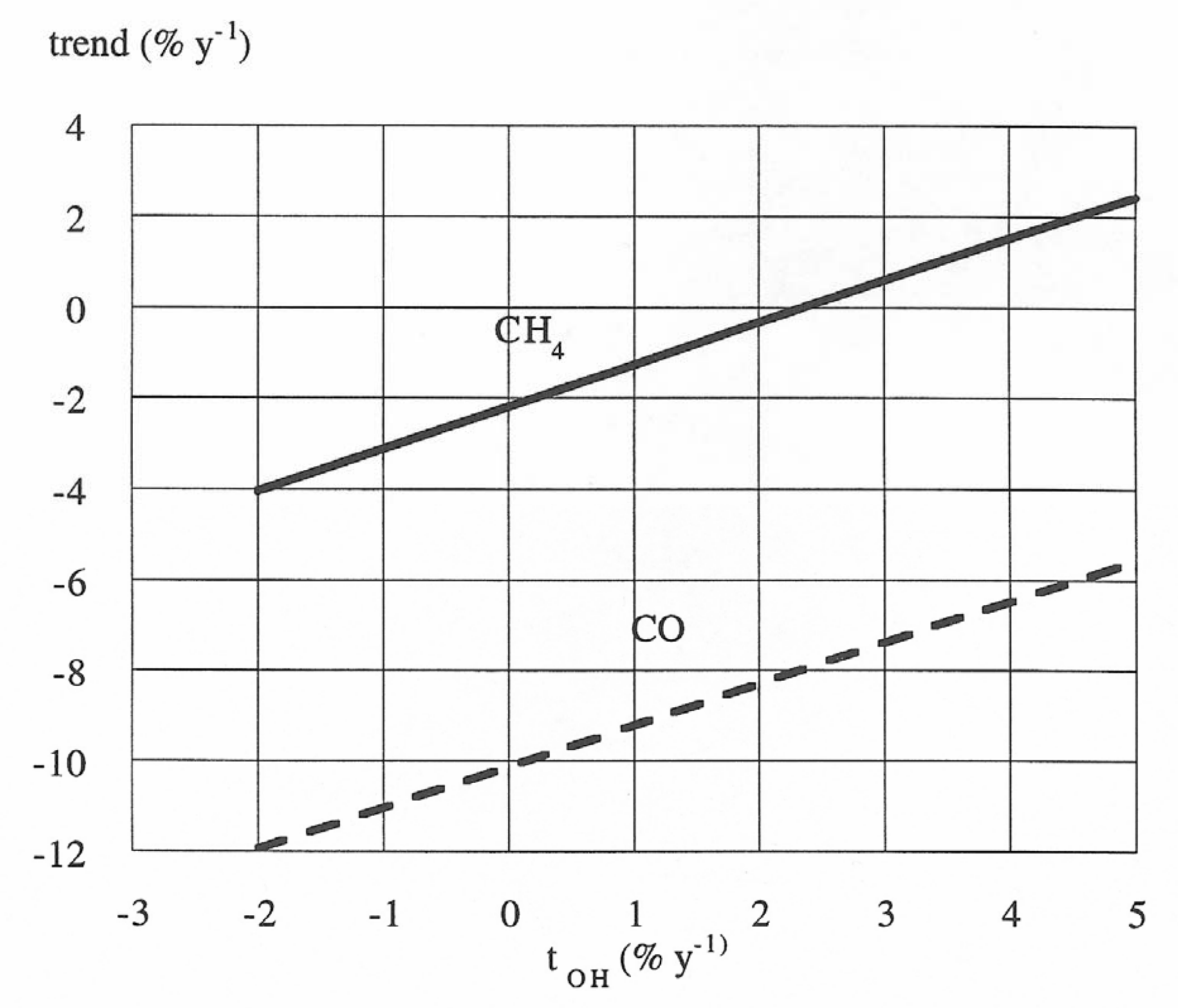
1970-1985 : 1.5 % / year

1985-1989 : 0.8 % / year

around 1993 : 0 %

1995-2003 : 0.3 % / year

Reason : CH_4-emission changes ??
OH increase ??


trend (% y-1)
4
2
0
-2
-4
-6
-8
-10
-12
CH4
CO
-3
-2
-1
0
1
2
3
4
5
t OH (% y-1)

Han van Dop and Maarten Krol

“Changing trends in tropospheric methane and carbon monoxide: a sensitivity analysis”. Tellus, 2001

Calculations with a 1-D transport-chemistry model

Ivar Isaksen and Oystein Hov

“Calculation of trends in the tropospheric concentration of O_3, OH, CO, CH_4 and NO_x .Tellus, 39 B, 271-285, 1987

Calculations with a 2-D global transport-chemistry model

I) Eiszeit Methan

Vor 38.000/14.500/11.500 Jahre :

Erwärmung in weniger hundert Jahren

Als reaction steigt auch CH_4 an-verstärkt Temperatur Erhöhung

Quelle unklar:

Im Eiskristalle gelagert $CH_4.H_2O$, vielleicht nicht??

Mehr bei Bacterien?

II) Nature Artikel, Januar 2006

***Frank Keppler et al*:**

Methane emissions from terrestial plants under aerobic conditions

A lot of discussions!

Tropospheric O_3-budget

A. Inflow from the stratosphere

B. Dry deposition at the surface

C. Chemical production

D. Chemical destruction

No wet deposition, O_3 does not desolves in water

Ad A. Stratosphere-Troposphere exchange

Change in tropopause height

Tropopause folding

Turbulent transport by jet-streams

Small scale turbulence

Estimate: NH 300-500 Tg/ year

SH 150-250 Tg/ year

(jet-streams stronger in NH)

ad B. Deposition flux

V_d deposition velocity

Oceans/snow	**0.001 m/s**
Grassland	**0.005 m/s**
Forest	**0.006 m/s**

Result: NH 425 Tg/ year

SH 275 Tg/ year

Ozone Production: NOx and RH

Ozone Destruction: by hν

Somewhat by $O_3 + OH \rightarrow HO_2 + O_2$

$O_3 + HO_2 \rightarrow 2O_2 + OH$

Conc. O_3 NH tropics 35 ppb

> 30 ° N 45 ppb

SH tropics 30 ppb

< 30 ° S 40 ppb

Total: NH 140 Tg

SH 120 Tg

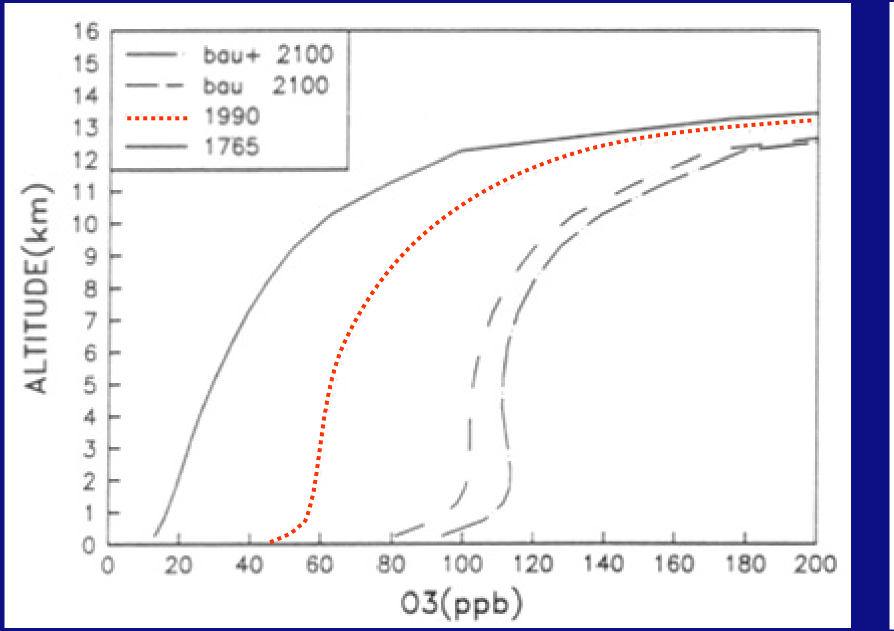
Atmospheric life time NH 100 days

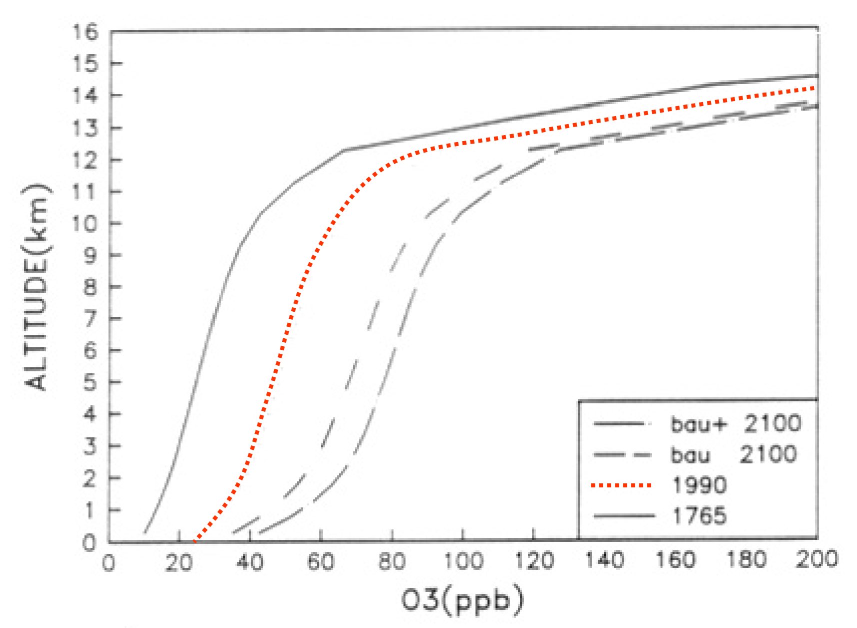
SH 120 days

Calculations with a global chemical transport model

	In Tg/year	
	Pre-industrial	2000
Chem. Prod.	1384	2212
Chem. Destr.	1327	2020
Netto	12	194
Dep.Flux	400	678
Strat. Flux	388	388

2-D model


ALTITUDE(km)
O3(ppb)
bau+ 2100
bau 2100
1990
1765
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0
20
40
60
80
100
120
140
160
180
200


ALTITUDE(km)
O3(ppb)
bau+ 2100
bau 2100
1990
1765
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0
20
40
60
80
100
120
140
160
180
200

Dry Deposition

$$\mathrm{Flux} = \mathrm{Fs}\ \ [\mathrm{conc.\ m/s}]$$

$$\mathrm{Fs} = \mathrm{Kz}\,(z)\,\frac{\partial C}{\partial_z}$$

$$-\,\mathrm{Fs} = (\,C\,(z)\mathrm{ref} - C\,(o)\,)\ /\int_{o}^{z}\frac{d_z}{K_z\ (z)}$$

$$= (\,C\ (z)\mathrm{ref} - C\ (o)\,)\ /\ \mathrm{ra}\ (z)$$

zref : reference hight, within the constant flux-layer

ra (z) : atmospheric resistance

rb : viscous sublayer

rc : surface resistance

$$-F_s = [\,C\,(z_{ref}) - c\,(o)\,] \,/\, r_a + r_b + r_c$$

with $C\,(o)$: concentration at $z = 0$, often zero:

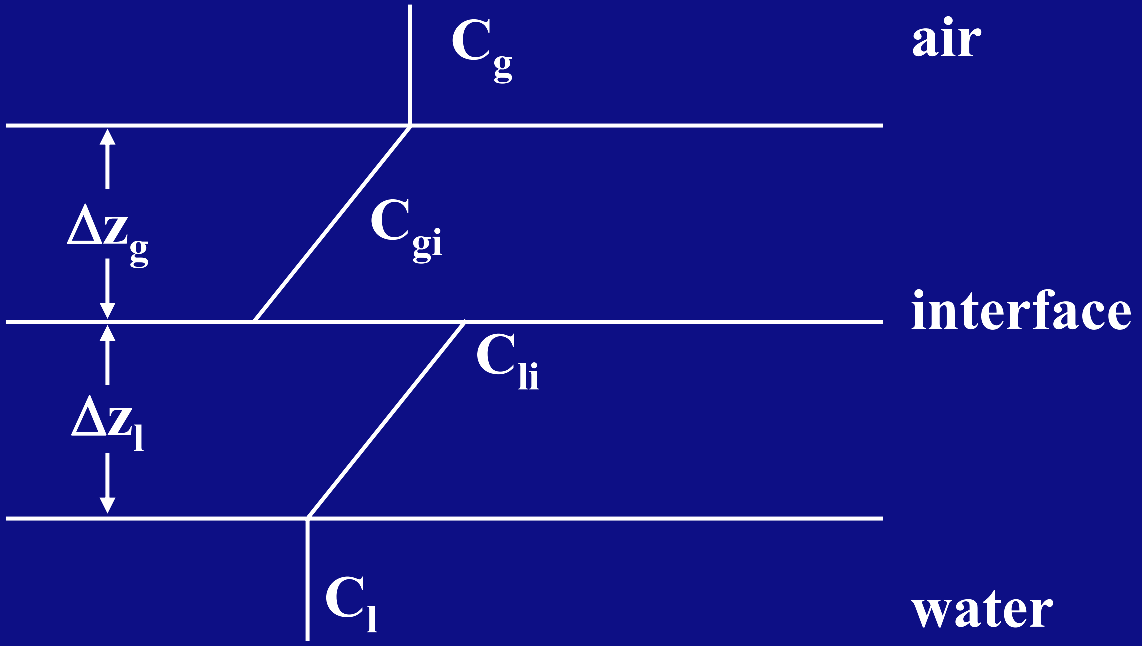
$$-F_s = V_d\;C\;(z_{ref})$$

V_d : Deposition velocity

Dry deposition velocity V_d in cm/ s

	Grassland	Water
SO_2	0.8	0.4
O_3	0.8	0.04
HNO_3	2.5	0
NO_2	0.5	0

Dissolve in water



$$F_s = \frac{D_g}{\Delta z_g}\,(C_{gi} - C_g)$$

$$= \frac{D_l}{\Delta z_l}\,(C_l - C_{li})$$

Dg, Dl = Moleculair Diffusion Coefficient in gasphase and liquid phase

Cgi = H . Cli

H : Henry Constant

Fs = (Cl – Cgi / H) / (1/kg H + 1/kl)

$$\frac{D_g}{\Delta z_g} = kg \qquad \frac{D_l}{\Delta z_l} = kl$$

kg, kl : fct (windspeed)

$$Fs = \frac{l}{r} \left(Cl - Cgi / H \right)$$

Dry deposition to watersurfaces

	Kg	K_l	H	V_d
SO_2	0.44	9.6	0.02	0.4
O_3	0.51	0.049	3	0.05

Kg, K_l, V_d in cm/s

Wet Deposition

Two processes:

- **In cloud processes: Gases absorbed in droplets followed by deposition when it rains:**

  Rain Out

- **Below cloud processes:**

  Wash out

Emissions

Anthropogenic

Biogenic (living species) and natural

Anthropogenic

Combustion:

- $C + O_2 \rightarrow CO_2$
- $C_xH_y + O_2 \rightarrow xCO_2 + 0.5y\ H_2O$

Incomplete Combustion:

- VOC, CO, CH_4, Dust (BLACK CARBON!!)

Contained in fuels

$S \rightarrow SO_2$

Heavy metals

$N \rightarrow NO_x$

in gas N	**about 0 %**
in coal	**about 0.5- 3 %**

Thermic NO_x

- $N_2 + O_2 \rightarrow NO_x$
- High T + high $O_2 \rightarrow$ NO high
- Low T + low $O_2 \rightarrow$ NO low
- Industrial processes:
  HF, CFC’s, heavy metals, pesticides, particles etc.

Emissie benzine-auto's

N_2	78	%
CO_2	12	%
H_2O	5	%
O_2	1	%
CO	2	%
H_2	2	%
NO	0.06	%
RH	0.08	%

Biogenic Emissions

- Animals: CO_2, CH_4, NH_3
- Forests: VOC
- Soil/Bacteria: NO, N_2O
- Wetlands: CH_4
- Plancton: DMS, H_2S

Natural emissions

- **Sea-salt (NaCl)**
- **Wind-blown dust (sahara-sand)**
- **Lightning (NO)**
- **Natural forest fires (CO_2, CH_4, CO, VOC, NO, particles)**
- **Meteorites (particles)**
- **Vulcano's (CO_2, SO_2, H_2S, HCl, particles)**

The basis of atmospheric transport-chemistry modelling

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial x} + v\frac{\partial C_i}{\partial y} + w\frac{\partial C_i}{\partial z} = \frac{\partial}{\partial x}\left(K_h \frac{\partial C_i}{\partial x}\right) +$$

$$\frac{\partial}{\partial y}\left(K_h \frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial C_i}{\partial z}\right) +$$

chemistry + emissions – dry deposition – wet deposition

3-D Eulerian grid modelling

Global scale, continental scale, urban scale.

Model system at TRUMF : REM/CALGRID (continental)
+ urban version

Model system at TNO : LOTOS (continental)
and LOTOS –zoom (urban)

Characteristics of the model –systems:

Horizontal grid resolution 0.25 x 0.5 latlong, with nesting down to about 4 x 4 km^2

Vertical layers: 5-10 upto about 3-5 km

Gasphase chemistry (O_3) and aerosol physics and chemistry

Required input data

- Boundary conditions from observations, or global modelling (TM-3)

- Anthropogenic and biogenic and natural emissions

- Land use data base

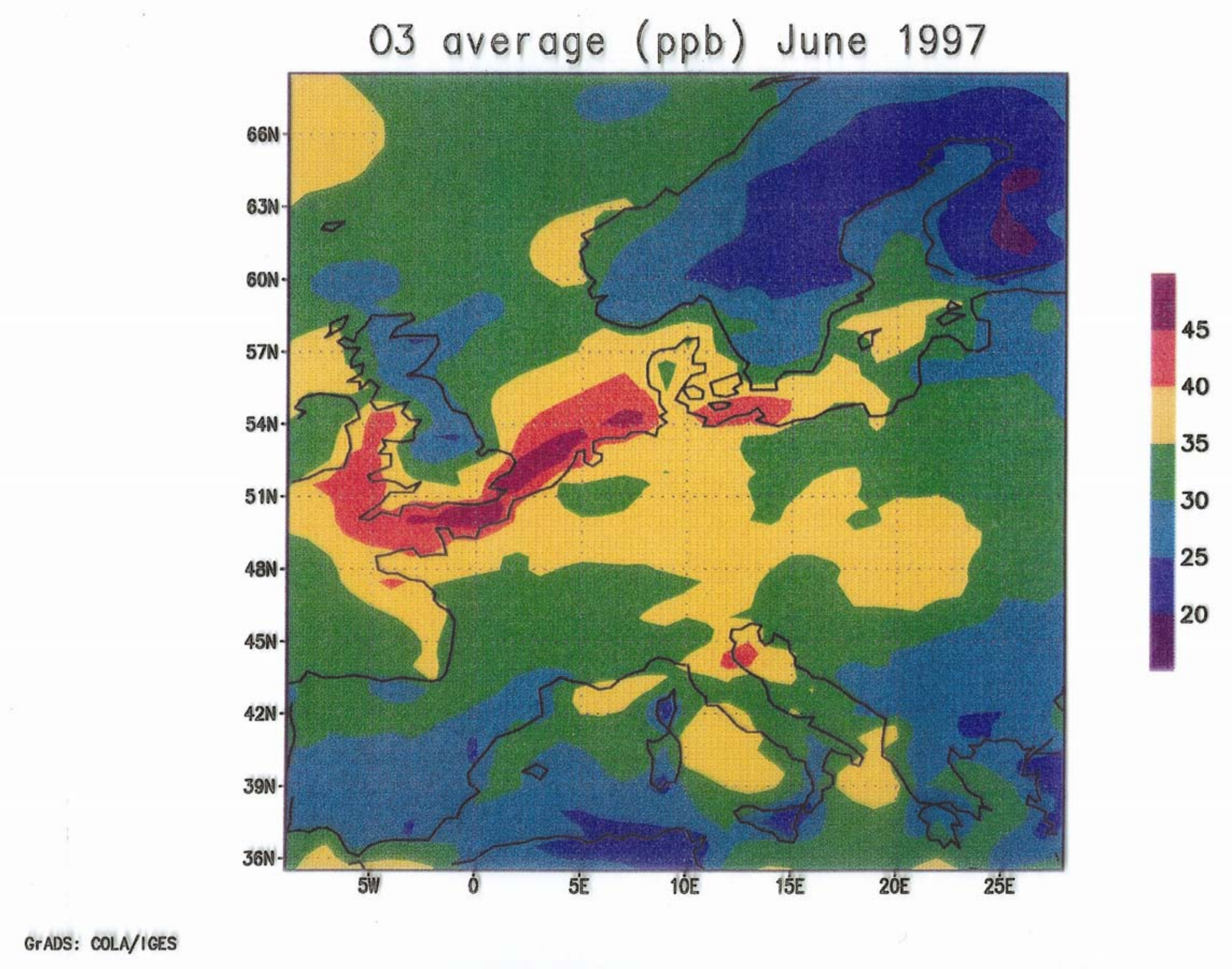
- Diagnostic meteorological fields (by Eberhard Reimer)
- Prognostic meteorological fields:
  - DWD-LM
  - NWP
  - MM5-reanalysis
  - ECMWF-ERA 40

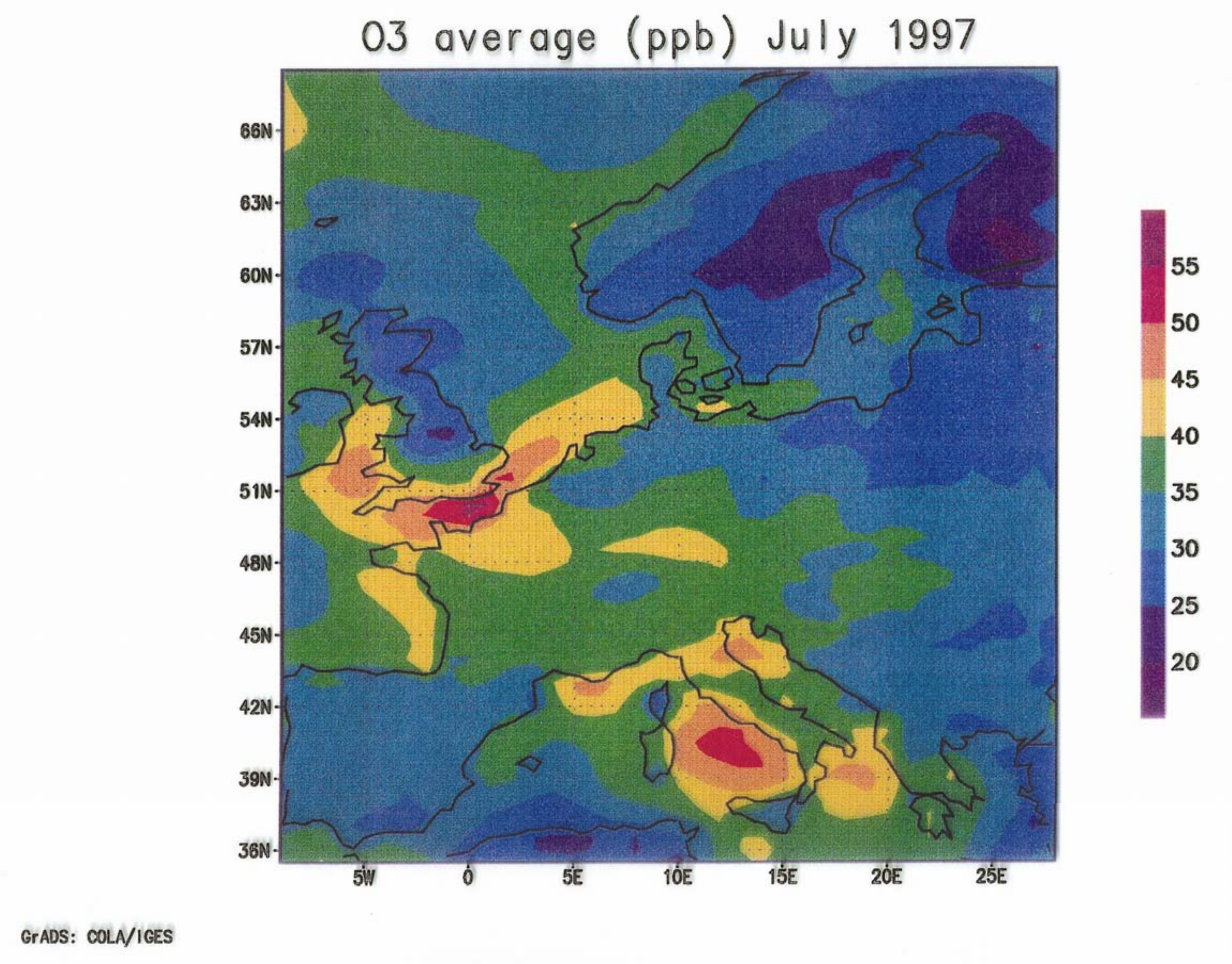
Model calculations hour-by-hour for one year, or more

Computer demand : several days on a PC

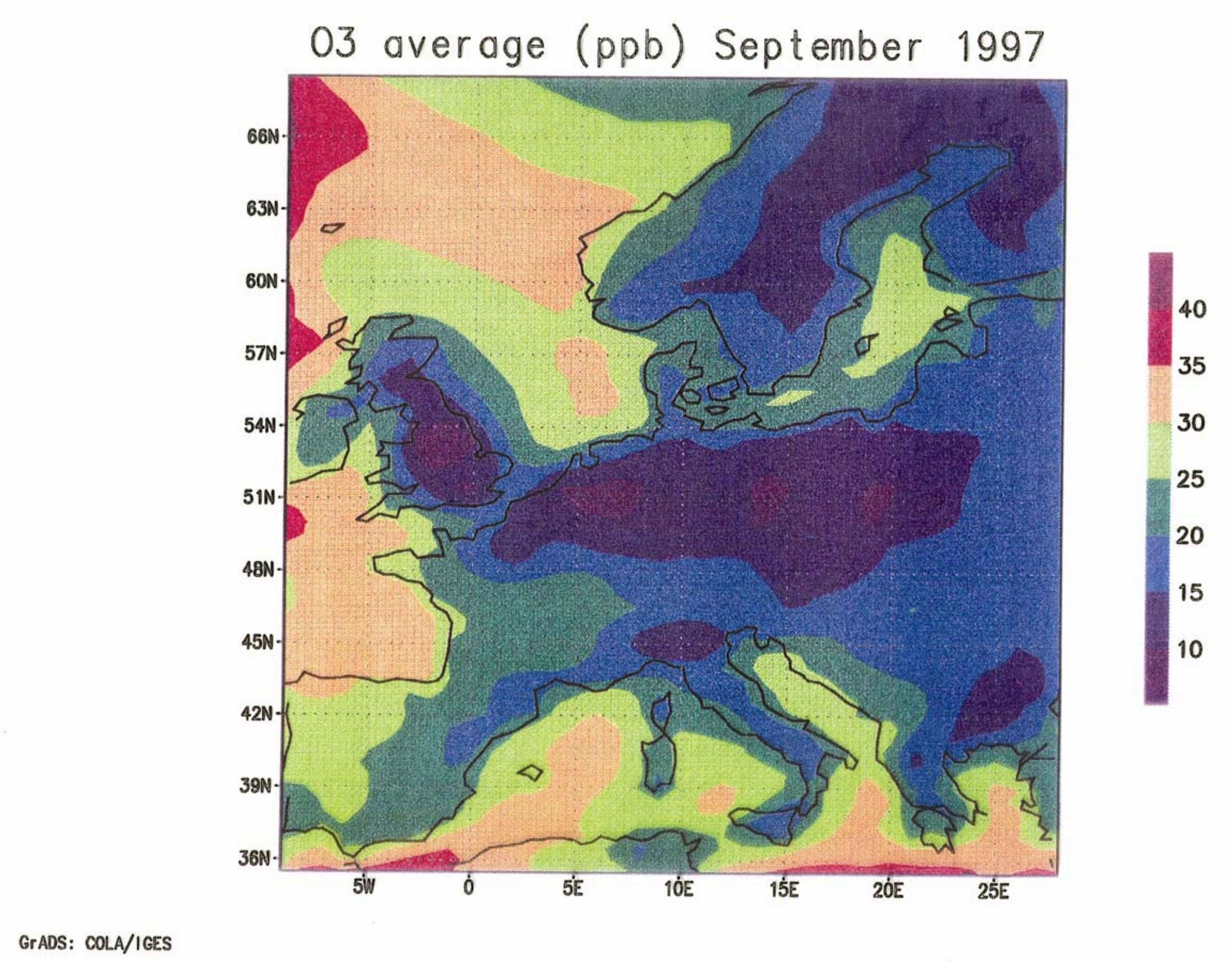
Purpose of modelling : Understanding the phenomena that control the chemical composition

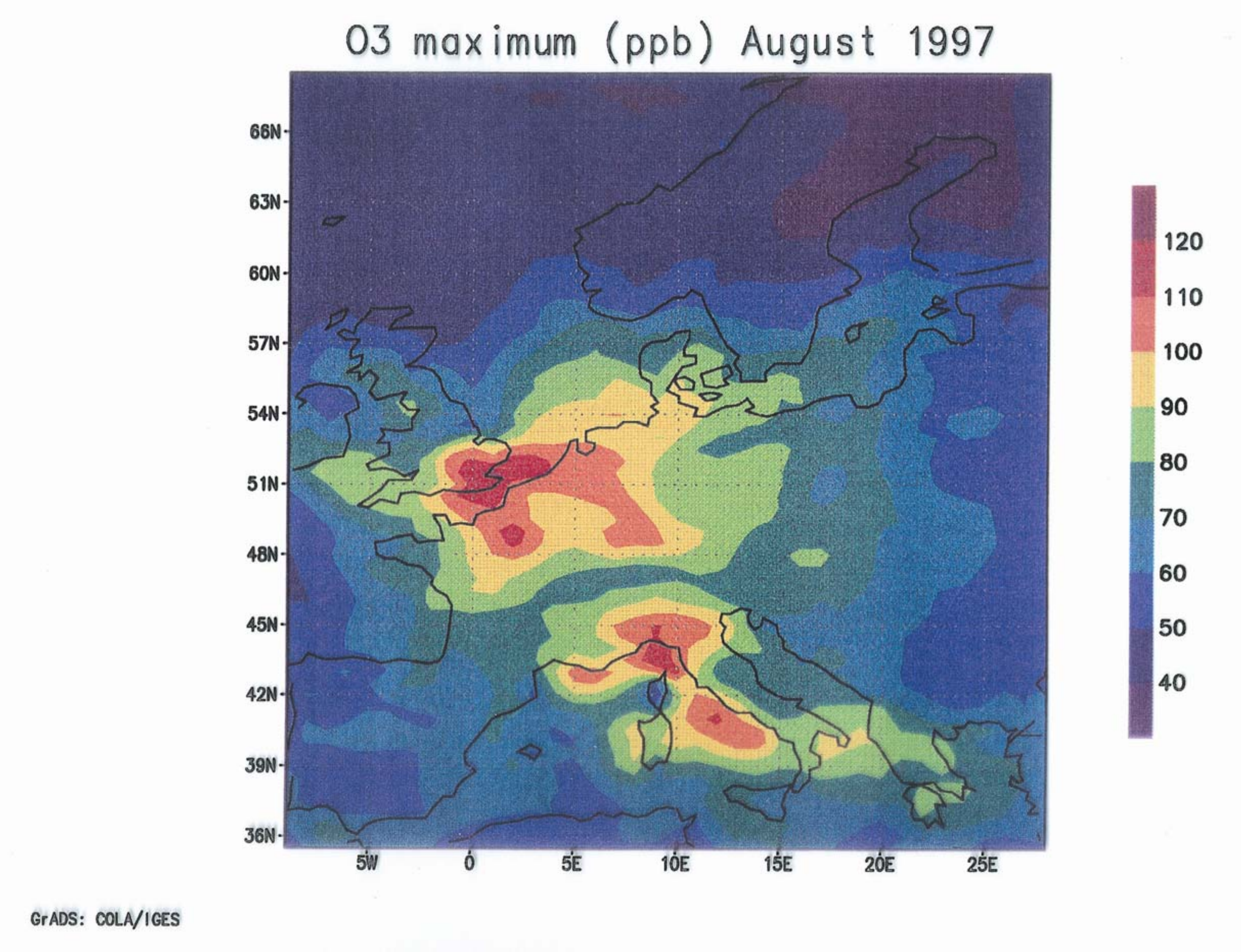
Policy applications : emission reduction strategies


O3 average (ppb) June 1997
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
5W
0
5E
10E
15E
20E
25E
45
40
35
30
25
20
GrADS: COLA/IGES



O_3 average (ppb) July 1997


O3 average (ppb) September 1997
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
5W
0
5E
10E
15E
20E
25E
40
35
30
25
20
15
10
GrADS: COLA/IGES

O3 maximum (ppb) August 1997
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
5W
0
5E
10E
15E
20E
25E
120
110
100
90
80
70
60
50
40
GrADS: COLA/IGES

Model evaluation: How reliable present the model the ‘reality’

Aspects:

- Model calculates volume averaged concentrations, observations are at a specific point
- Observations (might) contain errors, and their spatial representativity is (often) not well known
- Uncertainty and errors in input data: emissions
- Weak parts of the model as description of vertical exchange processes and the treatment of clouds
- Chemistry is non-linear: Right for the wrong reasons

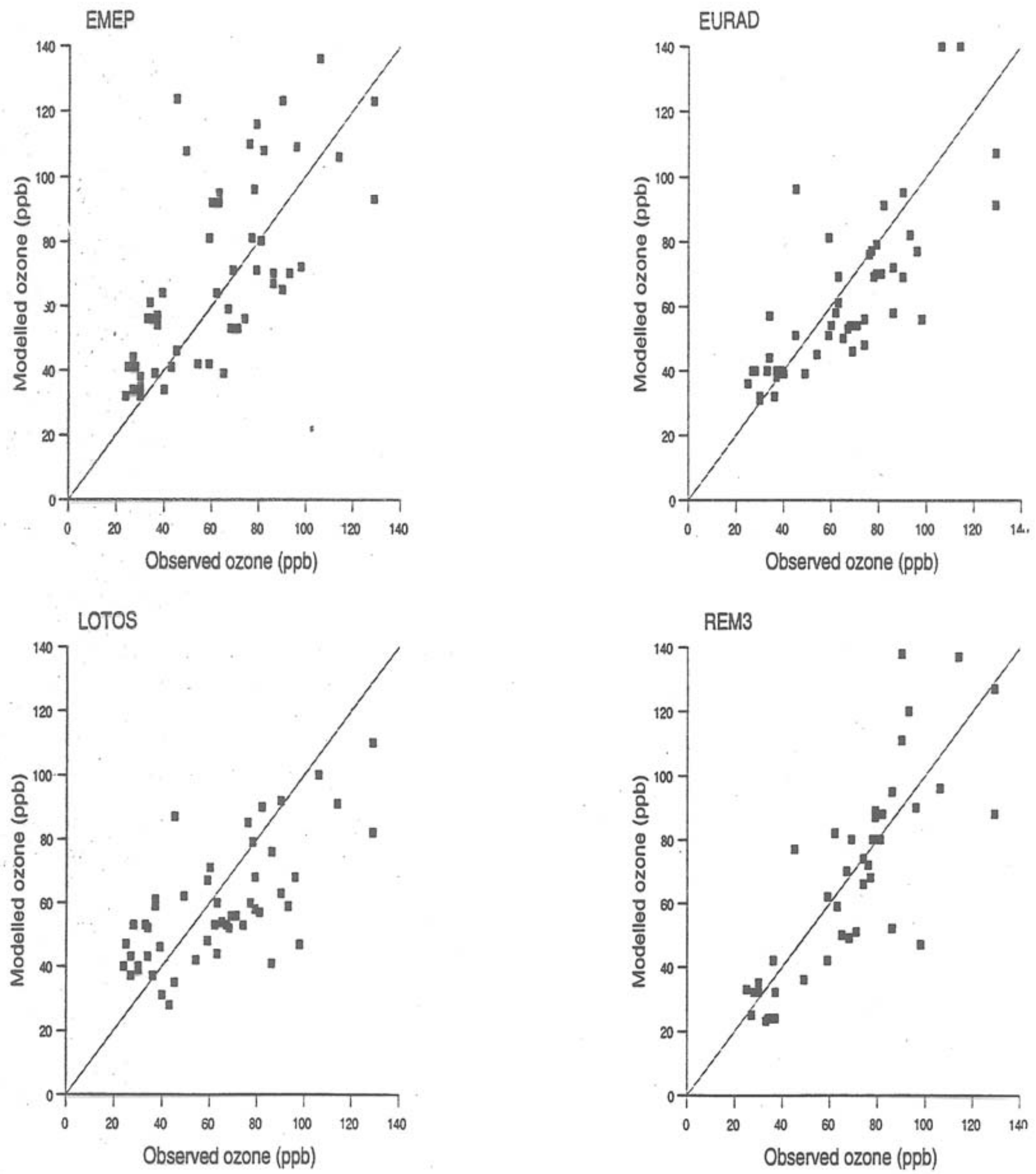
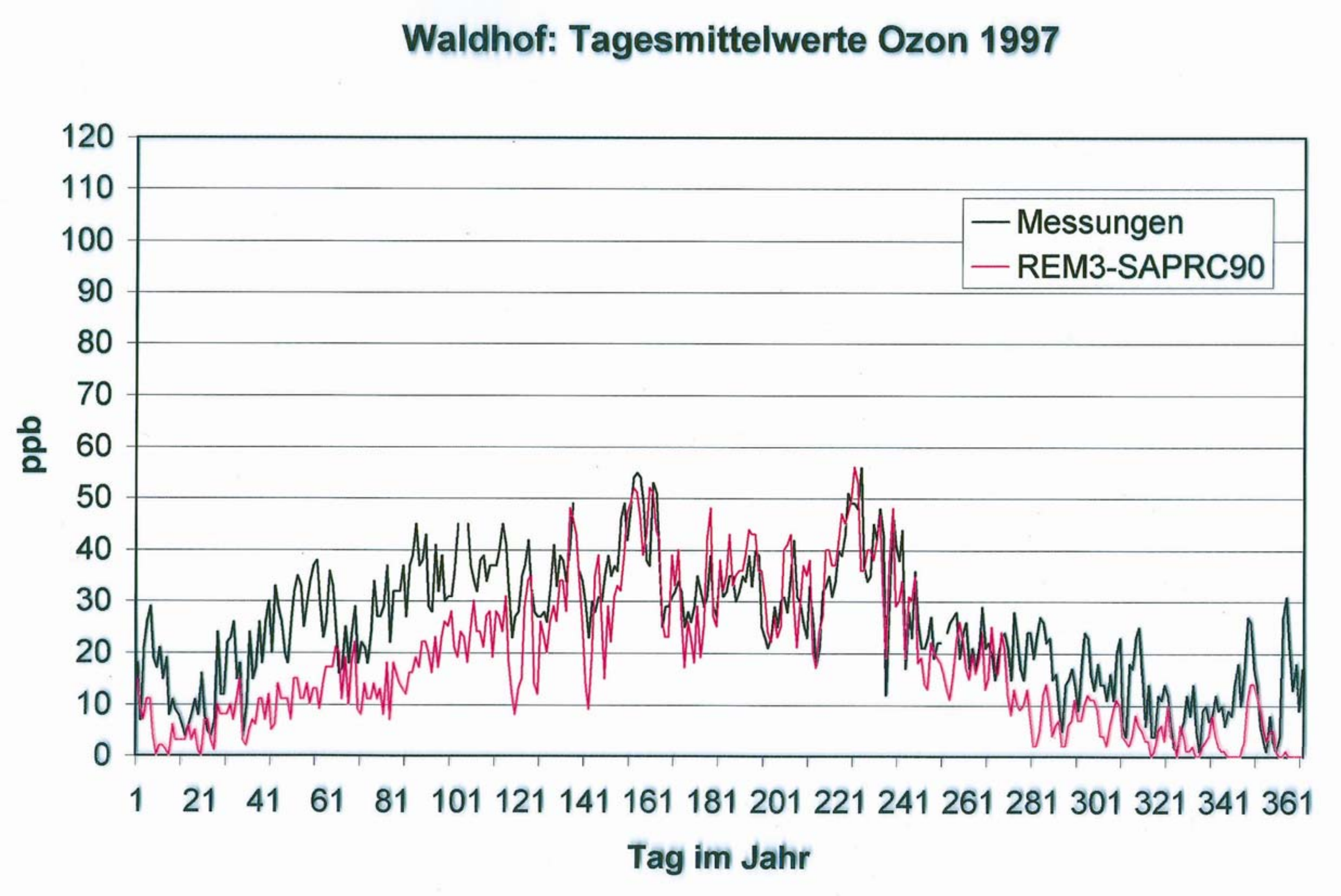
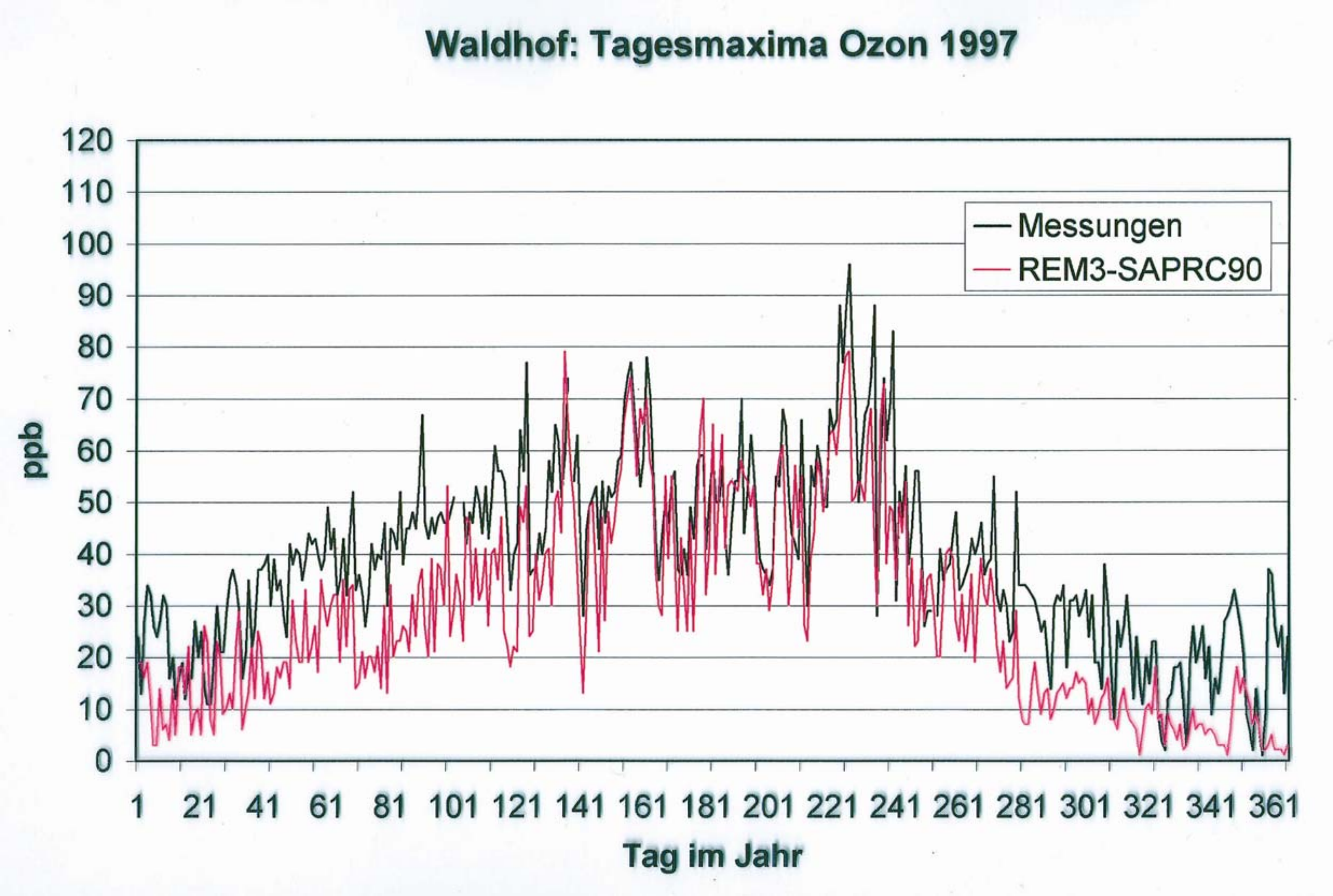
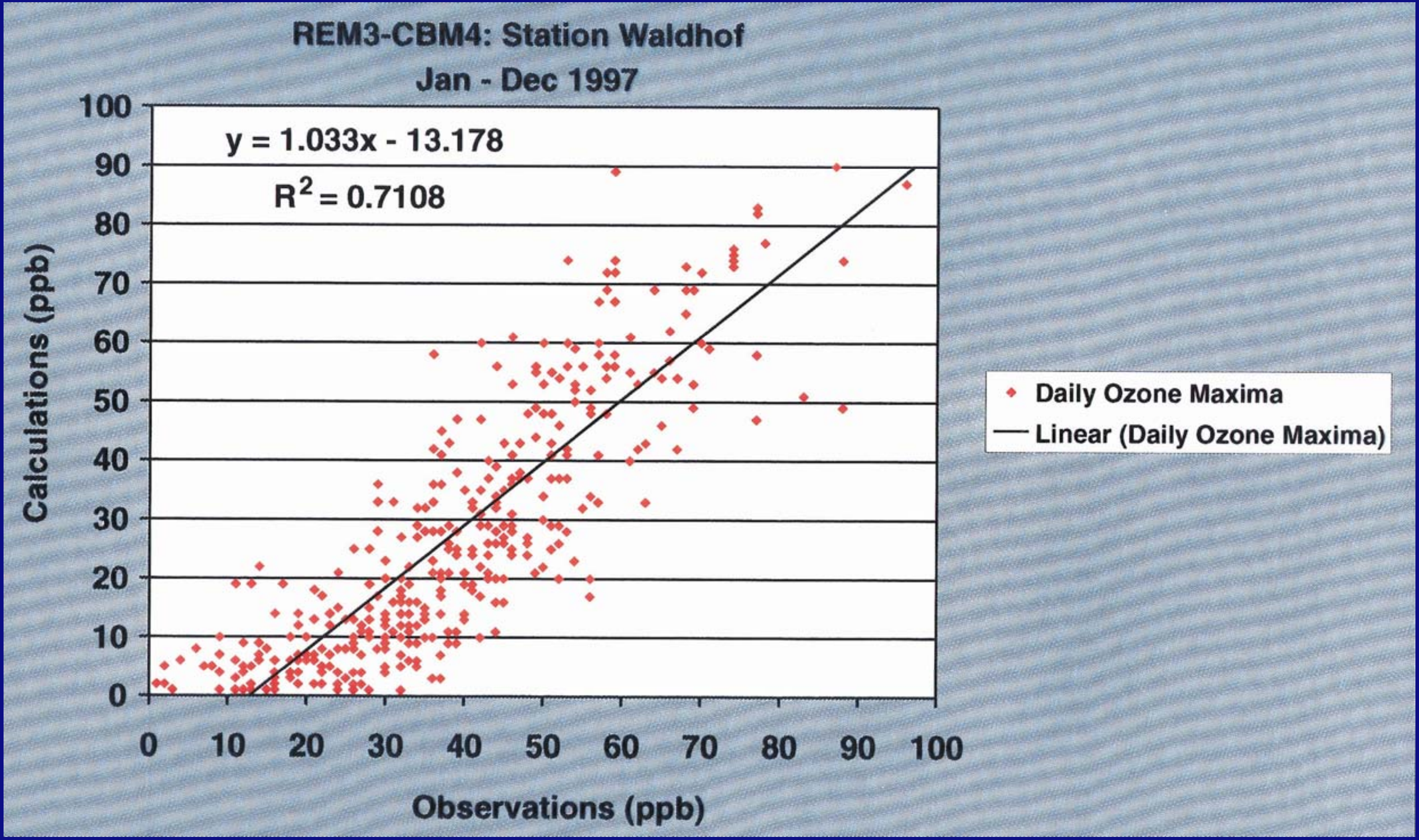


Figure 6.4: Scatter diagrams of modelled versus observed ozone at 12 UTC, 4th August, 1990.


Waldhof: Tagesmittelwerte Ozon 1997
120
110
100
90
80
70
60
50
40
30
20
10
0
ppb
Messungen
REM3-SAPRC90
1
21
41
61
81
101
121
141
161
181
201
221
241
261
281
301
321
341
361
Tag im Jahr

Waldhof: Tagesmaxima Ozon 1997
ppb
120
110
100
90
80
70
60
50
40
30
20
10
0
1
21
41
61
81
101
121
141
161
181
201
221
241
261
281
301
321
341
361
Tag im Jahr
— Messungen
— REM3-SAPRC90


REM3-CBM4: Station Waldhof
Jan - Dec 1997
y = 1.033x - 13.178
$R^2 = 0.7108$
Calculations (ppb)
Observations (ppb)
0
10
20
30
40
50
60
70
80
90
100
Daily Ozone Maxima
Linear (Daily Ozone Maxima)

Acidification / Eutrophication and Ground level ozone

Protection of the Ecos-systems: Freshwater, Forests, Vegetation

Critical loads of S- and N- deposition, depending on the character of the soil

S-Deposition: Acidification

N-Deposition: Acidification and Eutrophication

Ground level Ozone, averaged over the growing season

Data assimilation by combining models and observations
(Kalnay, E (2003). Atmospheric modelling, data assimilation and predictability.
Cambridge Univc. Press, UK)

Concept:
Model calculated and observed concentrations represent different sources of information about air quality concentration levels.
Necessary: Estimation of uncertainties in model calculated and observed concentrations
Necessary: Decision of weighting these uncertainties

Different methods:

- **Optimal Interpolation-OI**
- **3-D Var and 4-D Var**
- **Kalman filtering**

M.van Loon, P.Builtjes and A.Segers
“Modelling and data assimilation of ozone”
Air Pollution Modelling and its Application XIV
Kluwer/Plenum, 2001
Preliminary results of applying Kalman filtering for combining observed and modelled ozone concentrations over Europe

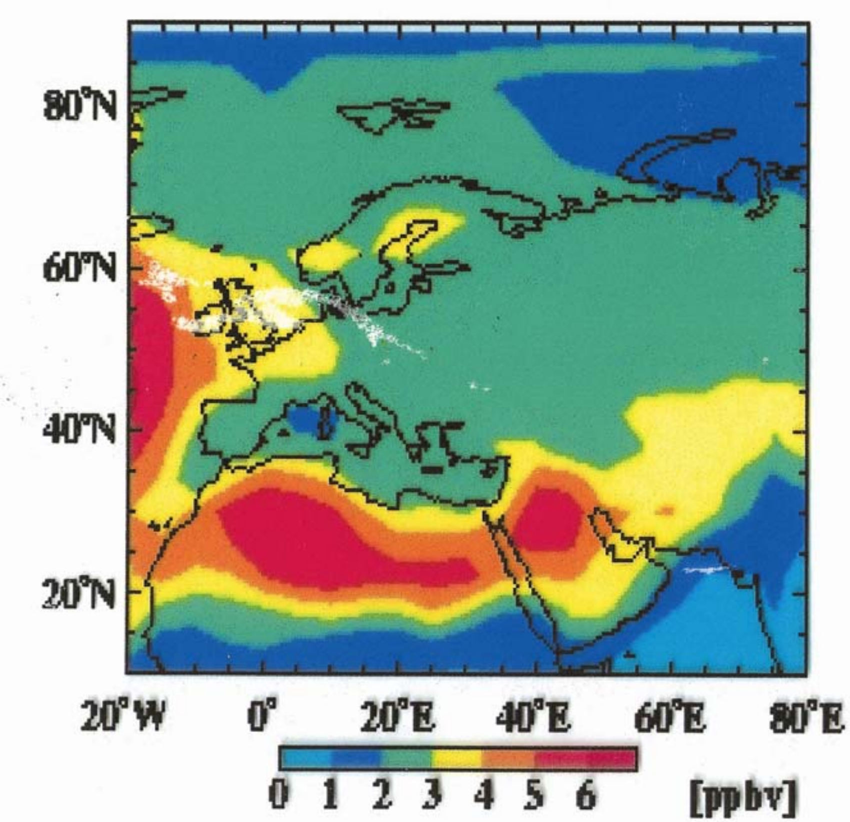
Some examples of global ozone modelling

Some recent calculations of the tropospheric ozone budget

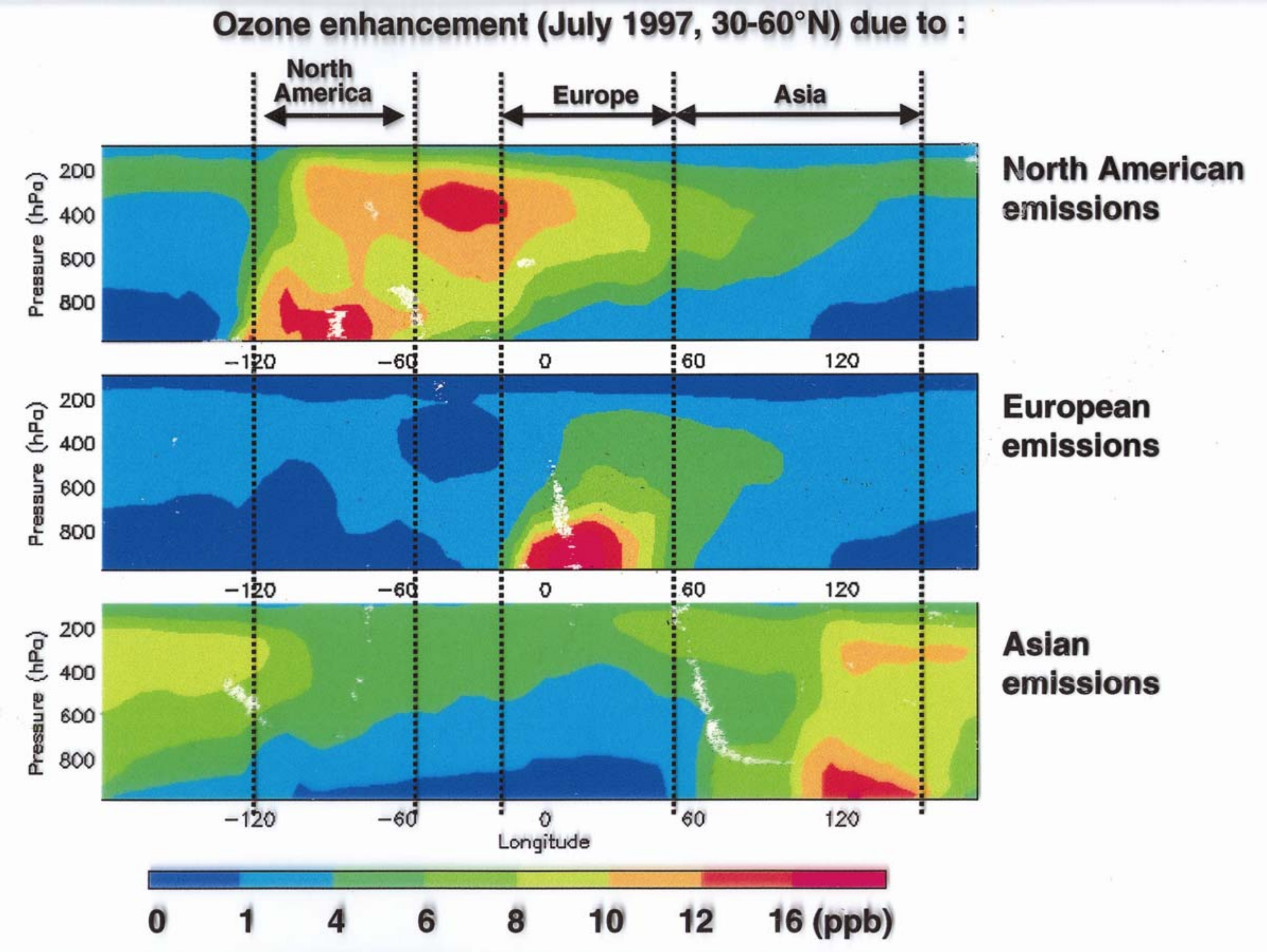
Ozone as greenhouse gas

Impact of climate change on air quality

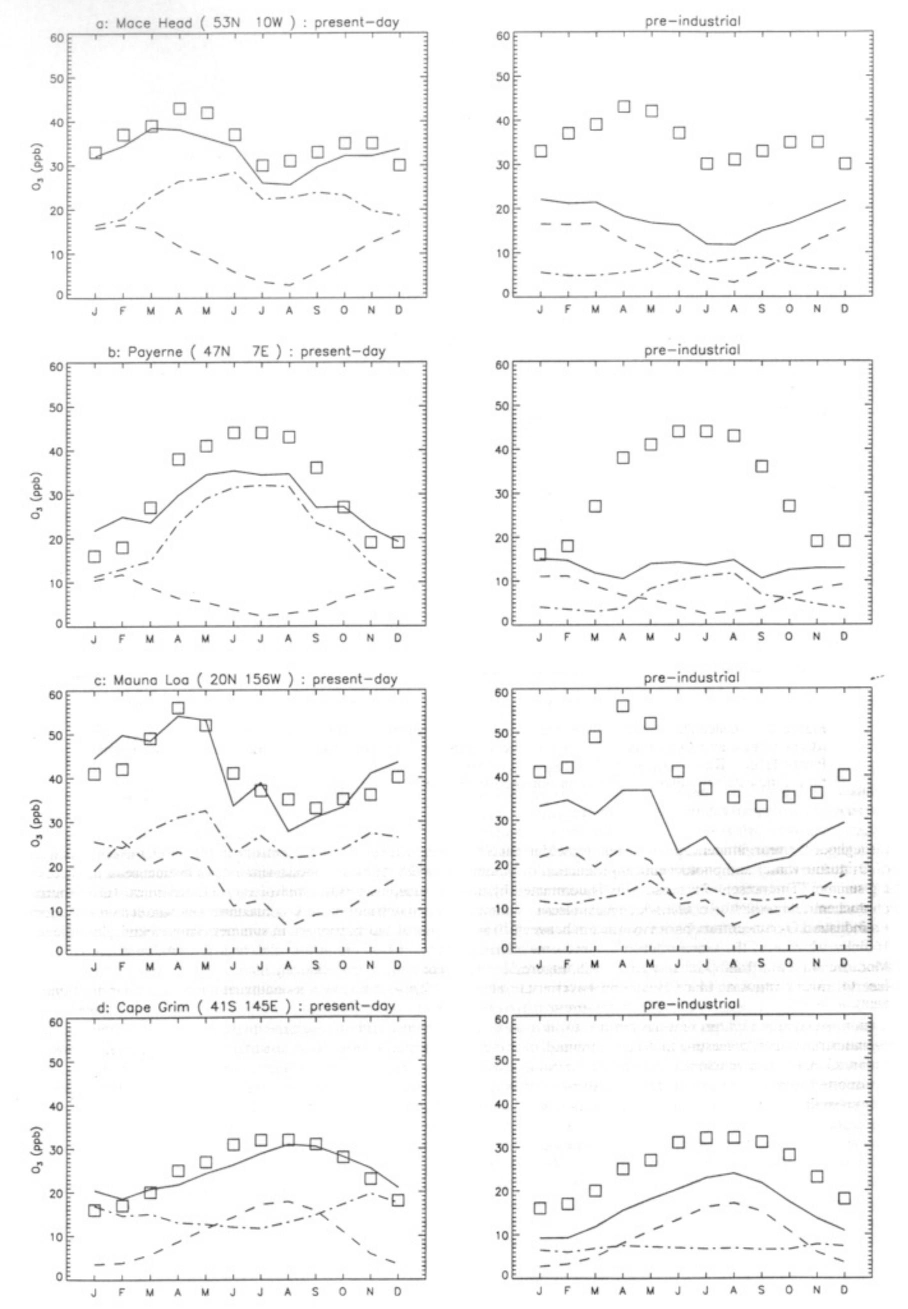
Increase in surface ozone from transatlantic transport of North American pollution (July 1997)



Li et al., 2001



Ozone enhancement (July 1997, 30-60°N) due to :


a: Mace Head (53N 10W) : present–day
pre–industrial
b: Payerne (47N 7E) : present–day
pre–industrial
c: Mauna Loa (20N 156W) : present–day
pre–industrial
d: Cape Grim (41S 145E) : present–day
pre–industrial
O₃ (ppb)
0
10
20
30
40
50
60
J F M A M J J A S O N D

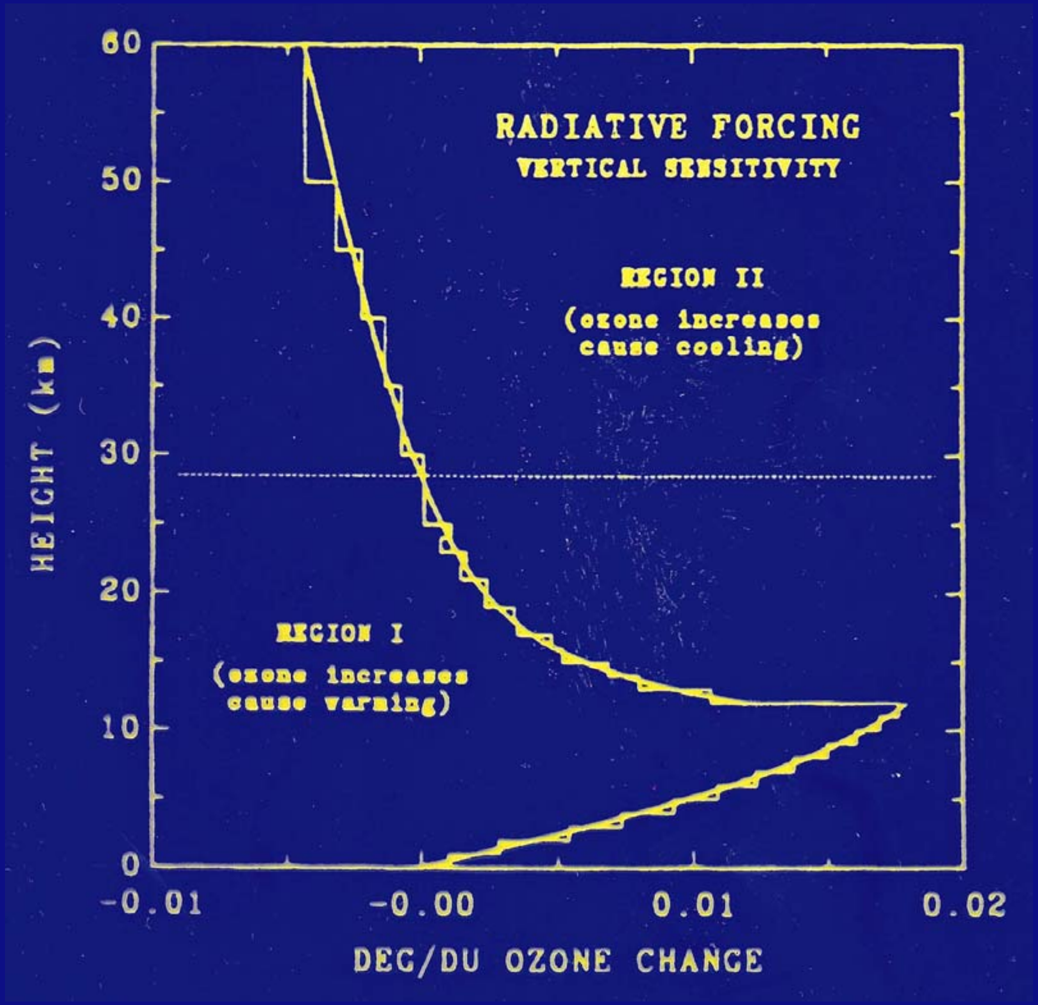
ECHAM

G.J.Roelofs, J. Lelieveld and R.van Dorland

“A three-dimensional chemistry/general circulation model simulation of anthropogenically derived ozone in the troposphere and its radiative climate forcing”

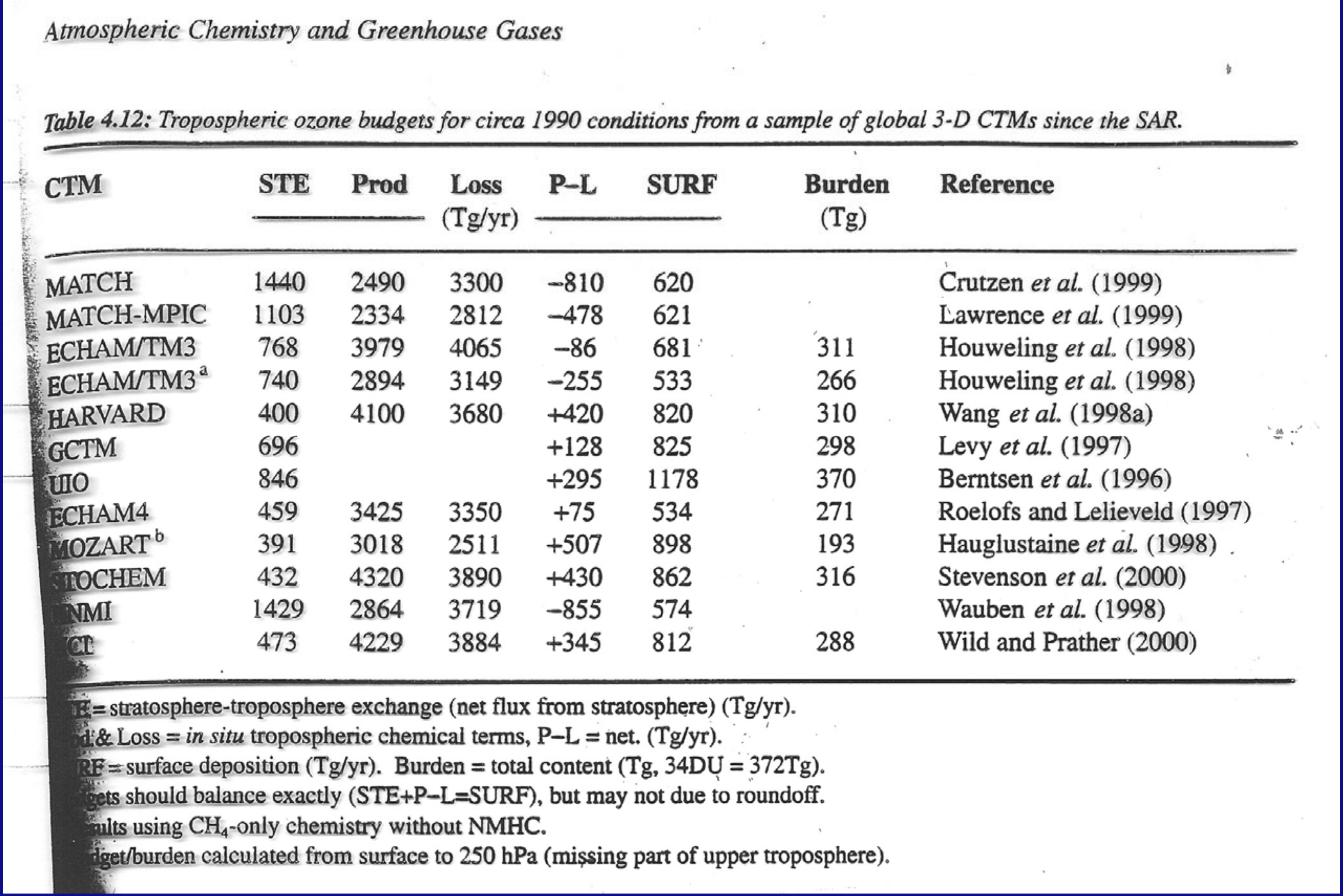
J. of Geoph. Res. 102, D19, 23389-23401, 1997

Model calculations with the European Center Hamburg Model-ECHAM, with pre-industrial and contemporary emissions



Radiative forcing sensitivity of global surface temperature to changes in vertical ozone distribution. The heavy solid line is a least squares fit to one-dimensional model radiative-convective equilibrium results computed for 10 Dobson unit ozone increment added to each atmospheric layer. Ozone increases in region I (below ≈ 30 km) warm the surface temperature. No feedback effects are included in the radiative forcing.

From: *Lacis et al.*, 1990



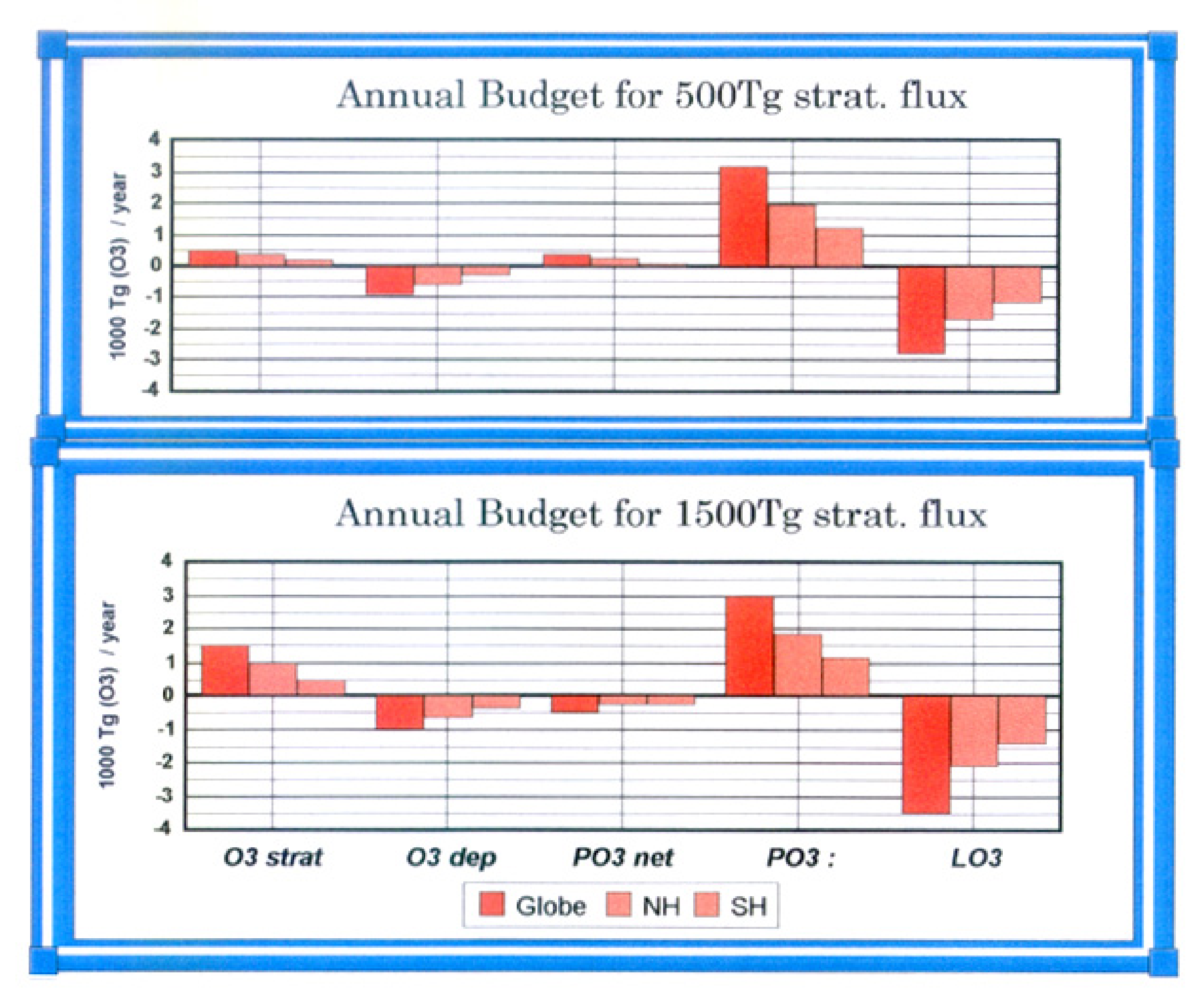
Atmospheric Chemistry and Greenhouse Gases

Table 4.12: Tropospheric ozone budgets for circa 1990 conditions from a sample of global 3-D CTMs since the SAR.

CTM	STE	Prod	Loss (Tg/yr)	P–L	SURF	Burden (Tg)	Reference
MATCH	1440	2490	3300	–810	620		Crutzen *et al.* (1999)
MATCH-MPIC	1103	2334	2812	–478	621		Lawrence *et al.* (1999)
ECHAM/TM3	768	3979	4065	–86	681	311	Houweling *et al.* (1998)
ECHAM/TM3[a]	740	2894	3149	–255	533	266	Houweling *et al.* (1998)
HARVARD	400	4100	3680	+420	820	310	Wang *et al.* (1998a)
GCTM	696			+128	825	298	Levy *et al.* (1997)
UIO	846			+295	1178	370	Berntsen *et al.* (1996)
ECHAM4	459	3425	3350	+75	534	271	Roelofs and Lelieveld (1997)
MOZART[b]	391	3018	2511	+507	898	193	Hauglustaine *et al.* (1998)
STOCHEM	432	4320	3890	+430	862	316	Stevenson *et al.* (2000)
NMI	1429	2864	3719	–855	574		Wauben *et al.* (1998)
CT	473	4229	3884	+345	812	288	Wild and Prather (2000)

E = stratosphere-troposphere exchange (net flux from stratosphere) (Tg/yr).
d & Loss = *in situ* tropospheric chemical terms, P–L = net. (Tg/yr).
RF = surface deposition (Tg/yr). Burden = total content (Tg, 34DU = 372Tg).
gets should balance exactly (STE+P–L=SURF), but may not due to roundoff.
ults using CH_4-only chemistry without NMHC.
dget/burden calculated from surface to 250 hPa (missing part of upper troposphere).

MOGUNTIA

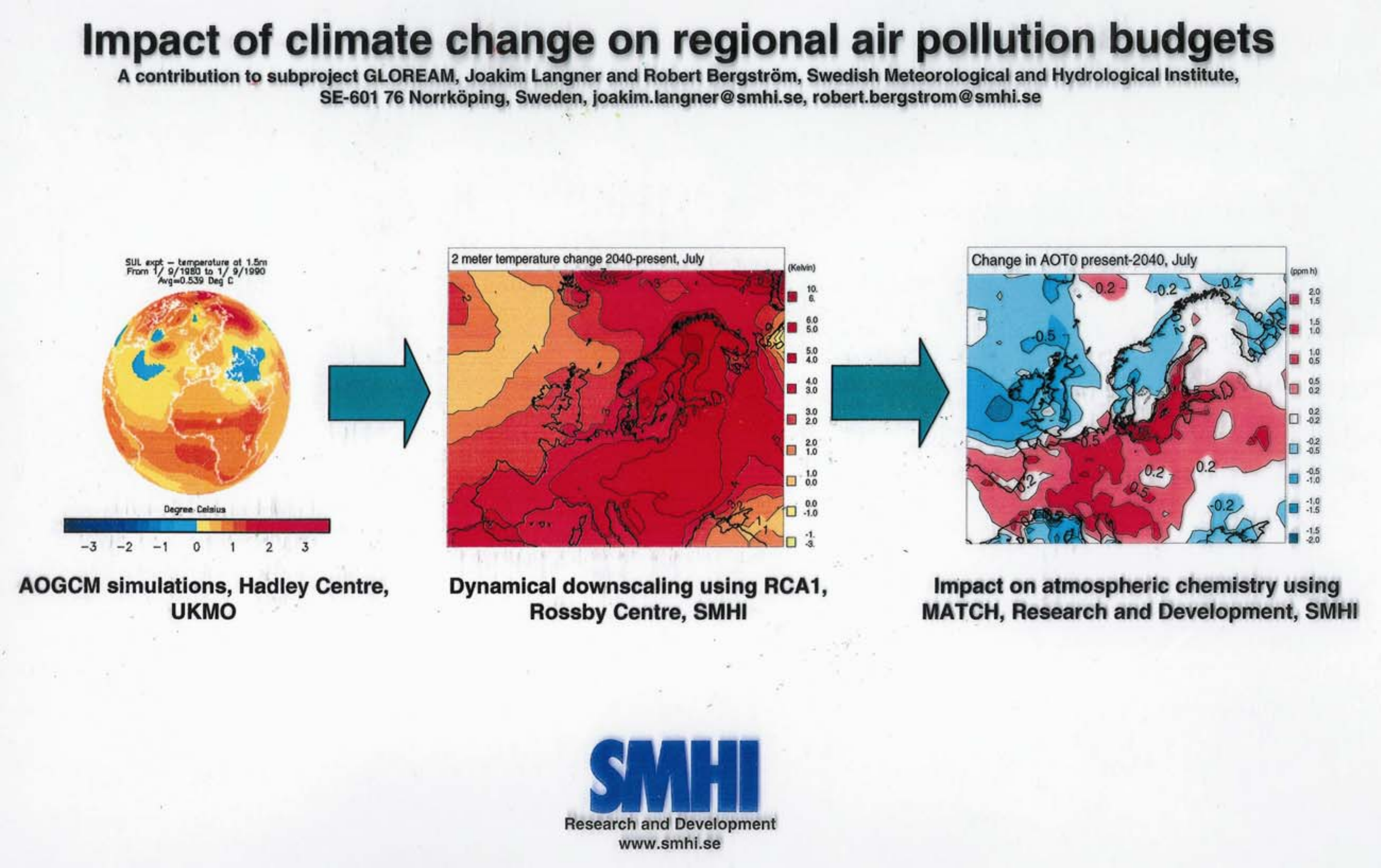

Annual Budget for 500Tg strat. flux
1000 Tg (O3) / year
4
3
2
1
0
-1
-2
-3
-4
Annual Budget for 1500Tg strat. flux
1000 Tg (O3) / year
4
3
2
1
0
-1
-2
-3
-4
O3 strat
O3 dep
PO3 net
PO3 :
LO3
Globe
NH
SH

Peter H.Zimmermann

“Moguntia: A handy global tracer model”

Air Pollution Modelling and its Application, Cambridge, 17th ITM, 1988

Global 3-D model using monthly averaged winds and eddy diffusion



Impact of climate change on regional air pollution budgets

A contribution to subproject GLOREAM, Joakim Langner and Robert Bergström, Swedish Meteorological and Hydrological Institute,
SE-601 76 Norrköping, Sweden, joakim.langner@smhi.se, robert.bergstrom@smhi.se

SUL expt – temperature at 1.5m
From 1/ 9/1980 to 1/ 9/1990
Avg=0.539 Deg C

AOGCM simulations, Hadley Centre, UKMO

2 meter temperature change 2040-present, July

Dynamical downscaling using RCA1, Rossby Centre, SMHI

Change in AOT0 present-2040, July

Impact on atmospheric chemistry using MATCH, Research and Development, SMHI

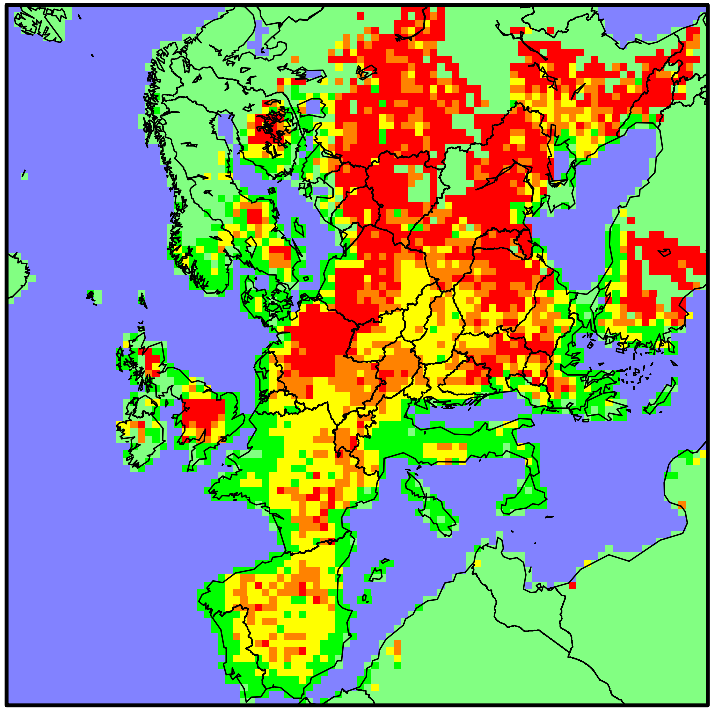
SMHI
Research and Development
www.smhi.se

DEM with climate change

DAYS WITH MORE THAN 60 PPB

Numbers of days in 1997 with 8–hour rolling
averages of ozone concentrations over 60 ppb
100(A/B): A=Climate Scenario 3
B=Basic Scenario
Maximum value in the domain: 800
Minimal value in the domain: 0

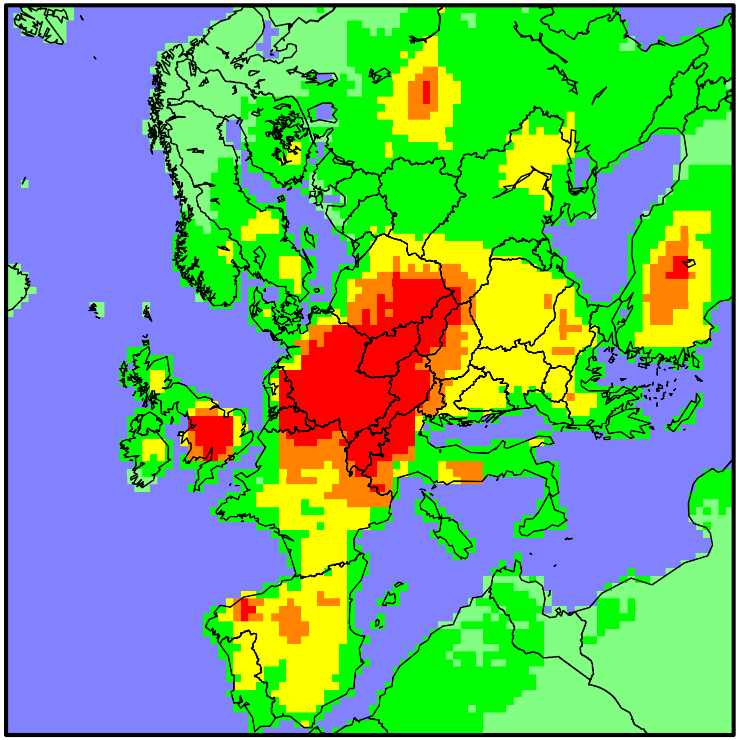
🟥 Above 160
🟧 140 – 160
🟨 120 – 140
🟩 100 – 120
🟩 Below 100
🟦 Water areas



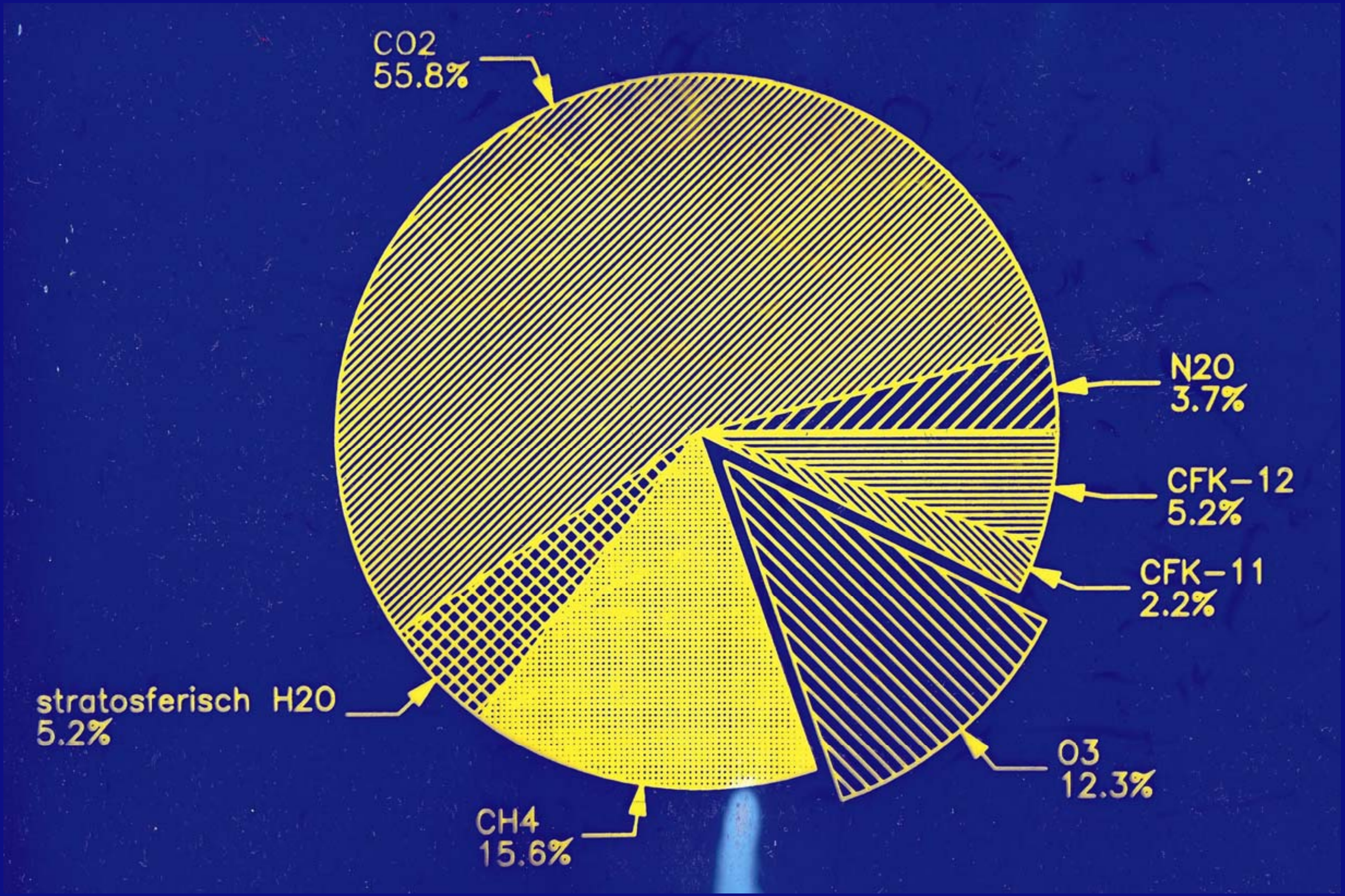
DAILY OZONE MAXIMA IN EUROPE

Runs on a (96x96) grid / (50 km x 50 km) cells
April–September 1997: averaged daily maxima
100(A/B): A=Climate Scenario 3
B=Basic Scenario
Maximal value in the domain: 131
Minimal value in the domain: 89

🟥 Above 115
🟧 110 – 115
🟨 105 – 110
🟩 100 – 105
🟩 Below 100
🟦 Water areas



1990 (globaal/mondiaal)



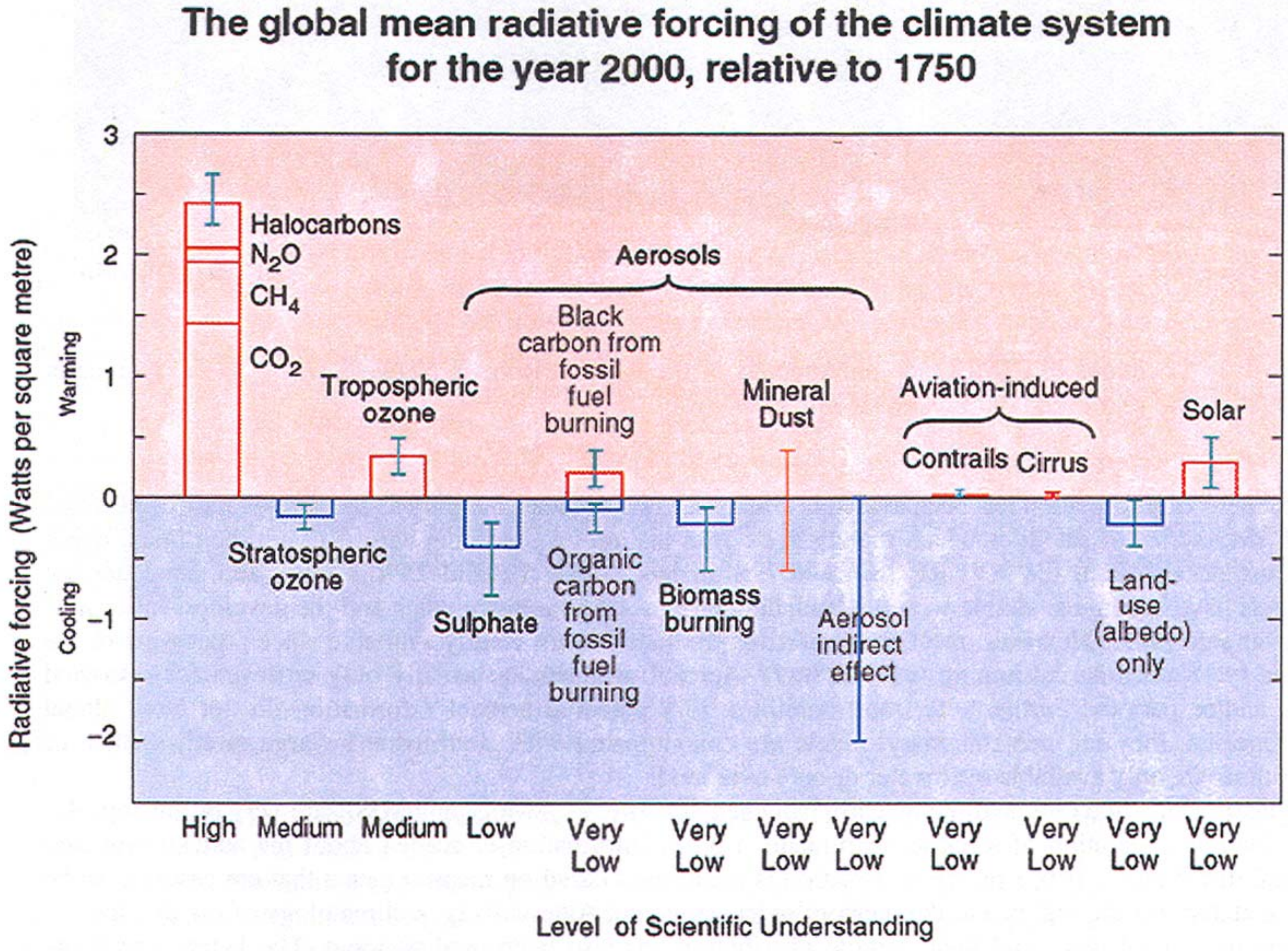
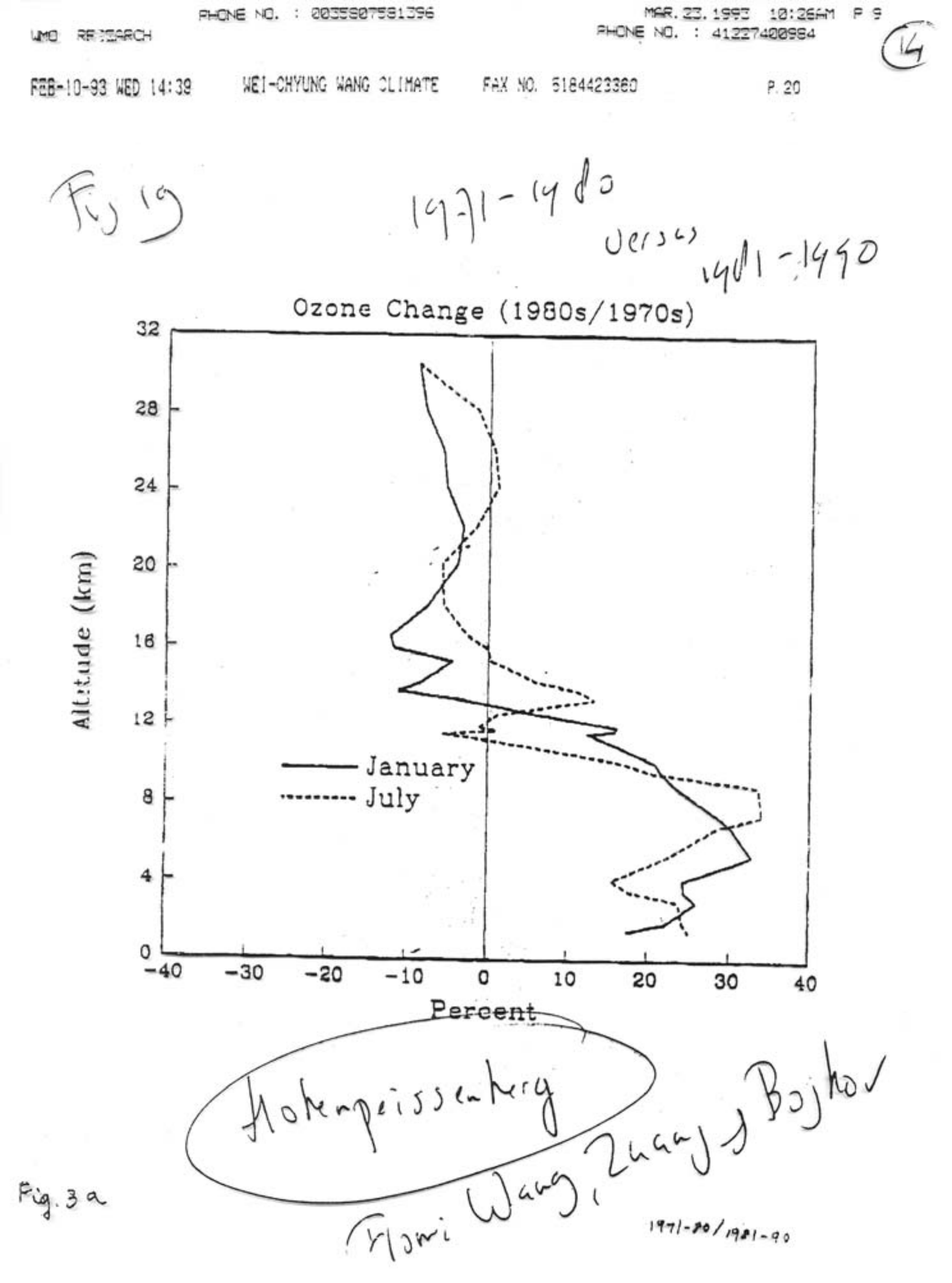


Figure 1.1 Radiative forcing of the climate system (IPCC, 2001)



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PHONE NO. : 41227400984

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FEB-10-93 WED 14:39 WEI-CHYUNG WANG CLIMATE FAX NO. 5184423360 P. 20

Fig 19

1971-1980 versus 1981-1990

Ozone Change (1980s/1970s)

Hohenpeissenberg

from Wang, Zhang & Bojkov

Fig. 3a

1971-80/1981-90

Aerosols, fine particles, particle matter

Definition:

Dispersed system containing solid or liquid particles suspended in air (cloud droplets are not considered to be aerosols)

Aerosols : Size-spectrum
Chemical composition

Aerosols : Radius > radius molecules
Mass > mass molecules

Aerosols : $> 10^{-3}$ µm

Aitken particles : $r < 0.1$ µm

Fine particles : $0.1 < r < 2.5$ µm

Coarse particles : $2.5 < r < 10$ µm

Fine particles : **r ~ wavelenght of light**

Particle size < wavelenght of light: Rayleigh scattering

~ wavelenght of light: Mie scattering

Grenzwerte in Europa

PM10 (diameter)

Jahresmittel wert: 40 µgr/m^3

Tagesmittel wert: 50 µgr/m^3, max 35 Tagen pro Jahr

Diese Grenzwert gillt überall !!!!

Im Gespäch: Zusätzlich:

PM2.5, Jahresmittel wert: 25 µgr/m^3, Stadthintergrund

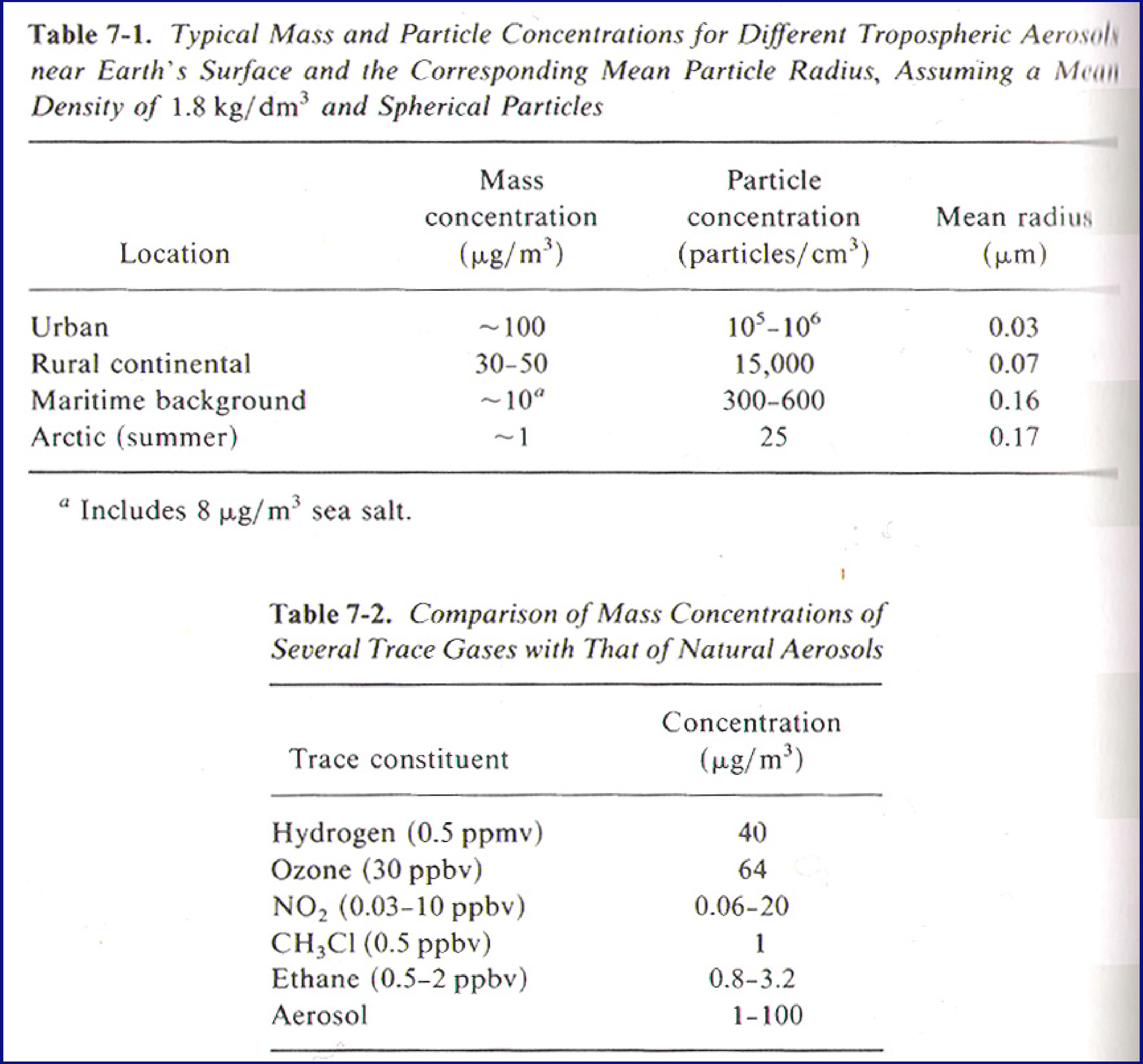


Table 7-1. *Typical Mass and Particle Concentrations for Different Tropospheric Aerosols near Earth's Surface and the Corresponding Mean Particle Radius, Assuming a Mean Density of* 1.8 kg/dm^3 *and Spherical Particles*

Location	Mass concentration (μg/m^3)	Particle concentration (particles/cm^3)	Mean radius (μm)
Urban	~100	10^5–10^6	0.03
Rural continental	30–50	15,000	0.07
Maritime background	~10[a]	300–600	0.16
Arctic (summer)	~1	25	0.17

[a] Includes 8 μg/m^3 sea salt.

Table 7-2. *Comparison of Mass Concentrations of Several Trace Gases with That of Natural Aerosols*

Trace constituent	Concentration (μg/m^3)
Hydrogen (0.5 ppmv)	40
Ozone (30 ppbv)	64
NO_2 (0.03–10 ppbv)	0.06–20
CH_3Cl (0.5 ppbv)	1
Ethane (0.5–2 ppbv)	0.8–3.2
Aerosol	1–100

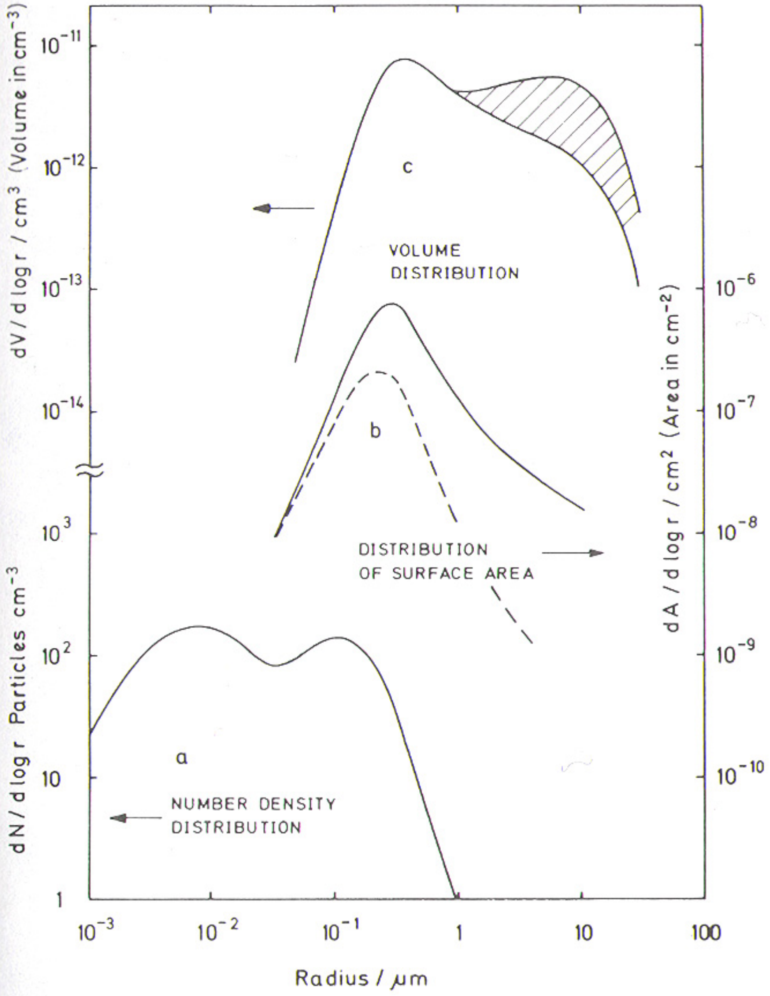
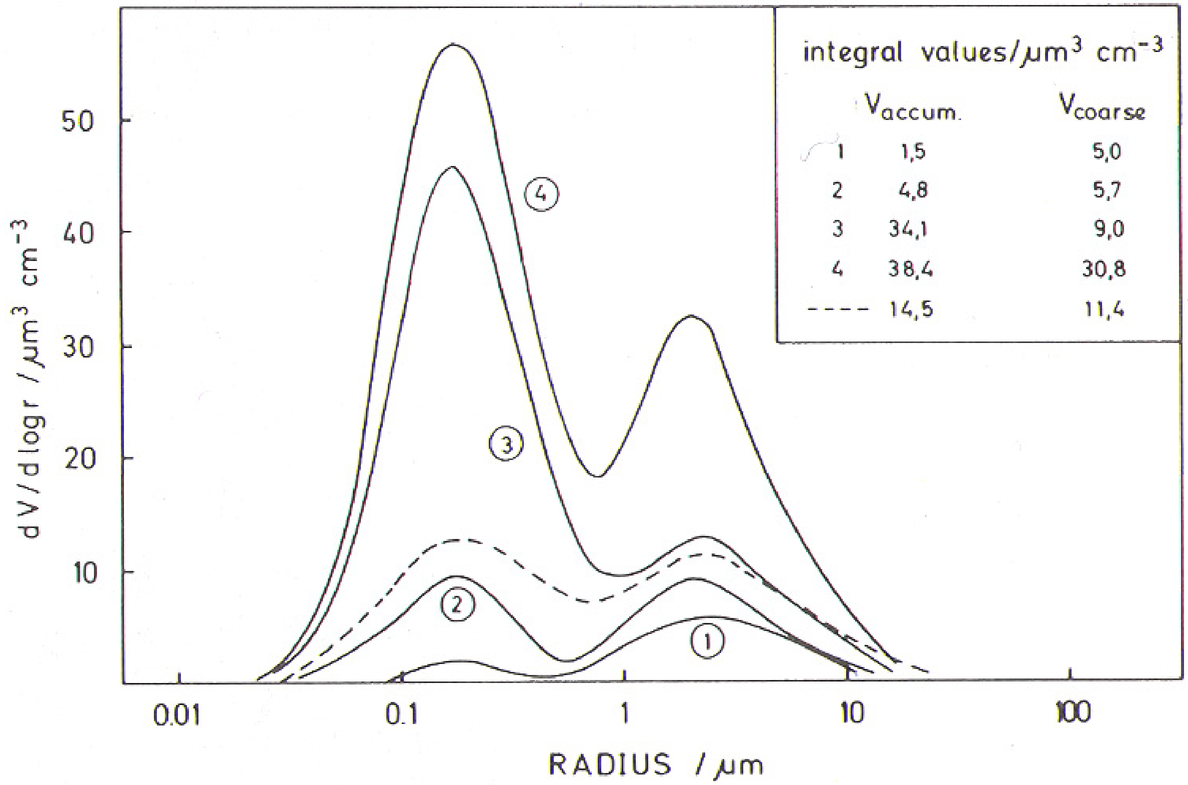


Fig. 7-2. Model size distributions of the marine background aerosol: (a) particle number density, (b) surface area, (c) volume. The contribution of sea salt to the volume distribution is indicated by the shaded area, and arrows indicate the appropriate scale. By integration one obtains a total number density $N = 290$ particles/cm³, a total surface area $A =$ [illegible] $\times 10^{-7}$ cm²/cm³, and a total volume $V = 1.1 \times 10^{-11}$ cm³/cm³. For an average density of 10^3 kg/m³, the mass concentration is 11 µg/m³ (5 µg/m³ of sea salt). The dashed curve gives the distribution of the surface area that is effective in collisions with gas molecules. For larger particles the collision rate is lowered by the rate of diffusion.



	$V_{accum.}$	V_{coarse}
1	1,5	5,0
2	4,8	5,7
3	34,1	9,0
4	38,4	30,8
----	14,5	11,4

Fig. 7-3. Average volume size distributions for continental aerosols. [Adapted from Whitby and Sverdrup (1980).] The measurement data were smoothed and idealized by fitting to them additive log-normal distributions. (1) Background aerosol, very clean; (2) normal background aerosol; (3) background aerosol disturbed by an urban plume (these data from measurements at Goldstone, California). (4) Average urban aerosol (from data taken at Minneapolis, Minnesota, Denver, Colorado, and various locations in California). The dashed curve gives the volume distribution resulting from the number density distribution for the rural continental aerosol shown in Fig. 7-1. The integrated volumina, given by the area underneath each curve, are shown in the insert.

Removal of aerosols by:

- **Coagulation + Accumulation**
- **Wet precipitation**
- **Sedimentation**

Coalescence by Brownian motion

$$-\frac{dN}{dt}=\tfrac{4}{3}\frac{kT}{\mu}\left(1+\frac{A\ell}{r}\right)N^{2}$$

N : numbers of particles

k : Bolzmann–constant

ℓ : mean free path

r : radius

μ: dynamic gas viscosity

A : Stokes – Cunningham correction

Wet deposition and aqueous phase chemistry

Cloud-formation by Cloud Condensation Nucleii-CCN

CCN’s are aerosol, size ~ 0.05 µm

In-cloud scaveging : Rain out

Below-cloud scaveging : Wash out

Example for in-cloud scaveging:

SO_2, gas $+ \; H_2O \leftrightarrow SO_2.H_2O$

In droplets:

$SO_2.H_2O \leftrightarrow H^+ + HSO_3^-$

$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$

$SO_3^{2-} + ½\, O_2 \rightarrow SO_4^{2-}$

Cloud-drops can evaporate Aerosols ”back”, called: processing

Cloud-drops can grow and precipitate

Wash out by raindrops

Wash out : R : Radius of drop :

$R^2 \pi h \quad (h : \textit{height above the surface})$

Total mass :

$$m = R^2 \pi h \int_o^r \tfrac{4}{3} \pi r^3 N(r)\, dr$$

N(r) : number concentration

r : radius of aerosol

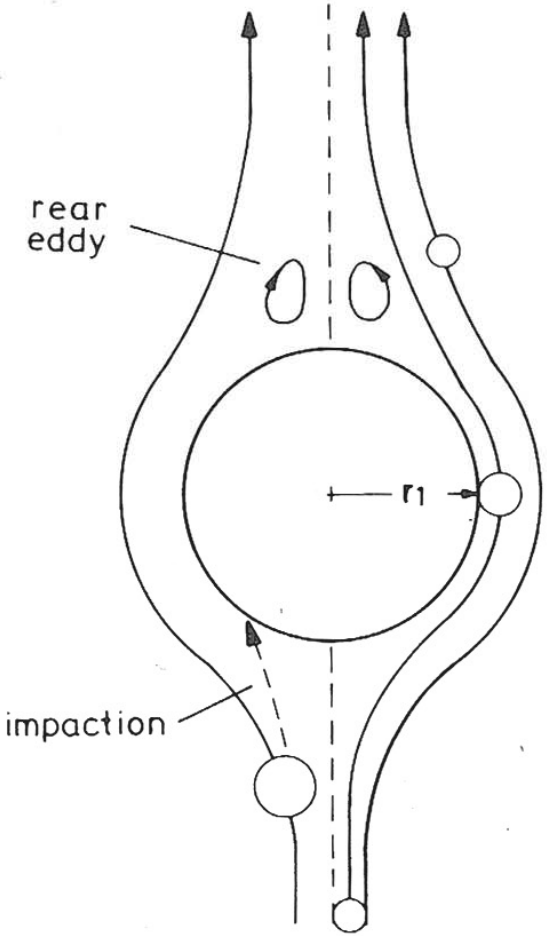


Fig. 8-4. Schematic representation of the air flow around a falling sphere.

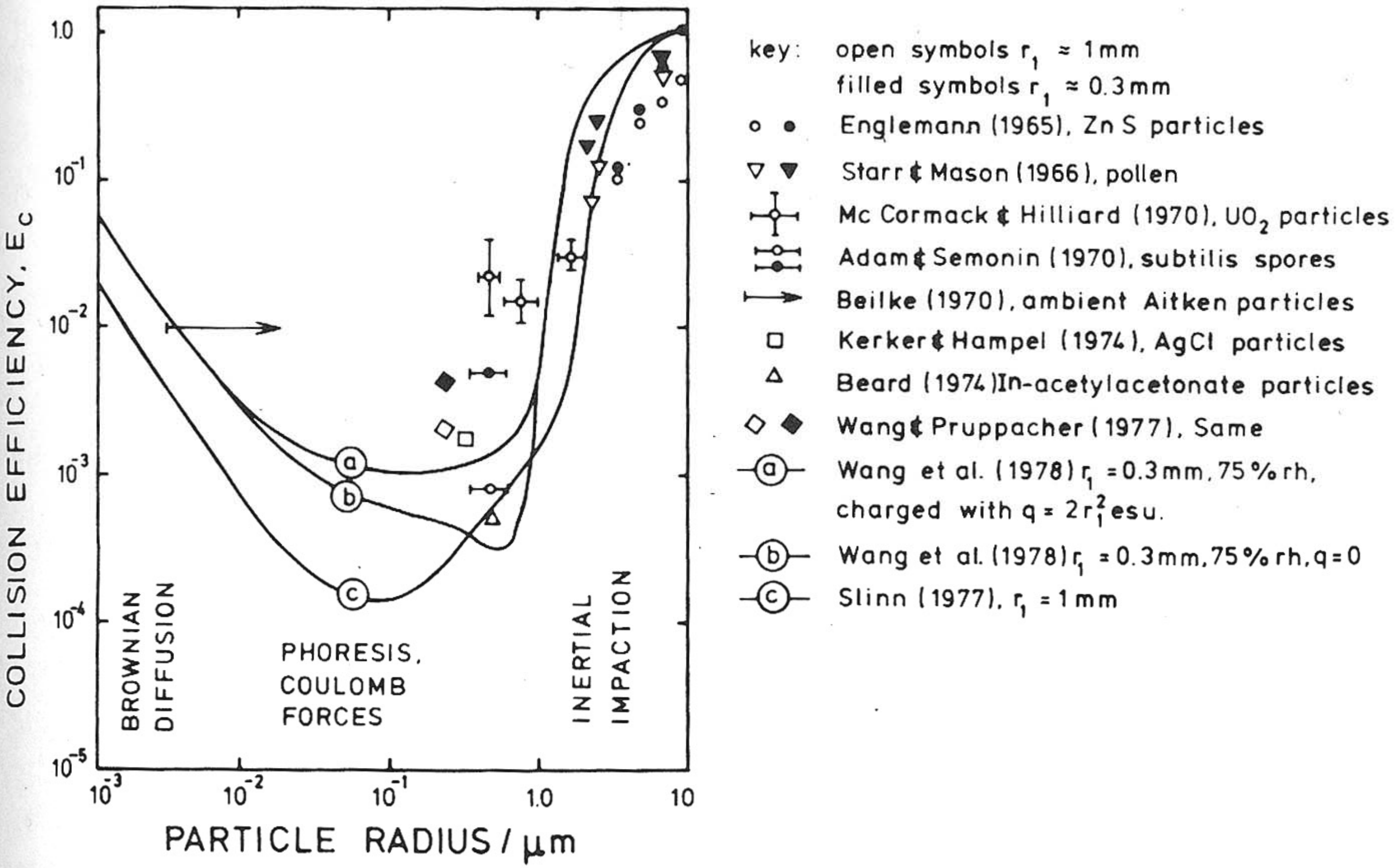


Fig. 8-6. Collision efficiency for the capture of particles by rain drops as a function of particle radius. Solid curves indicate calculations, and points represent laboratory results. Three size regimes may be distinguished depending on the dominant type of capture process.

Gravitation

Stokes' law

$$V_s = \tfrac{2}{9}\, r^2 \, \frac{\rho_p}{\mu} g$$

r : radius

ρ_p : particle density

μ : dynamic gas viscosity

$$for \quad \left.\begin{array}{c} r \cong 30\ \mu m \\ \rho \cong 2.10^3\ kg/m^3 \end{array}\right\} V_s \cong 0.1\, m/s$$

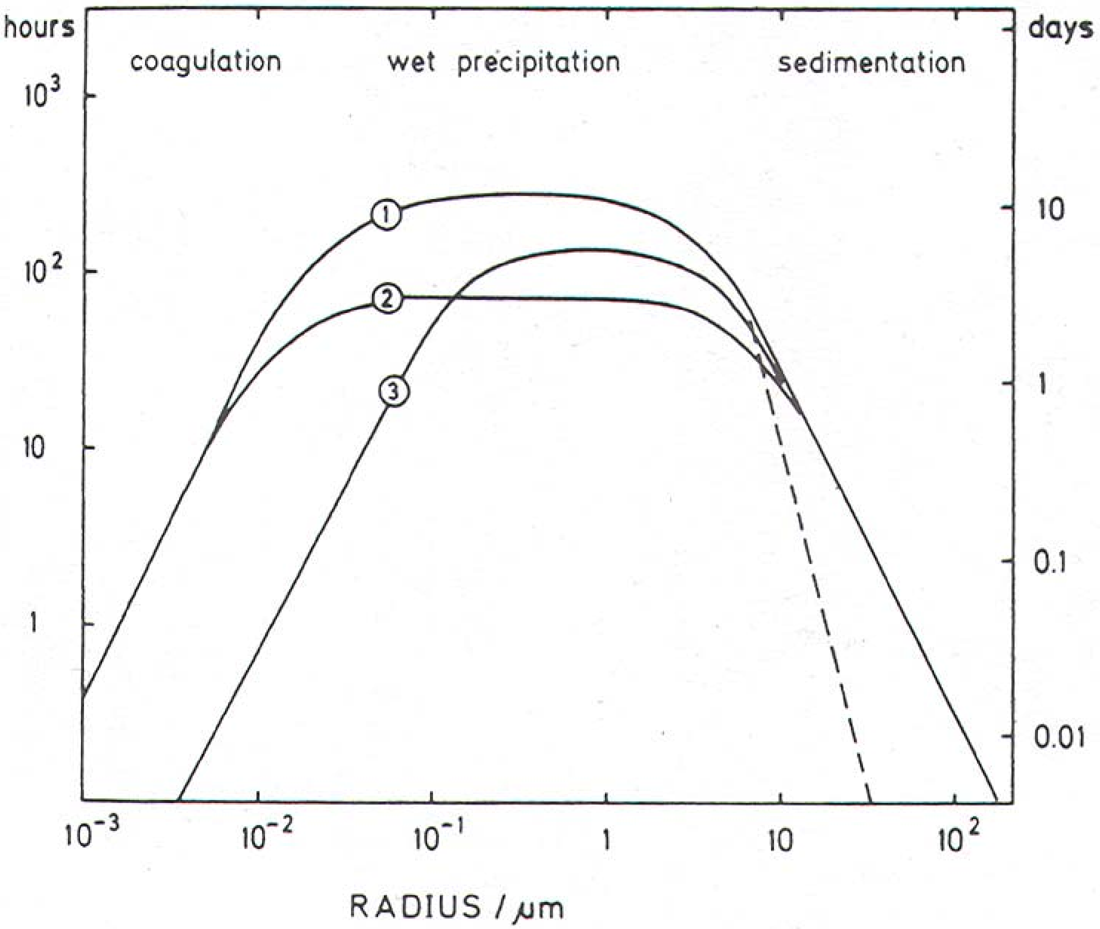


Fig. 7-28. Combined residence lifetimes of aerosol particles as a function of size. [Adapted from Jaenicke (1978c, 1980).] Important removal processes, active in various size ranges, are indicated. Coagulation and sedimentation time constants were calculated; the time constant for wet removal is the residence time derived from $^{210}Bi/^{210}Pb$ and $^{222}Rn/^{210}Pb$ ratios (Martell and Moore, 1974). Curves 1 and 2 represent the background aerosol for τ_{wet} equal to 12 and 3 days, respectively. Curve 3 represents the continental aerosol with $\tau_{wet} = 6$ days. The dashed line is calculated from a simple model for sedimentation equilibrium, as described in Section 7.6.3.

IV) Messungen von Aerosolen

- **Zusammensetzung:**
  - **primär, anthropogen und natürlich**
  - **sekundär anorganisch**
  - **sekundär organisch-biogen und anthropogen**

PM 10 und PM 2.5

- **Chemie sekundärer Aerosole**
- **Anzahl Messungen + Zusammensetzung sehr gering**
  - **AFO-2000 Projekt FU-Berlin-Reimer**
  - **Messungen Stadt Berlin-Lutz**

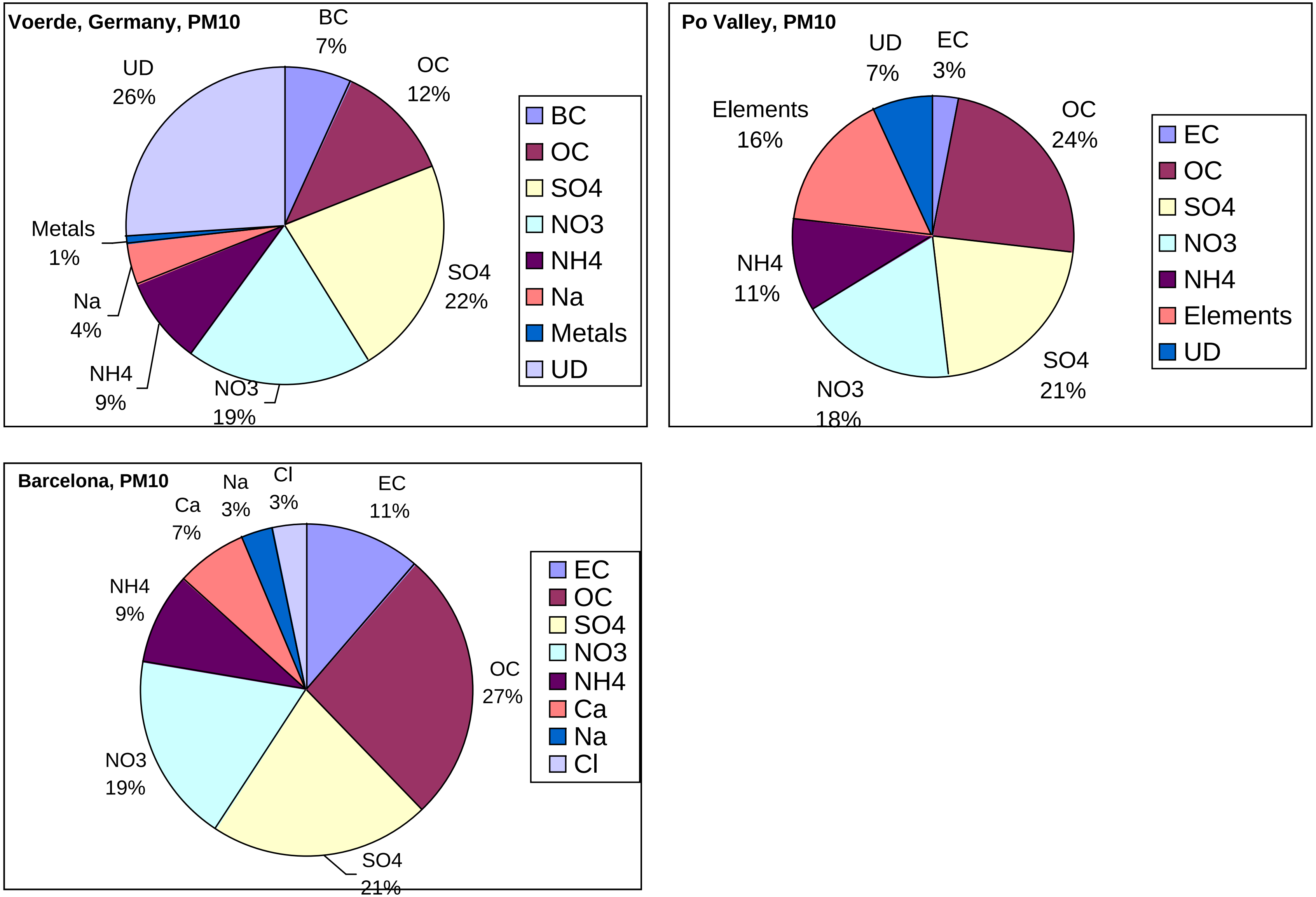


Figure 1 Composition of PM10 expressed in relative units at three sites in Europe.

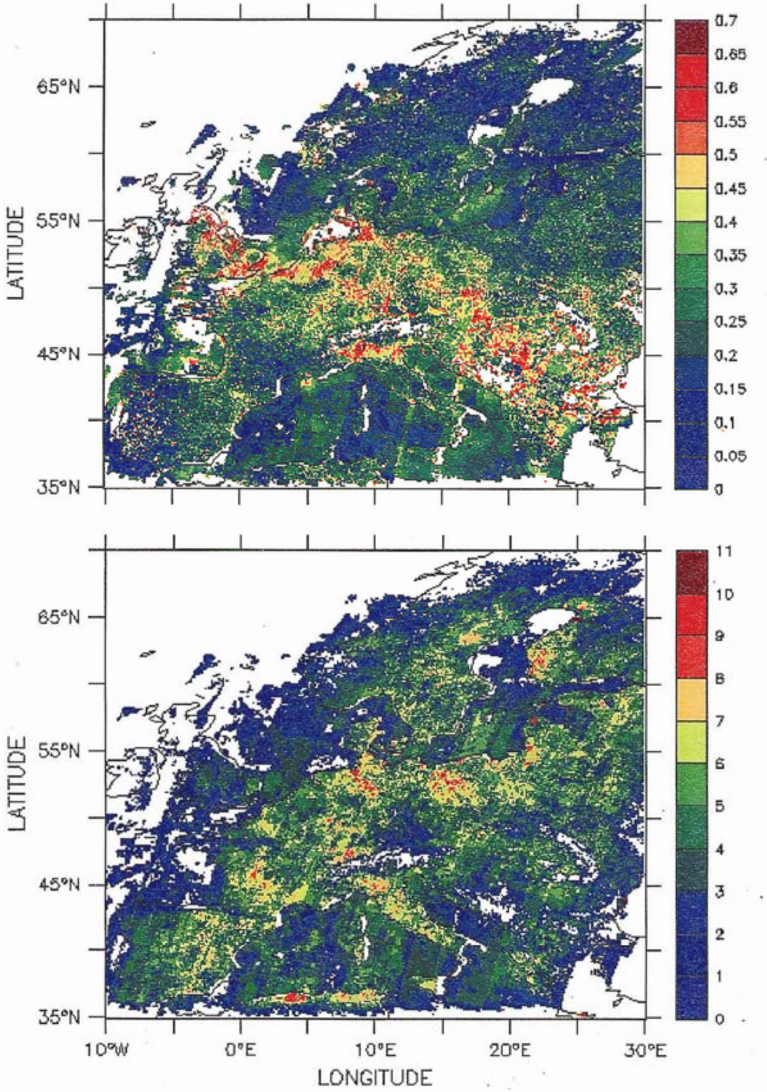
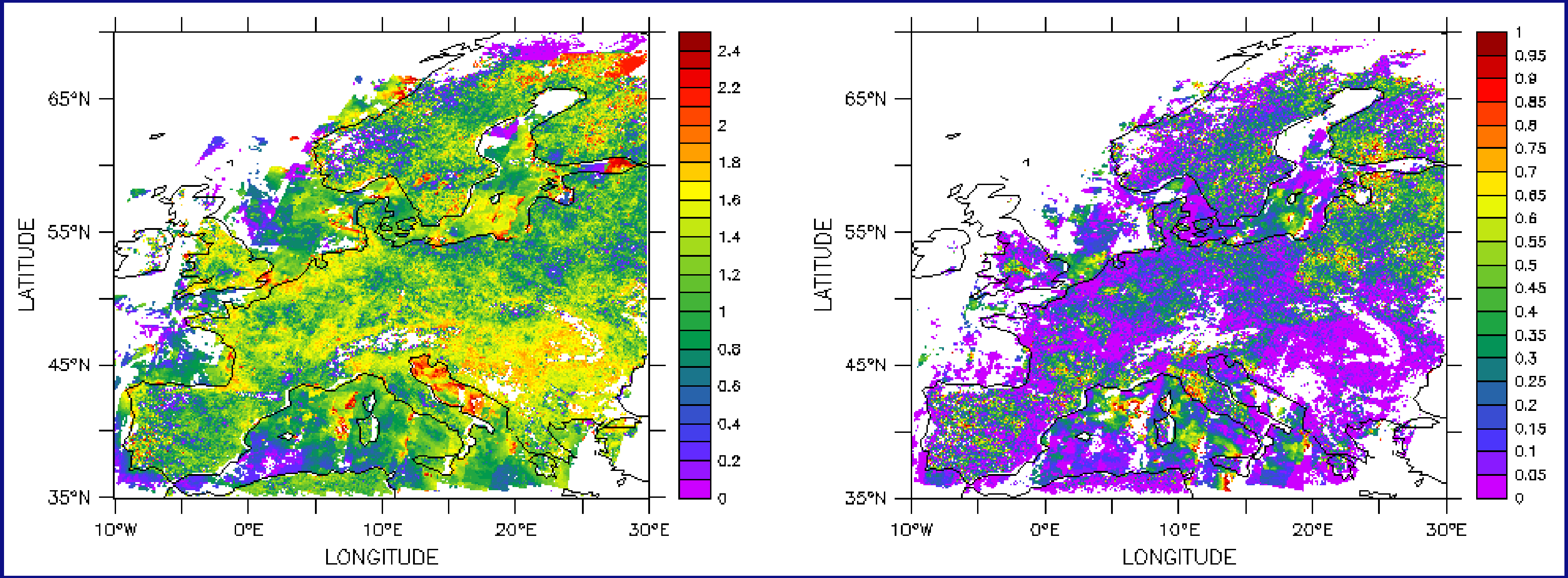


Figure 4.1. Composite map of the (a) mean aerosol optical depth at 0.555 µm over Europe for August 1997 and (b) the number of observations used to derive the mean value. AOD has been retrieved by application of the dual view algorithm to the ATSR-2 satellite data over land and the single view algorithm over ocean.



Mean Ångström coefficient (a) and its variance (b) for August 1997 computed from the Ångström law using all possible combination of wavelengths.

Secondary inorganic aerosol

$$NO_2 + OH \rightarrow HNO_3$$

$$HNO_3 + NH_3 \leftrightarrow NH_4\,NO_3$$

$$SO_2 + 2OH \rightarrow H_2SO_4$$

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2\,SO_4$$

secondary organic aerosol

$$\begin{array}{cccccc} ROG & + & OH & \rightarrow & \Sigma\,\alpha_i\,C_i \\ & + & NO_3 & & \\ & + & O_3 & & \end{array}$$

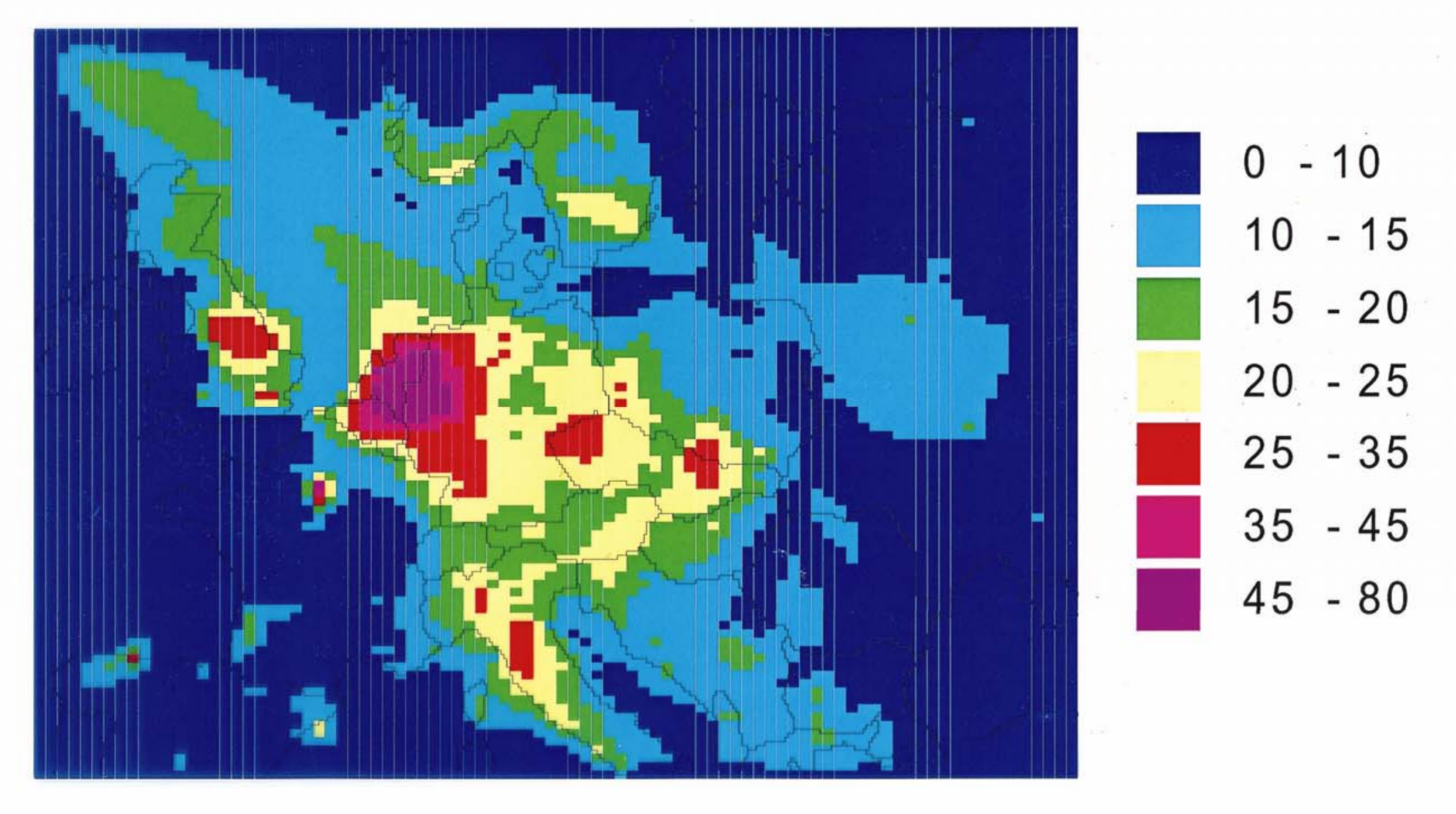
V) Erste Ergebnisse Modellierung von Aerosolen

- **REM-Calgrid/RCG und LOTOS und erste Validierung**
- **Additionelle Information AOD mit ATSR**

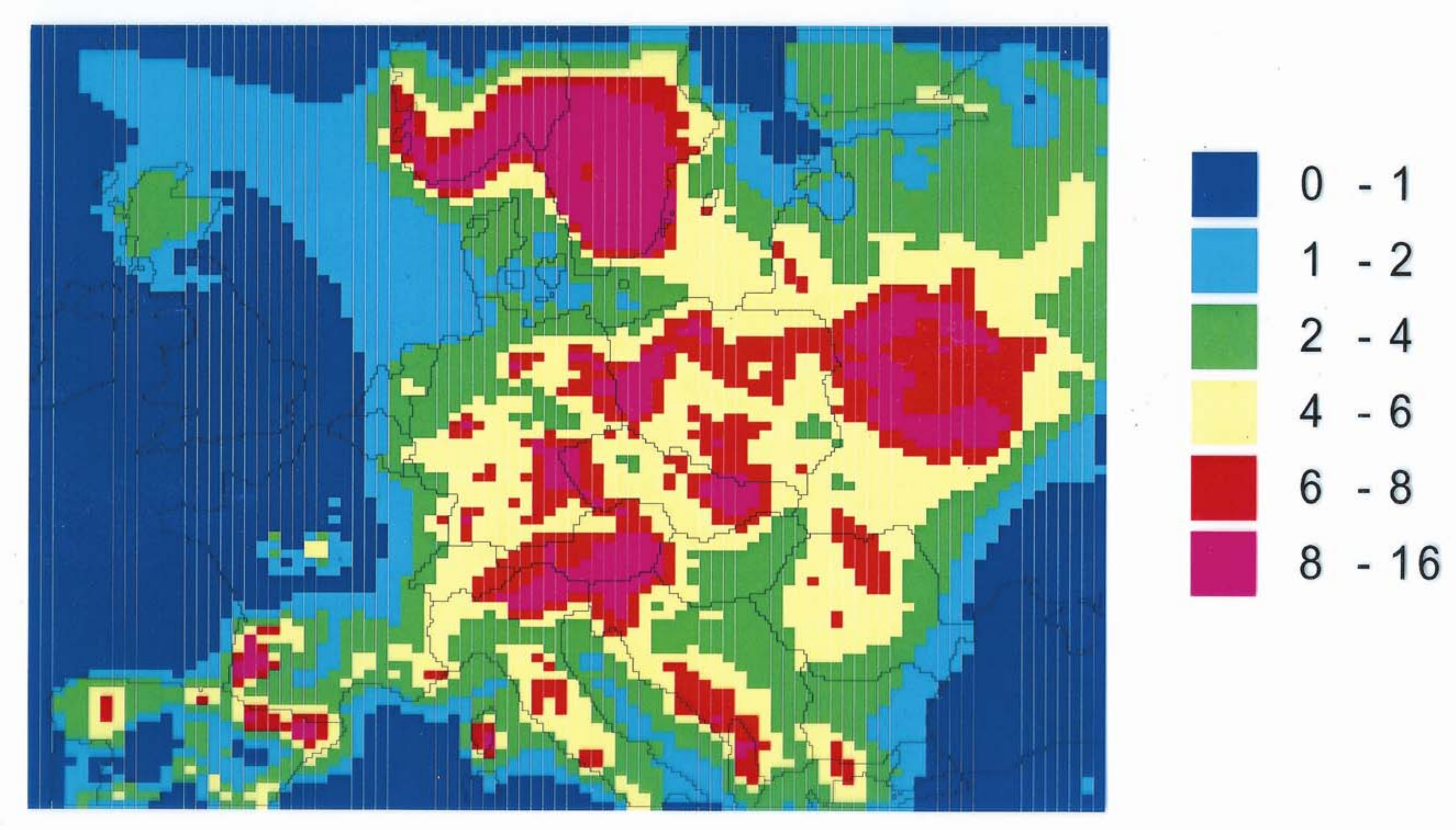
Hauptbeschränkungen Modellierung:

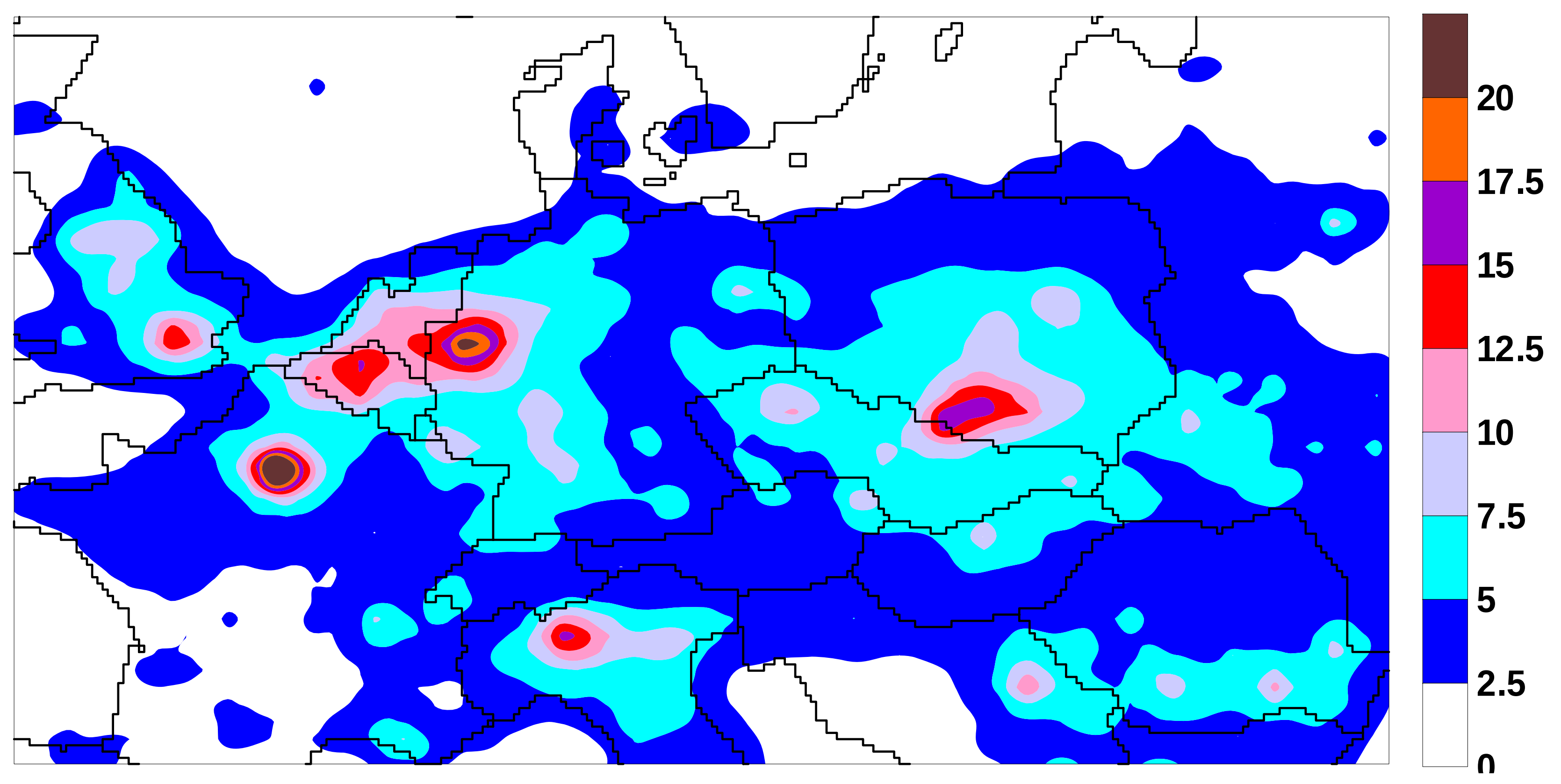
- **Zu wenig gute Beobachtungen**
- **Wolkenbeschreibung / Chemie / CCN**

Average $PM_{2.5}$ 28 July - 13 August 1997

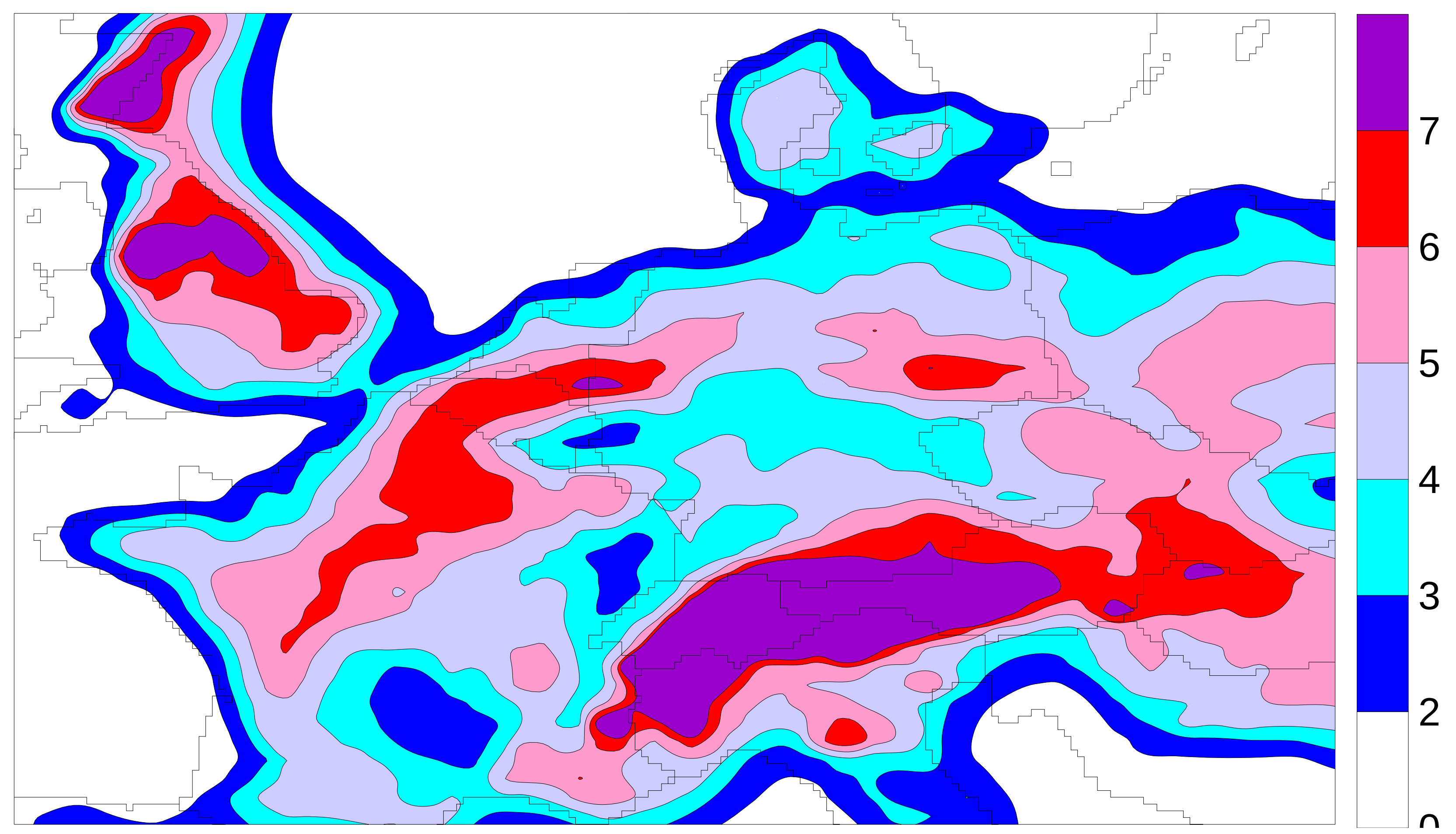


Average BSOA 28 July - 13 August 1997





Primary part of the PM_{10} concentrations in 1995 ($\mu g/m^3$)
as modeled by the LOTOS model

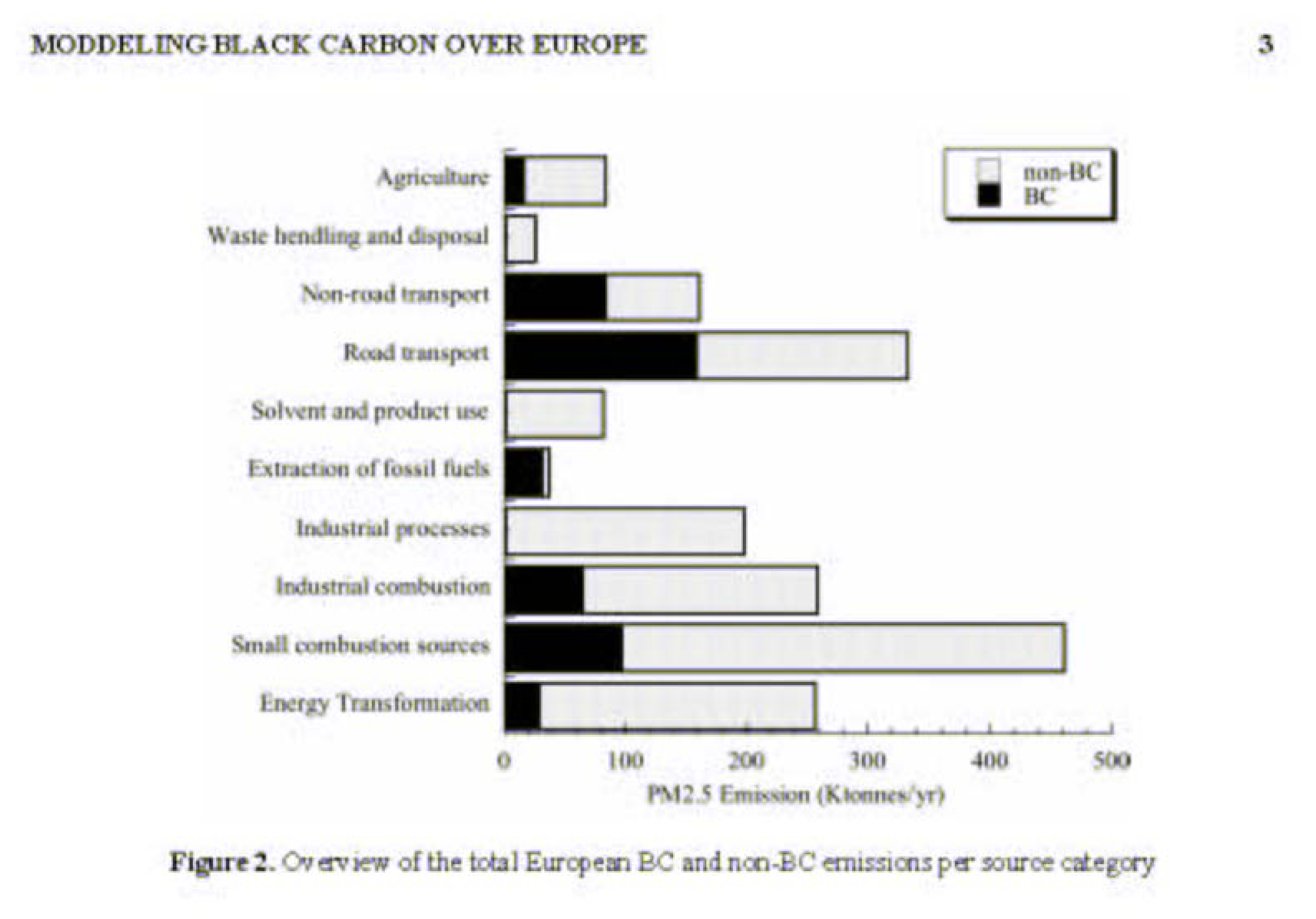


Average computed (LOTOS) wind blown dust concentration (µg/m³) in 1995

Soot (Russ) is the same as Black Carbon – BC- or Elementary Carbon-EC
It is produced by burning, so is part of the primary emissions of PM

PM 2.5 exists to a large extent of BC and Organic Carbon-OC

BC might be the health relevant part of PM 2.5
BC is a greenhouse “gas”, it absorbs light



MODELING BLACK CARBON OVER EUROPE 3

Figure 2. Overview of the total European BC and non-BC emissions per source category

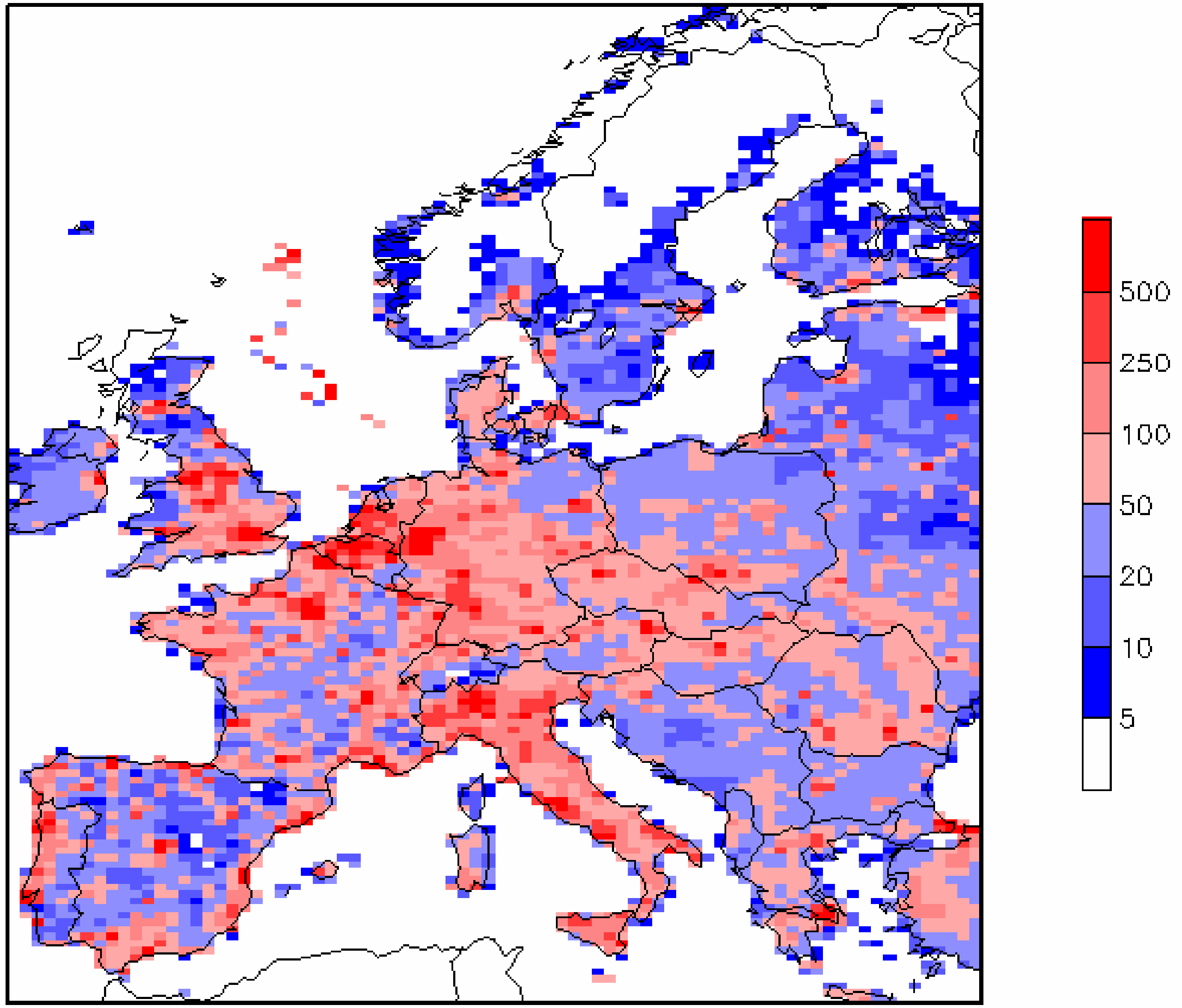
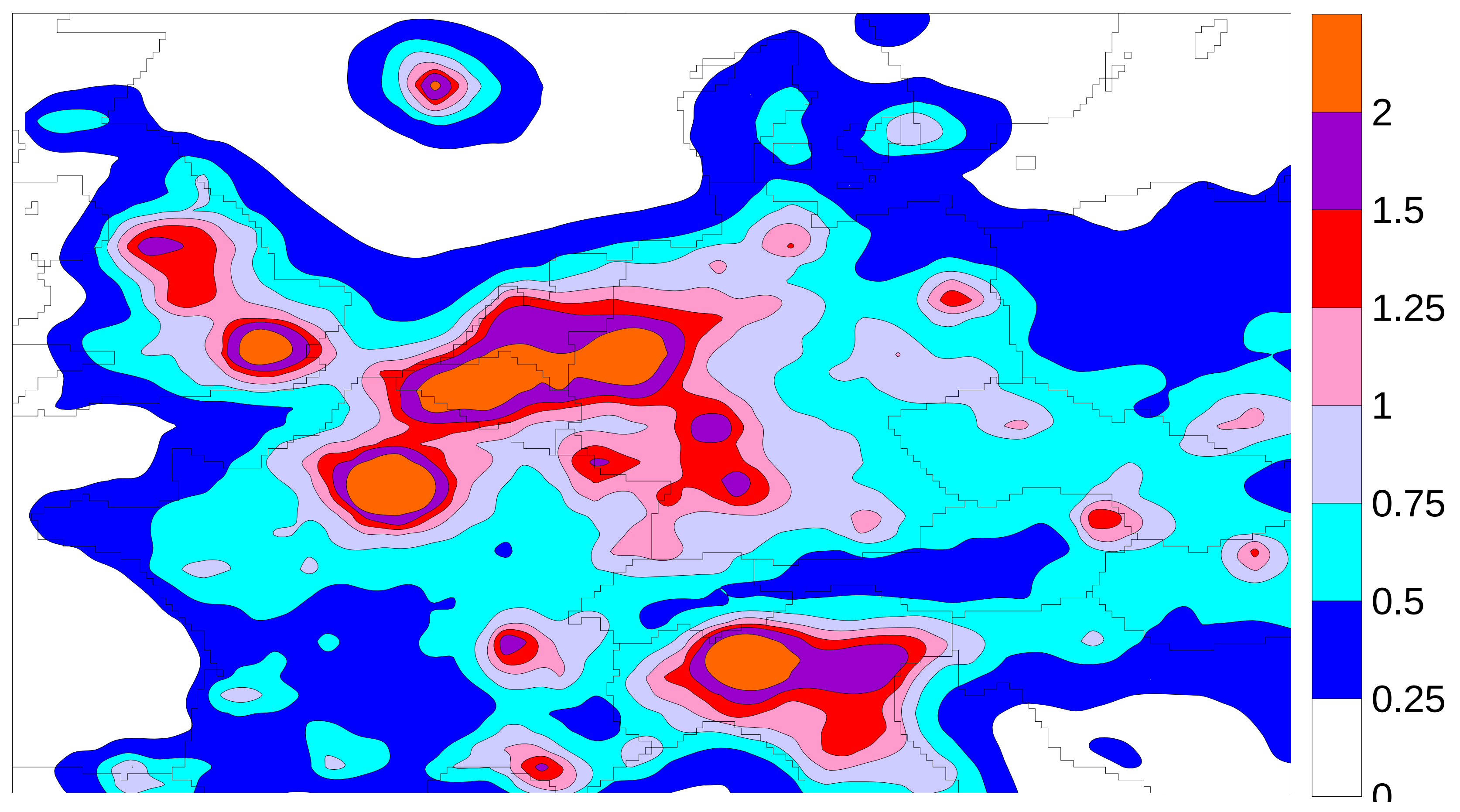


Figure 2 European BC emission (tonnes) derived in this study



Average computed (LOTOS) Black Carbon concentration (μg/m³) in 1995

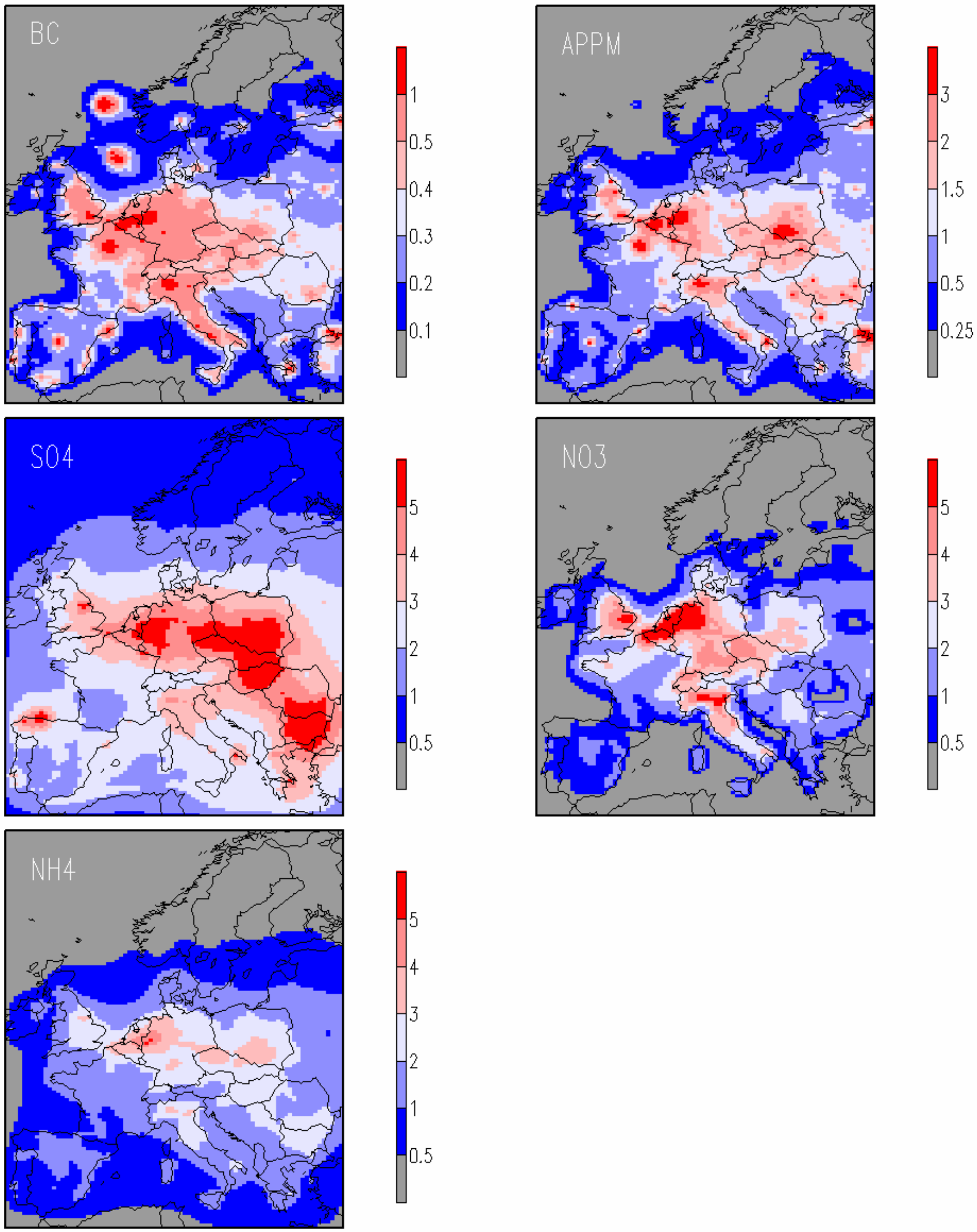


Figure 4

Annual average distribution of BC, APPM, SO_4, NO_3 and NH_4 over Europe ($\mu g/m^3$).

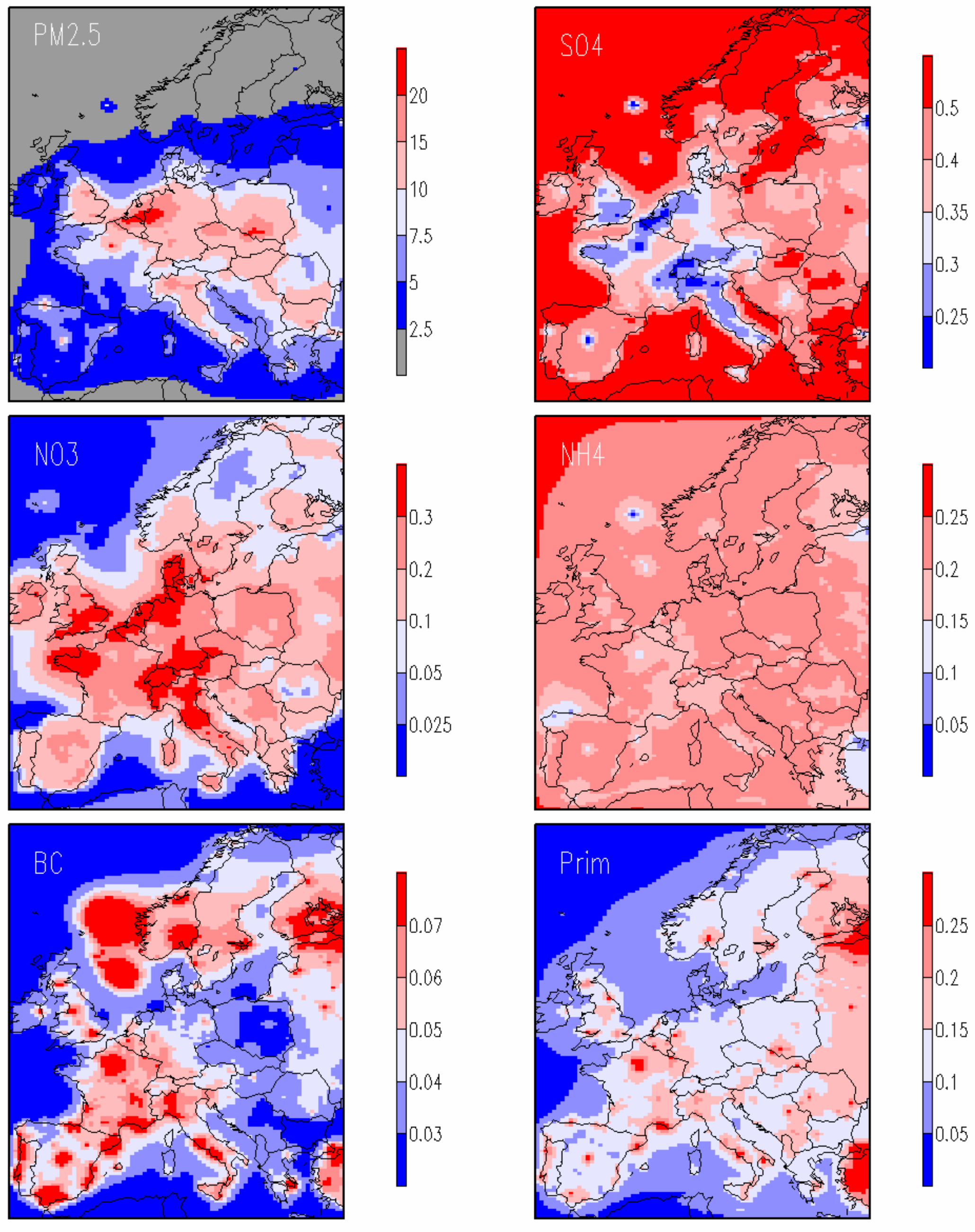
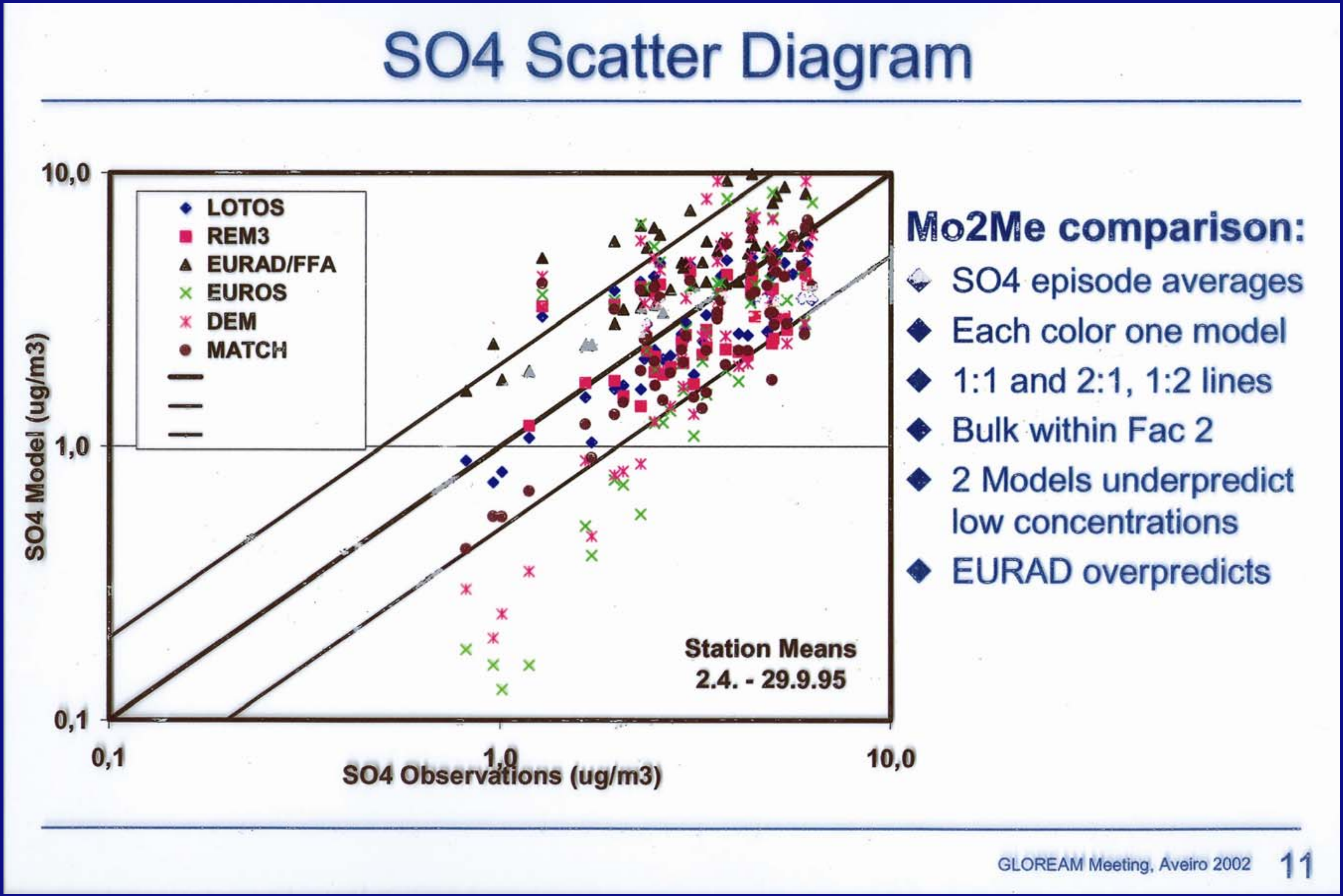


Figure 5

Annual average distribution of PM2.5 (µg/m^3) over Europe in the upper left panel and the associated fractions of BC, APPM, SO_4, NO_3 and NH_4 in the other panels.

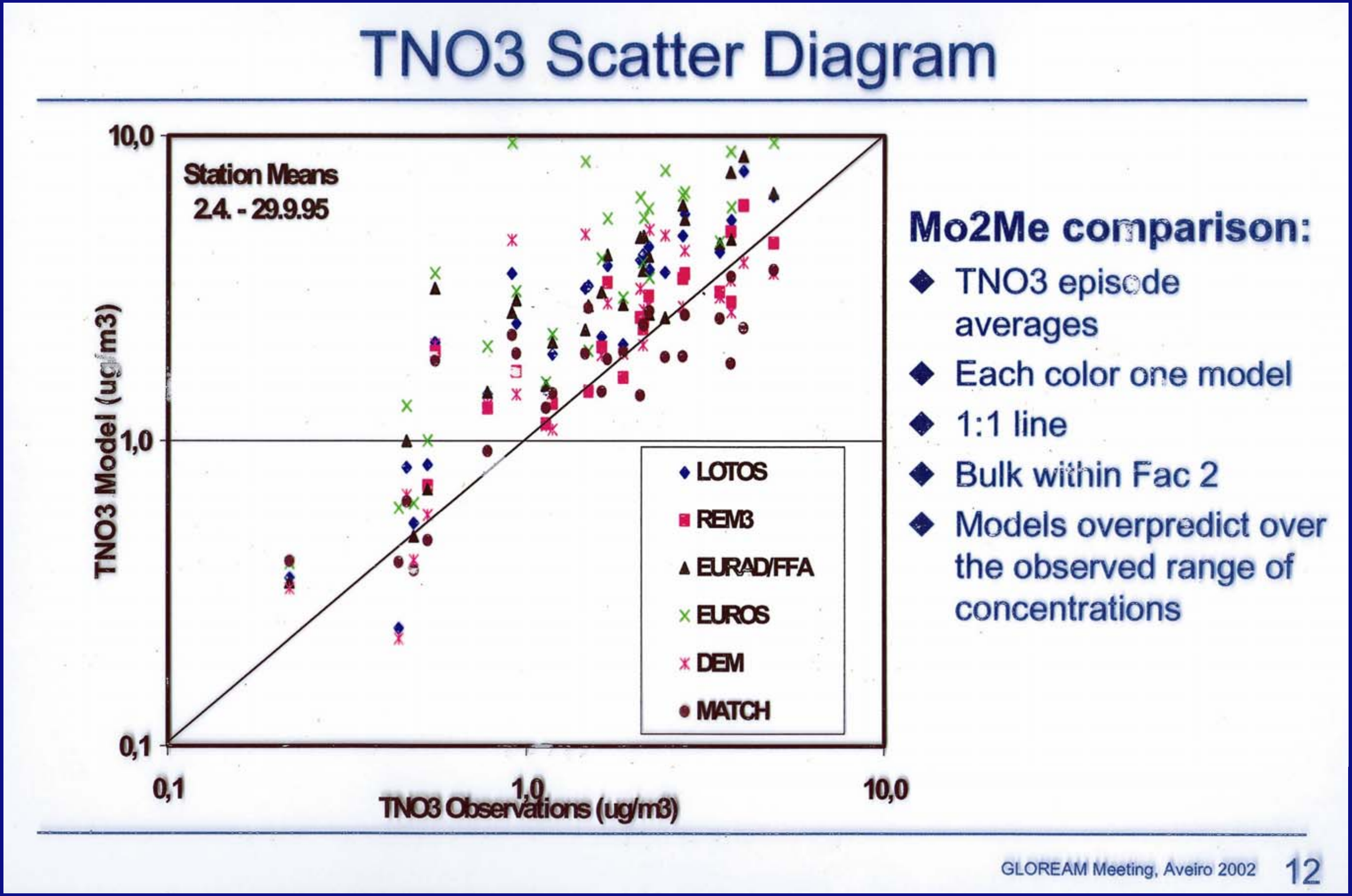


SO4 Scatter Diagram

Mo2Me comparison:

- SO4 episode averages
- Each color one model
- 1:1 and 2:1, 1:2 lines
- Bulk within Fac 2
- 2 Models underpredict low concentrations
- EURAD overpredicts

GLOREAM Meeting, Aveiro 2002 11



TNO3 Scatter Diagram

Mo2Me comparison:

- TNO3 episode averages
- Each color one model
- 1:1 line
- Bulk within Fac 2
- Models overpredict over the observed range of concentrations

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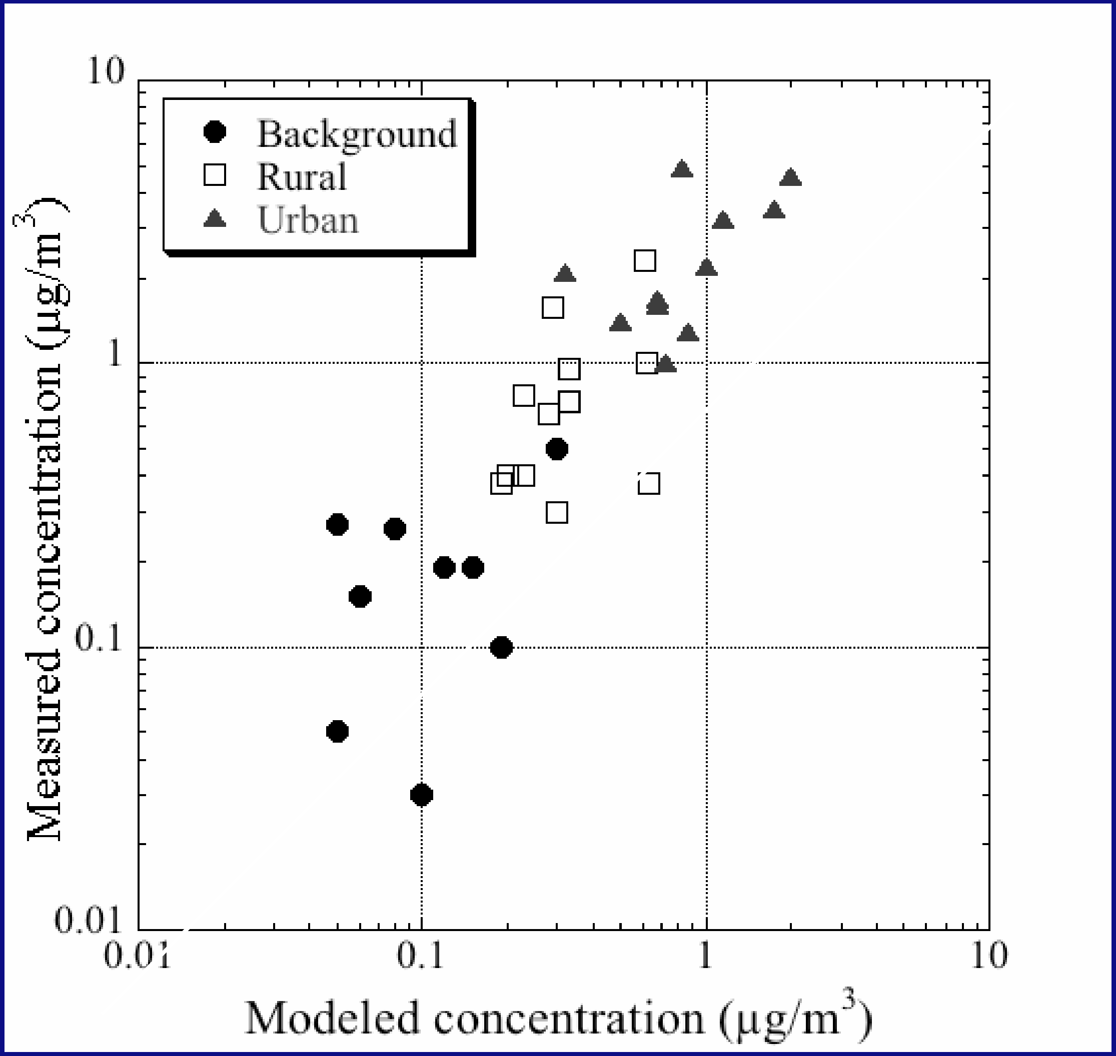
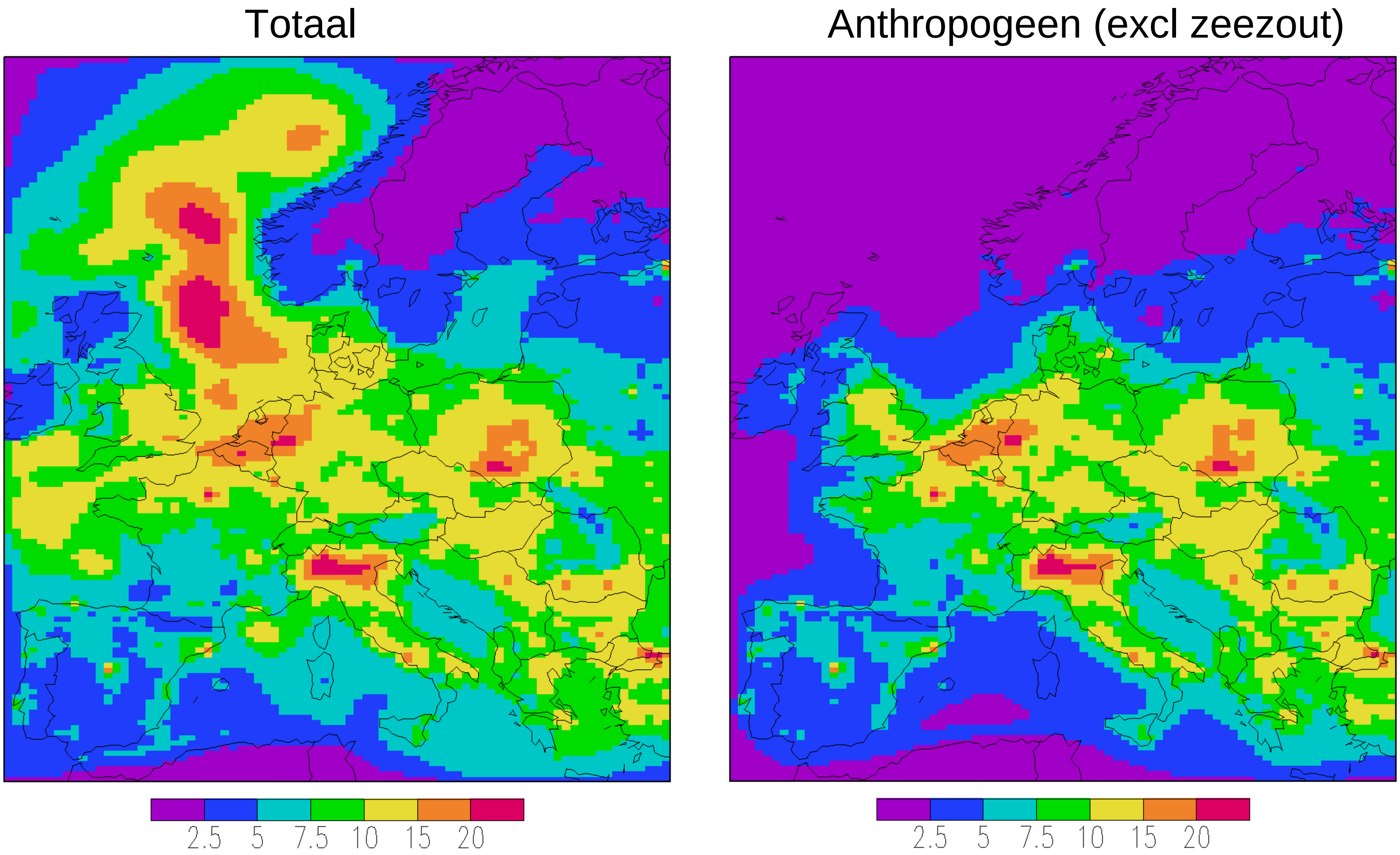
BC to measurements



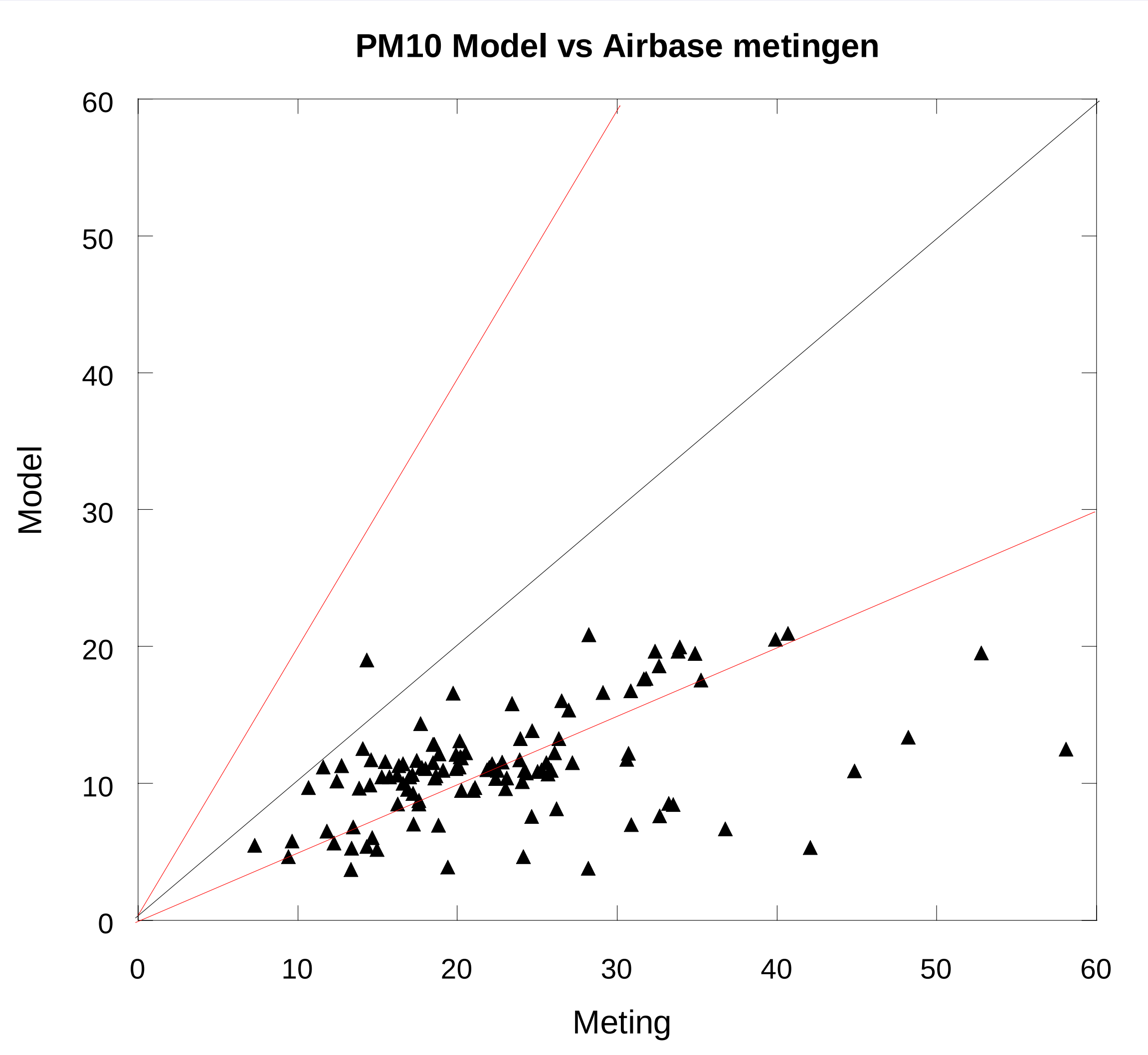
Gemodelleerde PM10 concentratie over Europa (2003)



Totaal

Anthropogeen (excl zeezout)

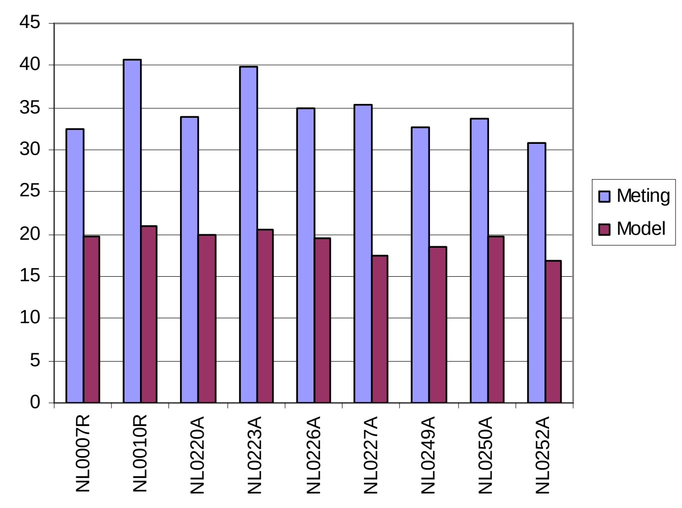
Verificatie van model resultaten: PM10



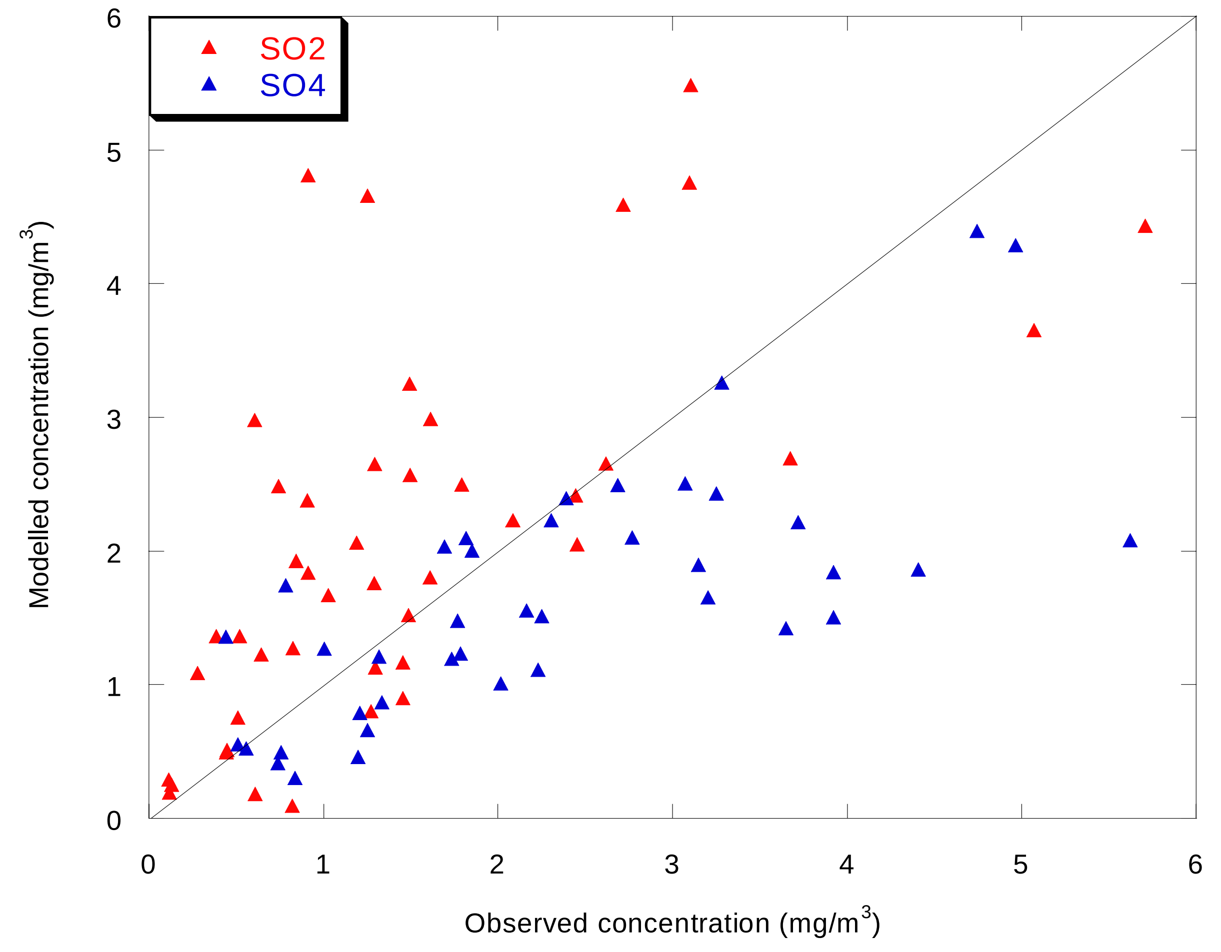
Nederland:

PM10 wordt 45 % onderschat

Correlatie: 0.52-0.62

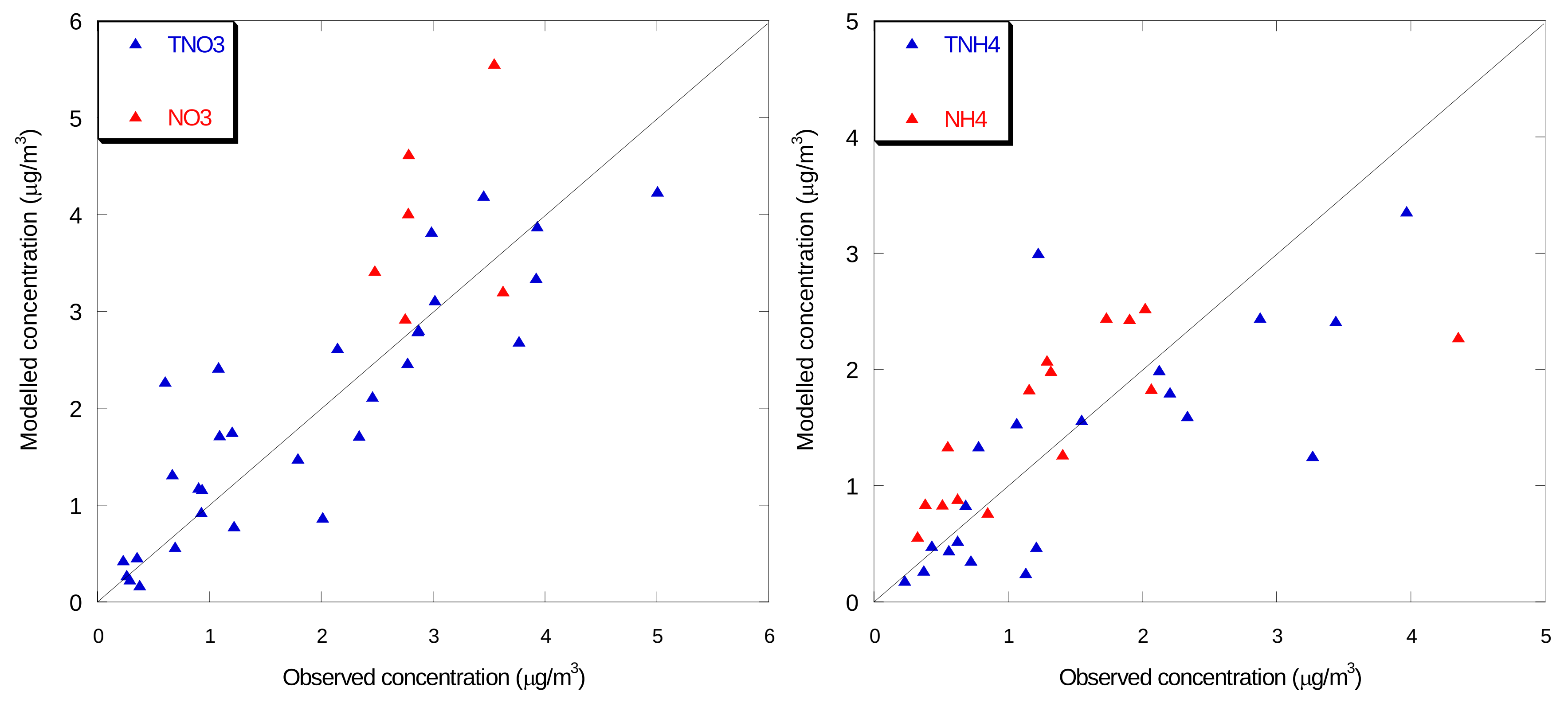


Verificatie van model resultaten: Sulfaat



Onzekerheid: Non-lineare trend in SO_2-SO_4 conversie snelheid (rol wolken/mist, heterogene reacties etc.)

Verificatie van model resultaten: Nitraat en ammonium



Onzekerheid: Representatie ammoniak

(in de zomer wanneer NH_3 de formatie limiteert

Konklusionen

Modellierung von Secondär Inorganisch Aerosol-SIA- geht gut

Modellierung von PM10 geht “nicht” gut

Noch laufende Studie, Artikel in Vorbereitung:

A model intercomparison study focussing on episodes with elevated PM10 concentrations

FU, TNO, LISA-Paris, Köln

I) Die EU-Rahmenrichtlinien und andere Massnahmen

Massnahmen in Brussel : Focus auf Gesundheit – Stadt

Massnahmen in Genf : Focus auf Eco-system – Laendliche Gebiete

Bruessel : EU-Rahmenrichtlinien, NEC-Directive (National Emission Ceilings)

Genf : UNECE-Grenzueberschreitende Luftverschmutzung-Gothenburg Protokoll

EU-Rahmenrichtlinien

Fuer SO_2, NO_2, NO_x, PM_{10} ($PM_{2.5}$), Pb, O_3
In der Zukunft: PAK und Schwermetalle

Fuer Stadtgebiete sind NO_2 und $PM_{10}/PM_{2.5}$ die wichtigsten Stoffen

(Im allgemeinen ist O_3 in der Stadt niedrig)

Grenzwerte

NO_2 40 µg/m^3 Jahresmittelwert
200 µg/m^3 Stundenmittel, max. 18 x pro Jahr

PM 10 40 µg/m^3 Jahresmittelwert
50 µg/m^3 Tagesmittel, max. 35 x pro Jahr

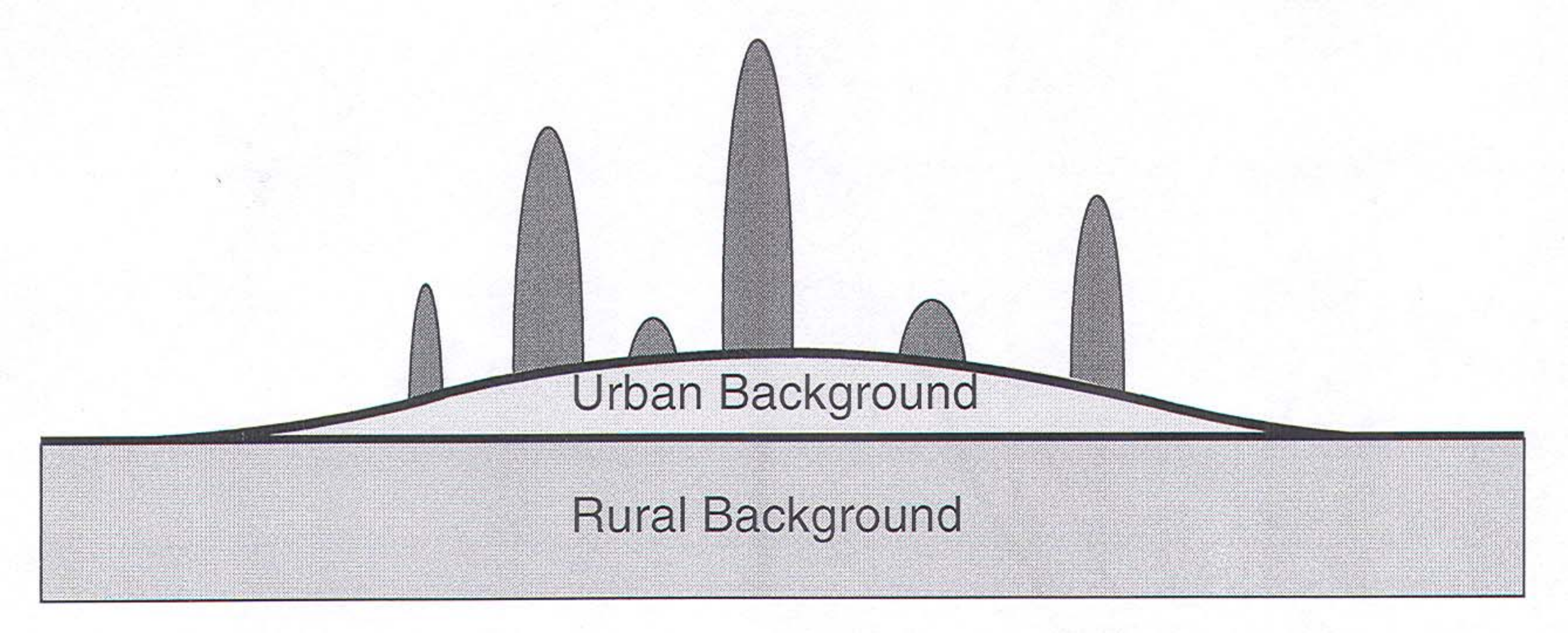
In Grossstaedten: Ueberschreitungen, auch in Berlin

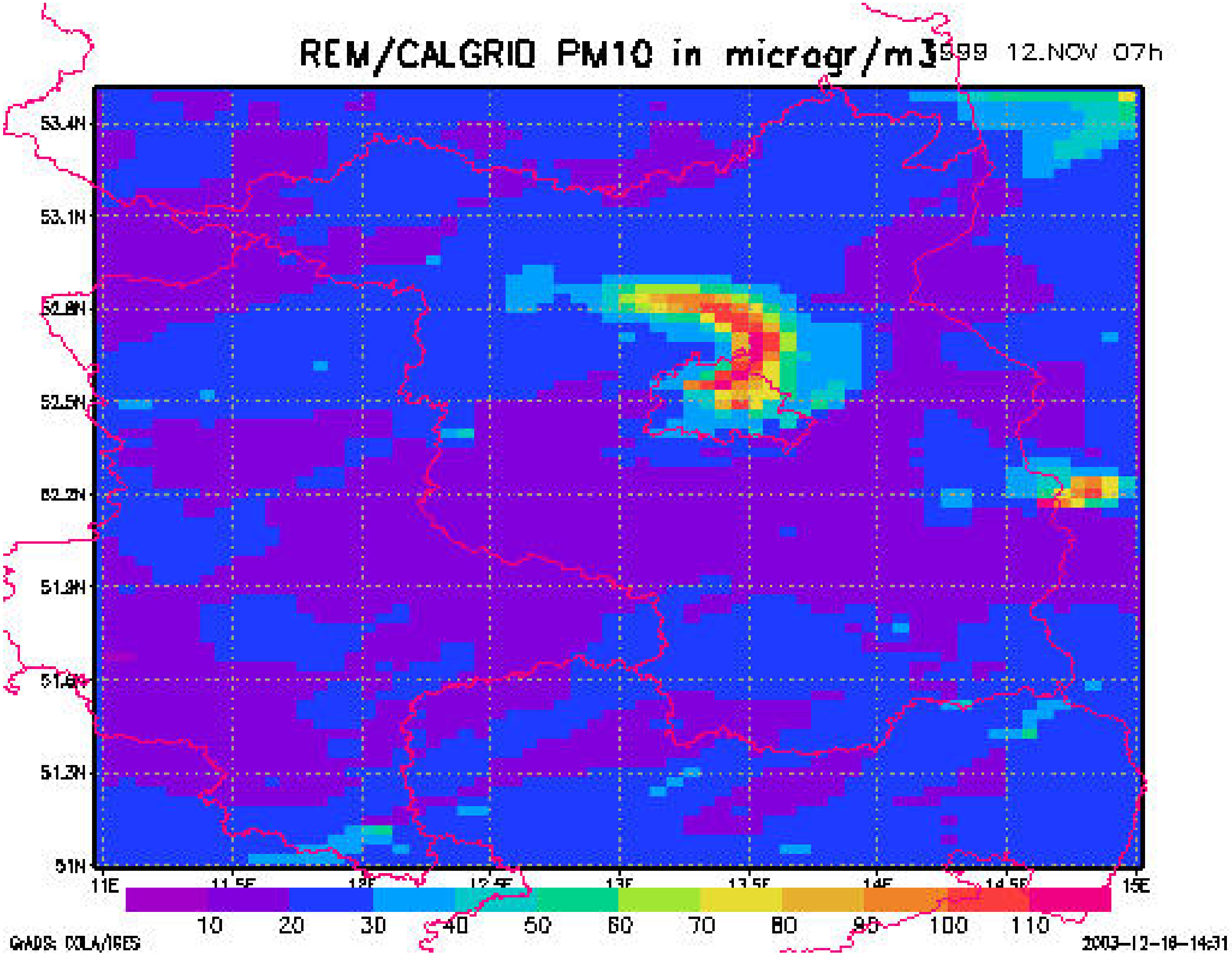
Konzentrationen in der Stadt sind bestimmt durch

Grossraeumigen Hintergrund

Allgemeinen Stadt-Hintergrund

Lokale Situation: Hot spots


Urban Background
Rural Background


REM/CALGRID PM10 in microgr/m3 1999 12.NOV 07h
53.4N
53.1N
52.8N
52.5N
52.2N
51.9N
51.6N
51.3N
51N
11E
11.5E
12E
12.5E
13E
13.5E
14E
14.5E
15E
10
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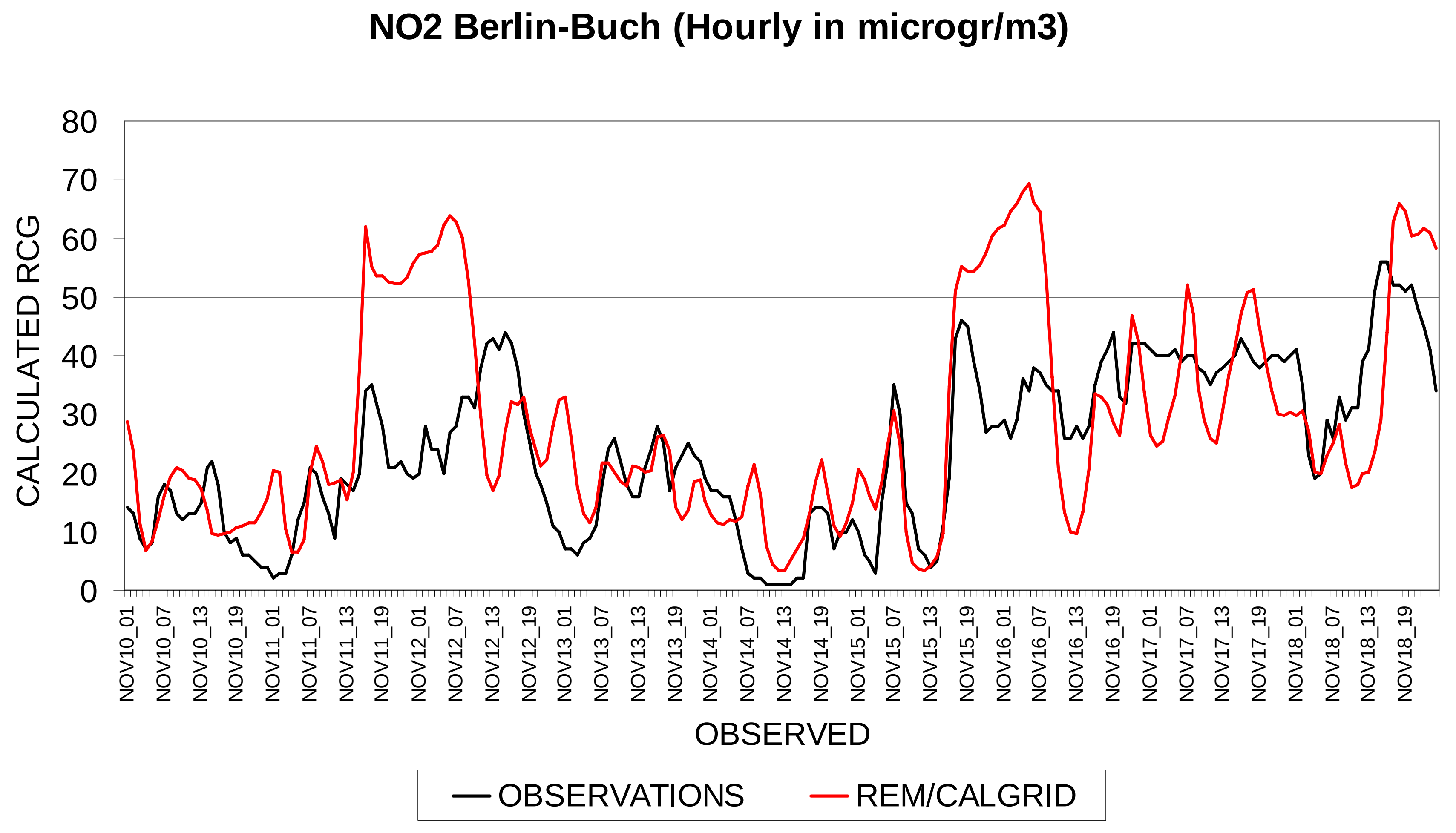
30
40
50
60
70
80
90
100
110
GrADS: COLA/IGES
2003-12-18-14:31


NO2 Berlin-Buch (Hourly in microgr/m3)
CALCULATED RCG
80
70
60
50
40
30
20
10
0
NOV10_01
NOV10_07
NOV10_13
NOV10_19
NOV11_01
NOV11_07
NOV11_13
NOV11_19
NOV12_01
NOV12_07
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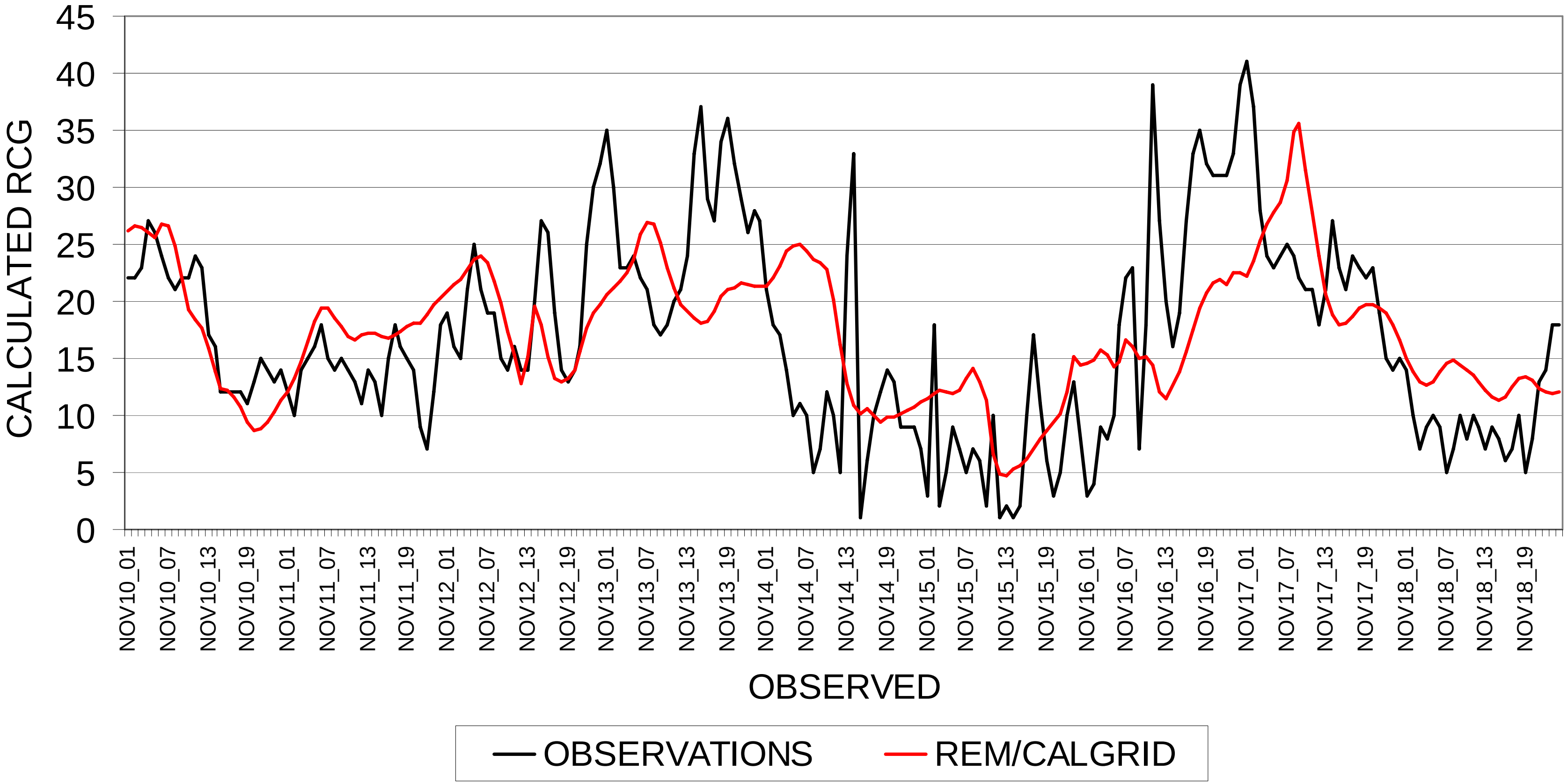
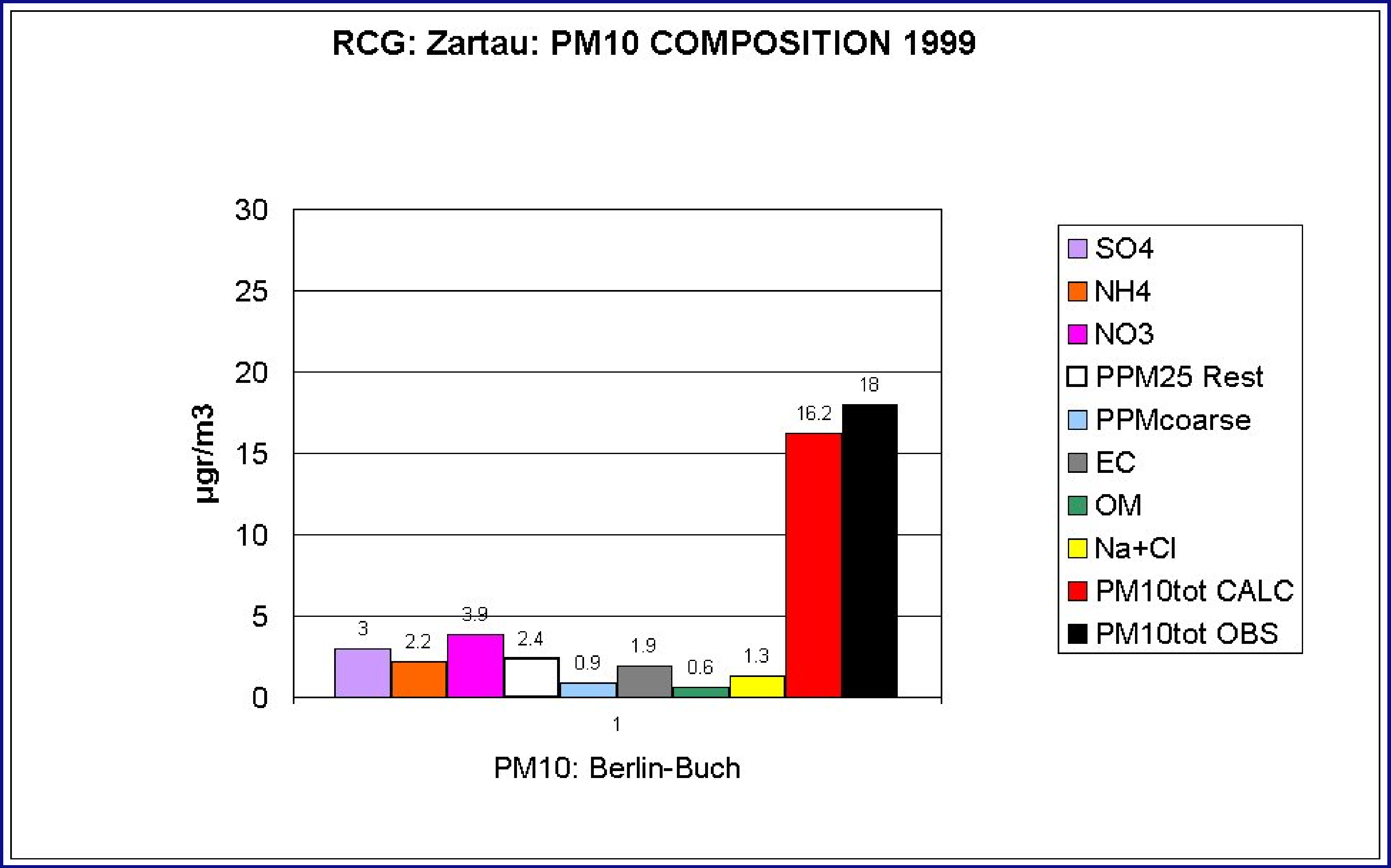
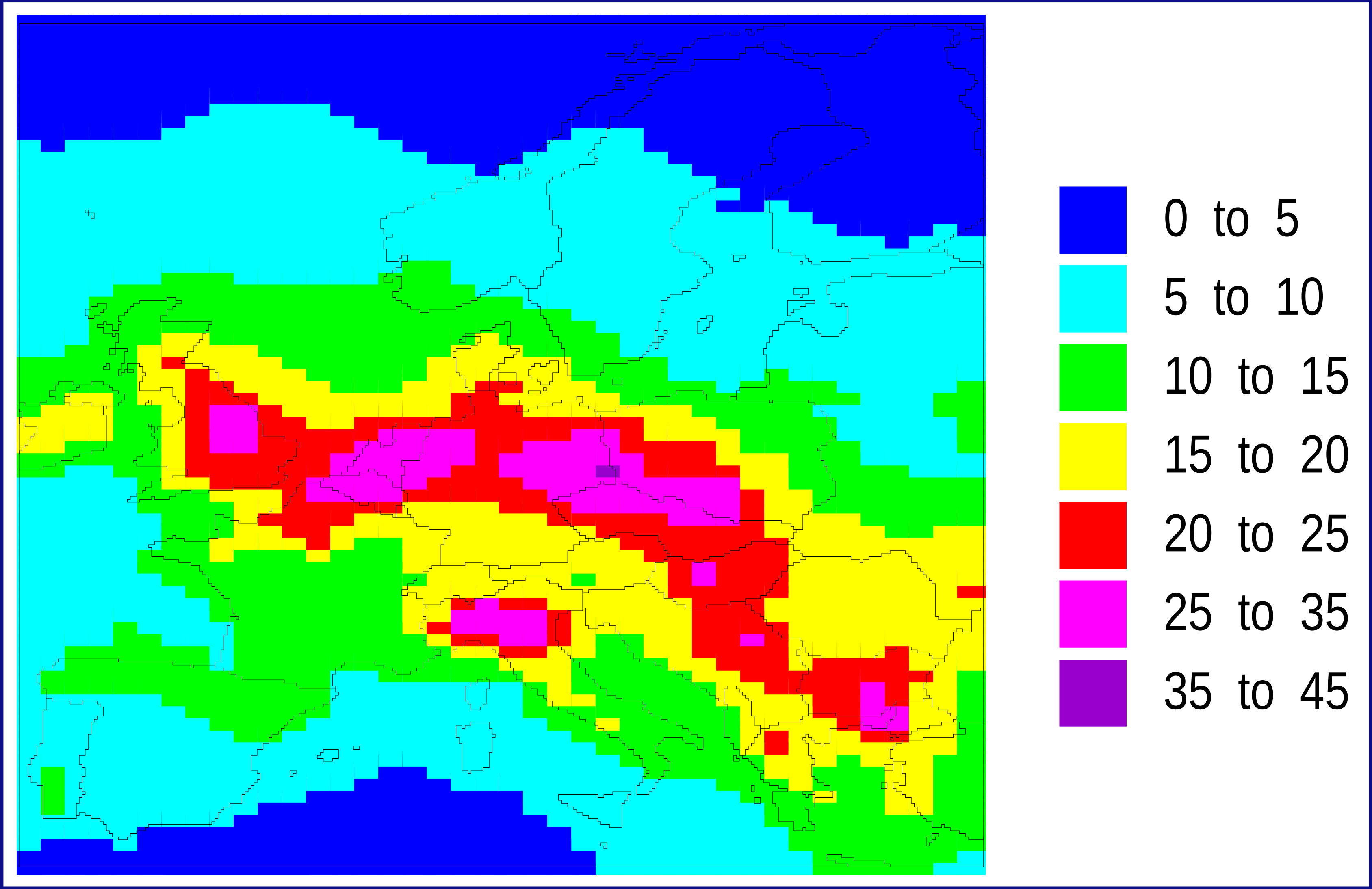
NOV18_01
NOV18_07
NOV18_13
NOV18_19
OBSERVED
OBSERVATIONS
REM/CALGRID

PM10 ZARTAU (Hourly in microgr/m3)





RCG: Zartau: PM10 COMPOSITION 1999



Preliminary estimate of the average $PM_{2.5}$ ($\mu g/m^3$)concentration for August 1997, based on ATSR-2 data.

Many problems in understanding / modelling of PM10 and PM2.5

In observations : PM2.5 1/3 Anorganic
1/3 Organic
1/3 Primary

Coarse Particles: PM10- PM2.5

In general: Modelled concentrations of especially PM10 are lower than observations

Possible explanations :

Missing emission-sources : Wind-blown dust
Road abrasion
Tyres and brakes

Aerosols are also relevant for Climate Change

Most aerosols are cooling (reflection)

Estimate over Europe ~ -2 W/m^2

Black Carbon is warming (absorption)

Estimate over Europe $\sim +1$ W/m^2

MODDELING BLACK CARBON OVER EUROPE 7

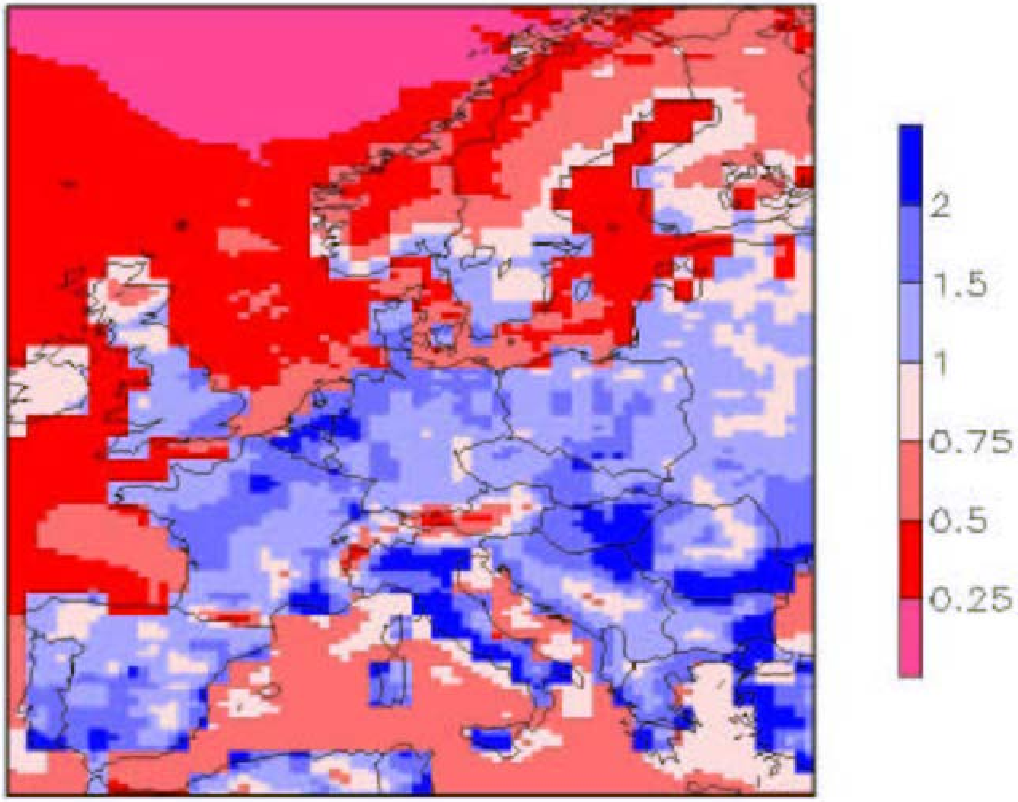
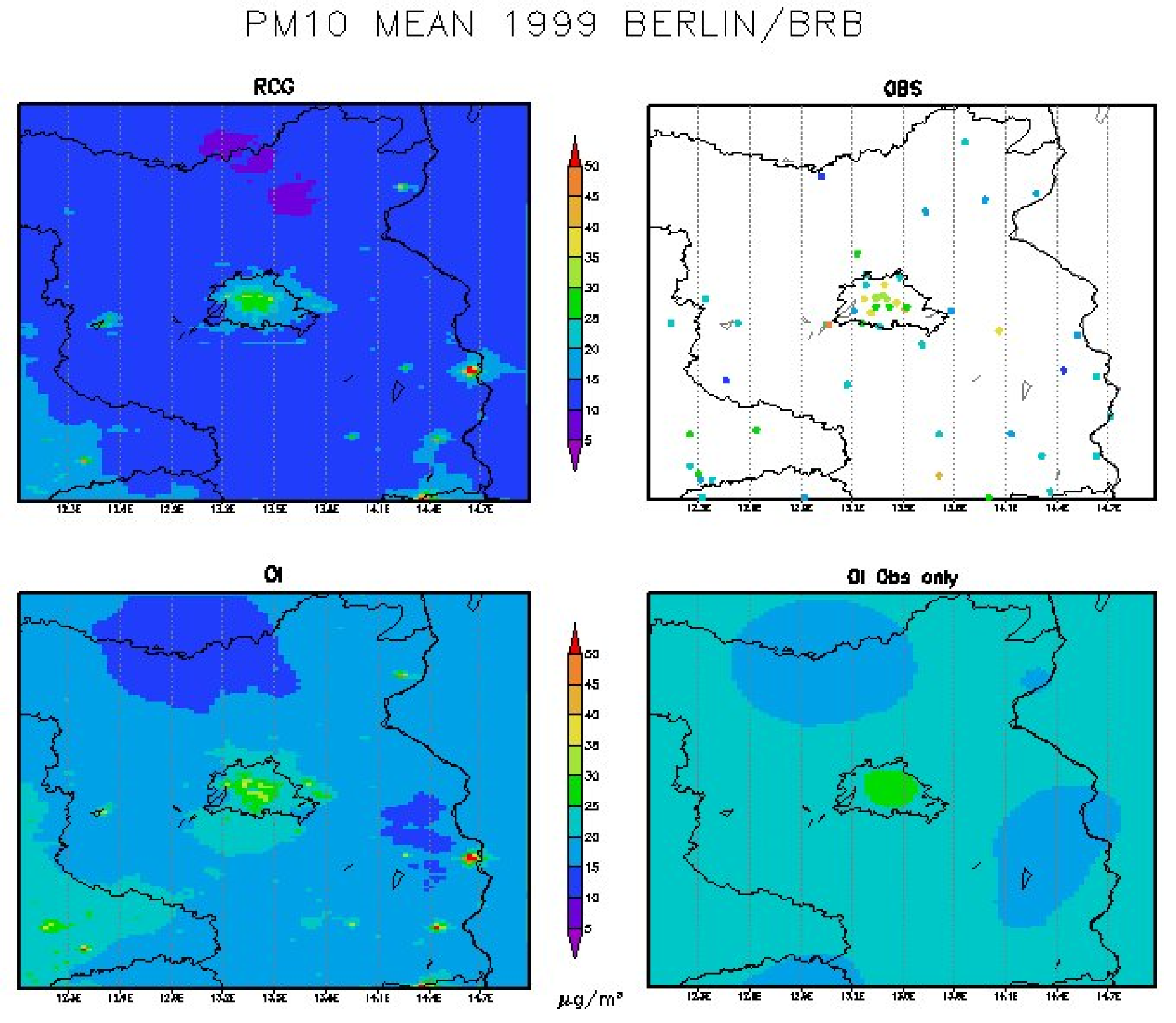


Figure 5. Radiative forcing (W/m^2) of BC over Europe

M.Schaap et al.
“Anthropogenic black carbon and fine aerosol distribution over Europe.
J. of Geoph. Res. 109, D 18207, 2004
Model calculations over 1995 over Europe using the LOTOS-model, overview paper.

IV) Schlussbemerkungen

- **Weitere Untersuchung notwending in der Messung von $\mathrm{PM}_{10/2.5}$ mit chemische Aufsplittung**
- **Weitere Untersuchung notwending in der Modellierung von $\mathrm{PM}_{10}/\mathrm{PM}_{2.5}$, einschliesslich der Emissionen**
- **Herausforderung: Kombination von Messungen und Modellierung bei Data-assimilation / Optimale Interpolation**



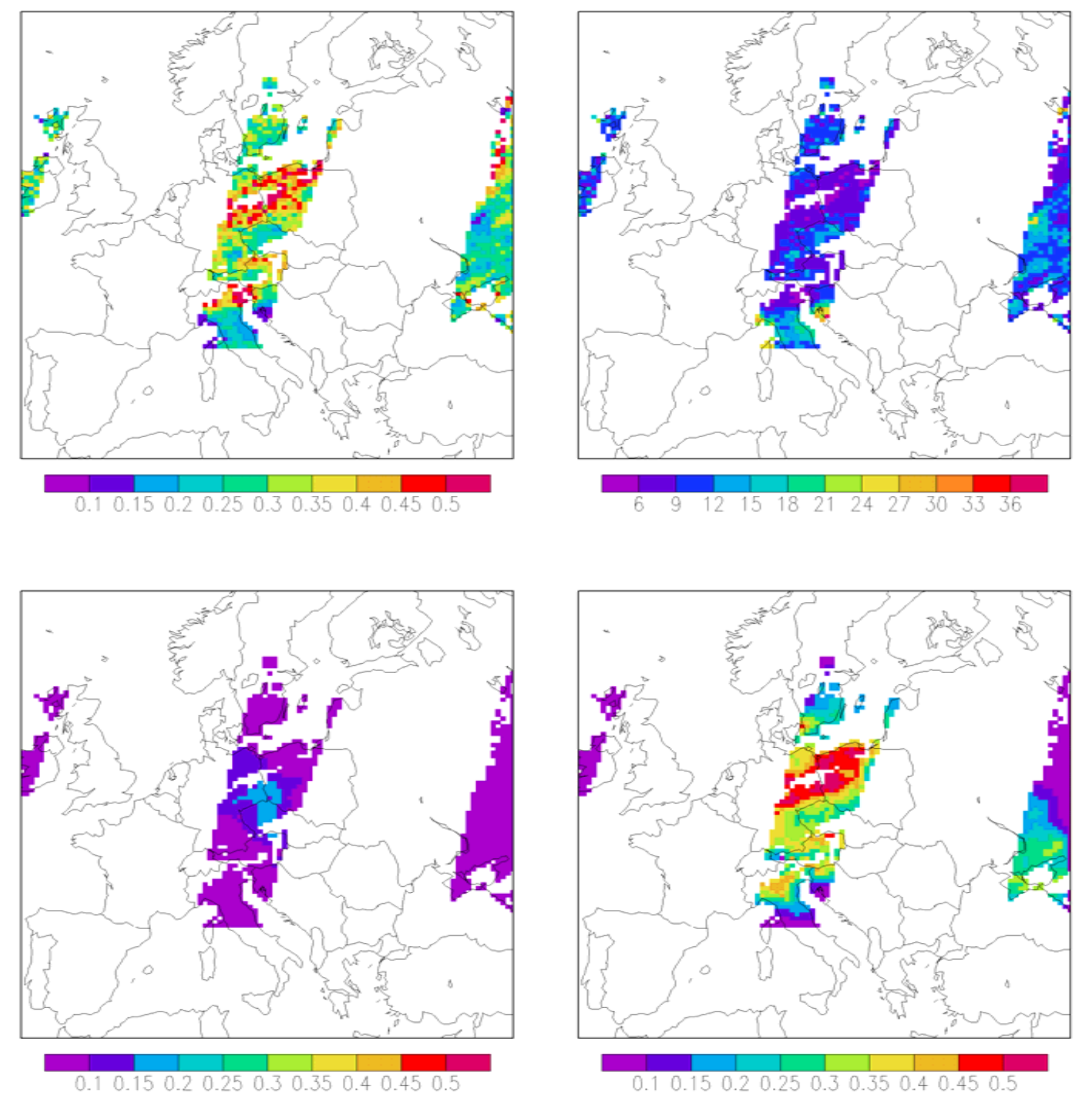
Jahresmittelwert der PM10-Konzentration für Berlin\Brandenburg aus der kleinräumigen Modellrechung (links, oben), der OI-Methode aus Modell und Beobachtung (links unten) und der Beobachtung (rechts oben) und der OI-Methode ausschließlich aus Messungen für das Jahr 1999.

Data assimilatie AOD en PM in LOTOS-EUROS

23-5-2000

Exp 2.

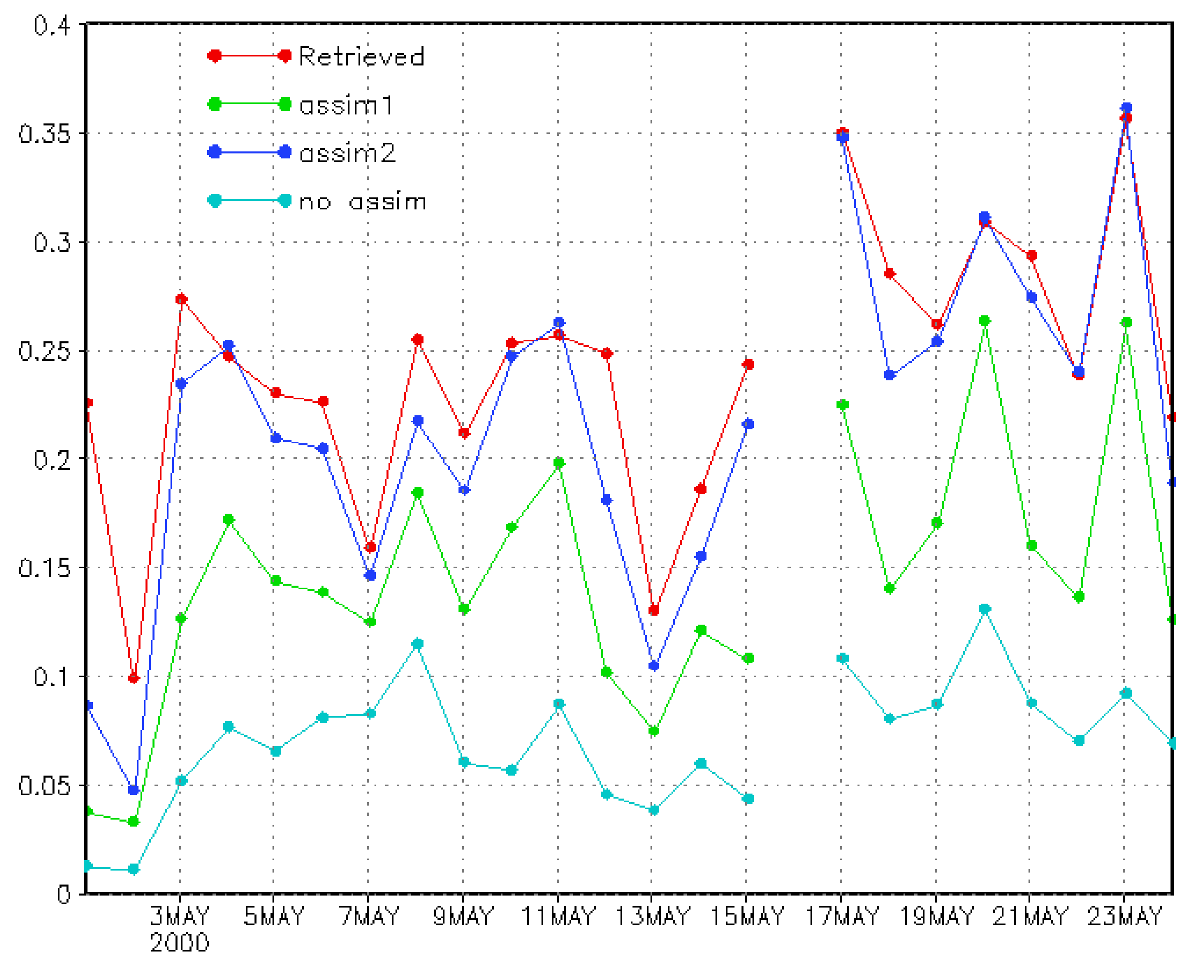
Retrieved



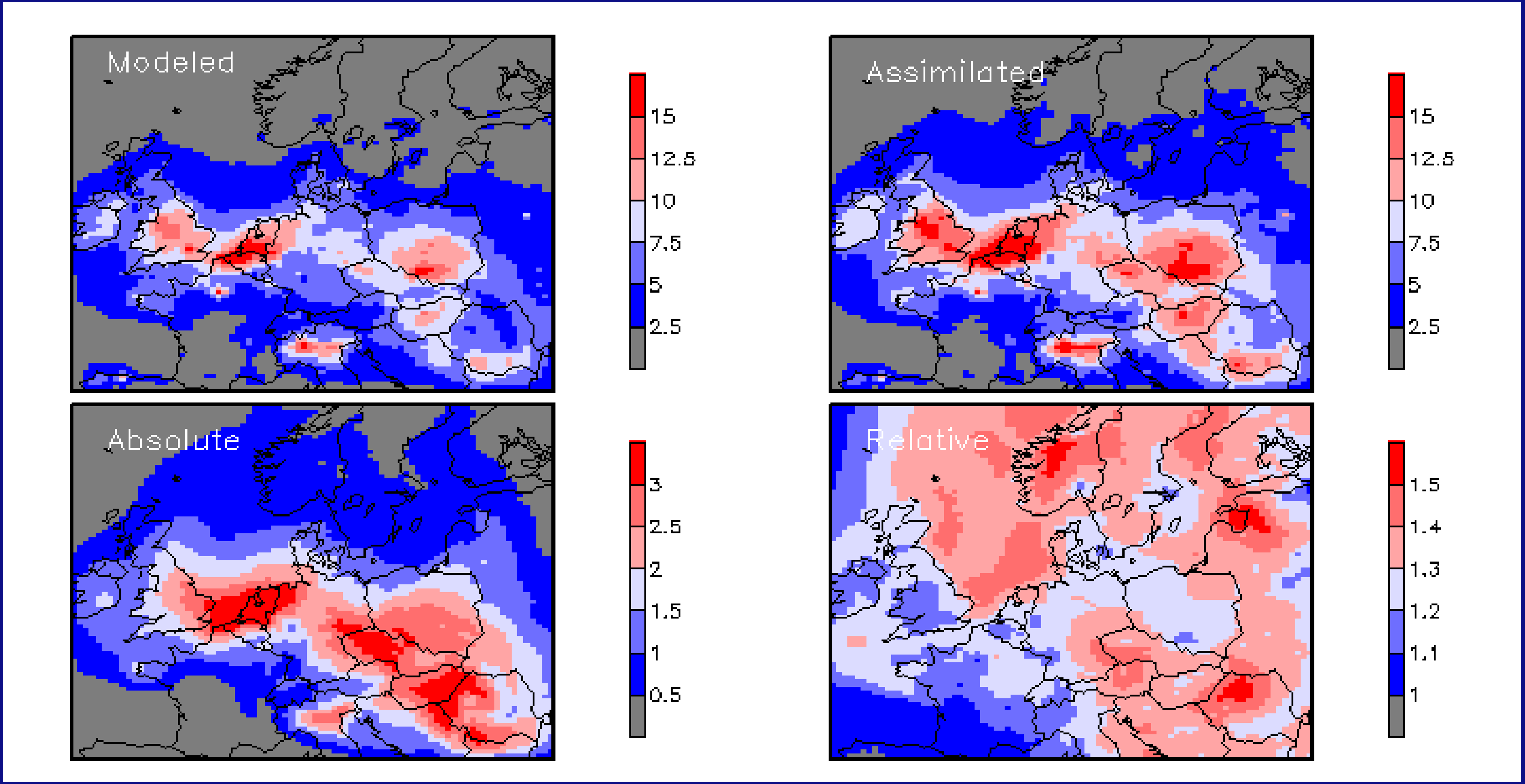
Model

geässimileerd

Validatie AOD → systeem werkt!



Geschatte PM2.5 concentraties



PM2.5 schattingen nog zeer onzeker door laag aantal AOD observaties en de grote onzekerheden in de AOD-PM2.5 relatie

Atmospheric Chemistry / Air quality and Climate Change are coupled phenomena.

- Example: High ozone concentrations in the hot period of August 2003
- Tropospheric ozone is a greenhouse gas
- Most aerosols are cooling, BC is warming
- Research question:
- Air quality/atmospheric chemistry situation over Europe in 2050/2100, so in a modified climate.
- Detailed question: OH-radical in 2050/2100 ???

Angebot zum EU-Brussel, eingereicht März 2, 2006

RACER: Role of Aerosols in Climate Forcing and European Regional Air Quality:

With U.Cubasch, H. Hübener, J.Fischer, and P.Builtjes and many more!

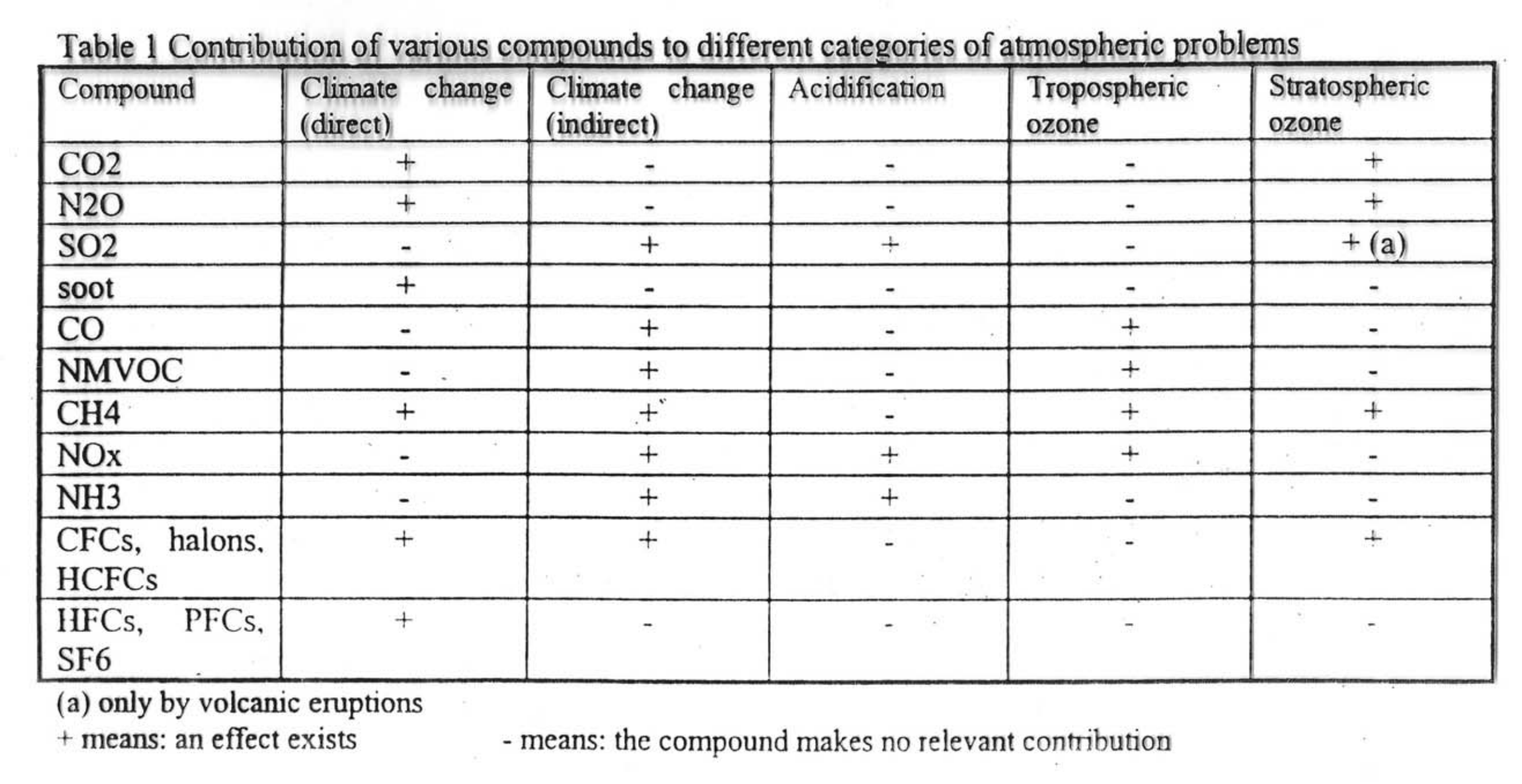


Table 1 Contribution of various compounds to different categories of atmospheric problems

Compound	Climate change (direct)	Climate change (indirect)	Acidification	Tropospheric ozone	Stratospheric ozone
CO2	+	-	-	-	+
N2O	+	-	-	-	+
SO2	-	+	+	-	+ (a)
soot	+	-	-	-	-
CO	-	+	-	+	-
NMVOC	-	+	-	+	-
CH4	+	+	-	+	+
NOx	-	+	+	+	-
NH3	-	+	+	-	-
CFCs, halons, HCFCs	+	+	-	-	+
HFCs, PFCs, SF6	+	-	-	-	-

(a) only by volcanic eruptions

+ means: an effect exists

- means: the compound makes no relevant contribution