Block-Kurs Luftchemie

16 – 20 Februar 2009

TNO | Knowledge for business

Freie Universität Berlin, FB Geowissenschaften
Institut für Meteorologie

Arbeitsgruppe TRUMF – TRopospha̋rische UMweltForschung

9.00 - 13.00 / Nachmittag Selbststudie

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

Ziel von der Block-Kurs

- Einführung in Atmosphärische Chemie
- Lesen/Studieren zwei algemeine - kurze - Artikeln
- Studieren/Verstehen von ein ausgewählte Artikel
- Kurze Presentation am Freitag über dieses Artikel

Struktur des Kurses (1)

Montagmorgen : Entwicklung Erdatmosphäre/Basisprinzipen
Chemie/Stratosphäre 1

Montagnachmittag : “Aerosols Before Pollution” Meinrat Andreae,
Science Jan. 2007

Dienstagmorgen : Stratosphäre II / Troposphäre I

Dienstagnachmittag : “On avoiding dangerous anthropogenic interference
with the climate system”.
V.Ramanathan and Y.Feng, PNAS, vol 105, 38,
14245-14250, Sept.23, 2008

Mittwochmorgen : Troposphäre II und III

Mittwochnachmittag : Anfang studieren ausgewählte Artikel

Struktur des Kurses (2)

Donnerstagmorgen : Aerosolen

Donnerstagnachmittag : Weiter studieren ausgewählte Artikel

Freitag : Präsentationen

- Erst Stratosphäre/Ozonschicht, dann Troposphäre
- Fokus: Luftqualität, aber auch Bemerkungen über Klima
- Fokus: Feinstaub/Aerosolen

I) Entwicklung der Zusammensetzung der Erdatmosphäre

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

Detlev Möller, Luft, Chemie Physik Biologie Reinhaltung Recht, Walter de Gruyter, 2003

Richard Wayne, Chemistry of Atmospheres, Clarendon Press, 1993

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

Junge, Air Chemistry and Radioactivity, Academic Press, 1963

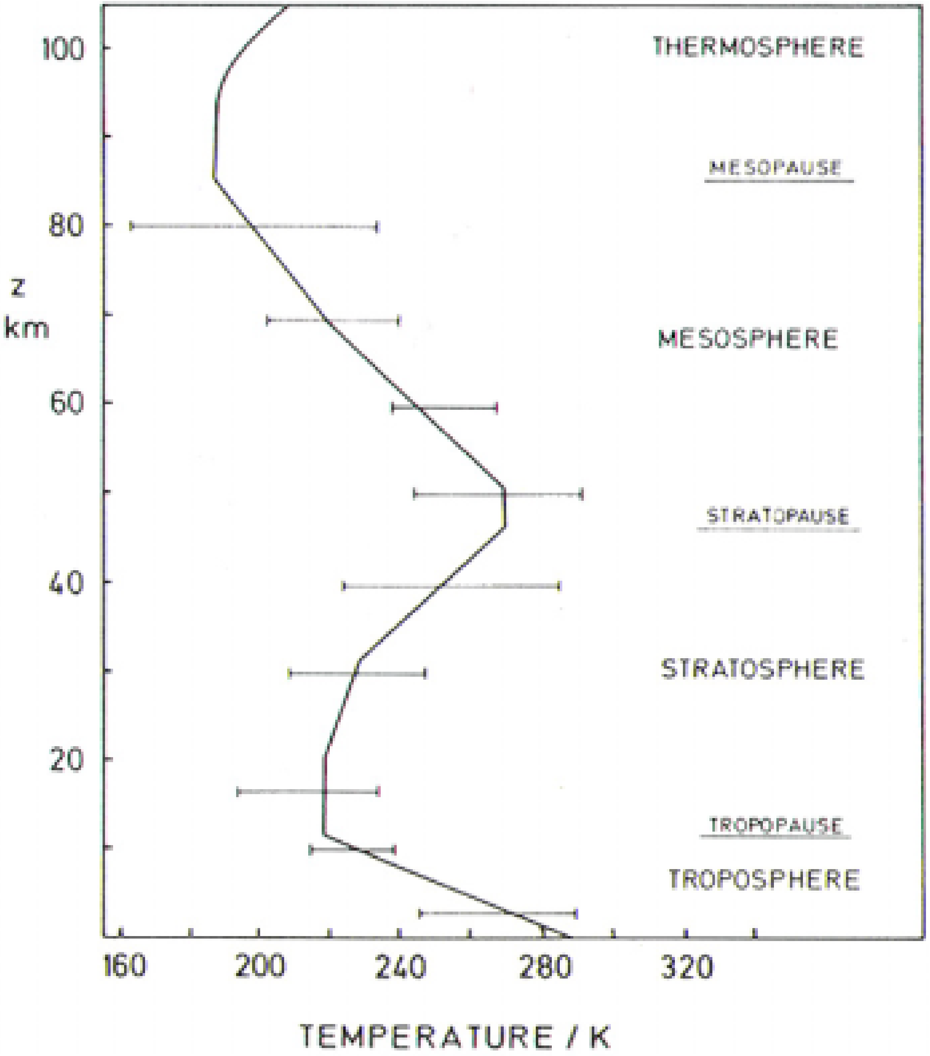


Fig. 1-5. Vertical temperature structure of the atmosphere. The solid curve represents the U.S. Standard Atmosphere, and the horizontal bars indicate the range of monthly means observed between equator and north pole. [Adapted from U.S. Standard Atmosphere (1976).]

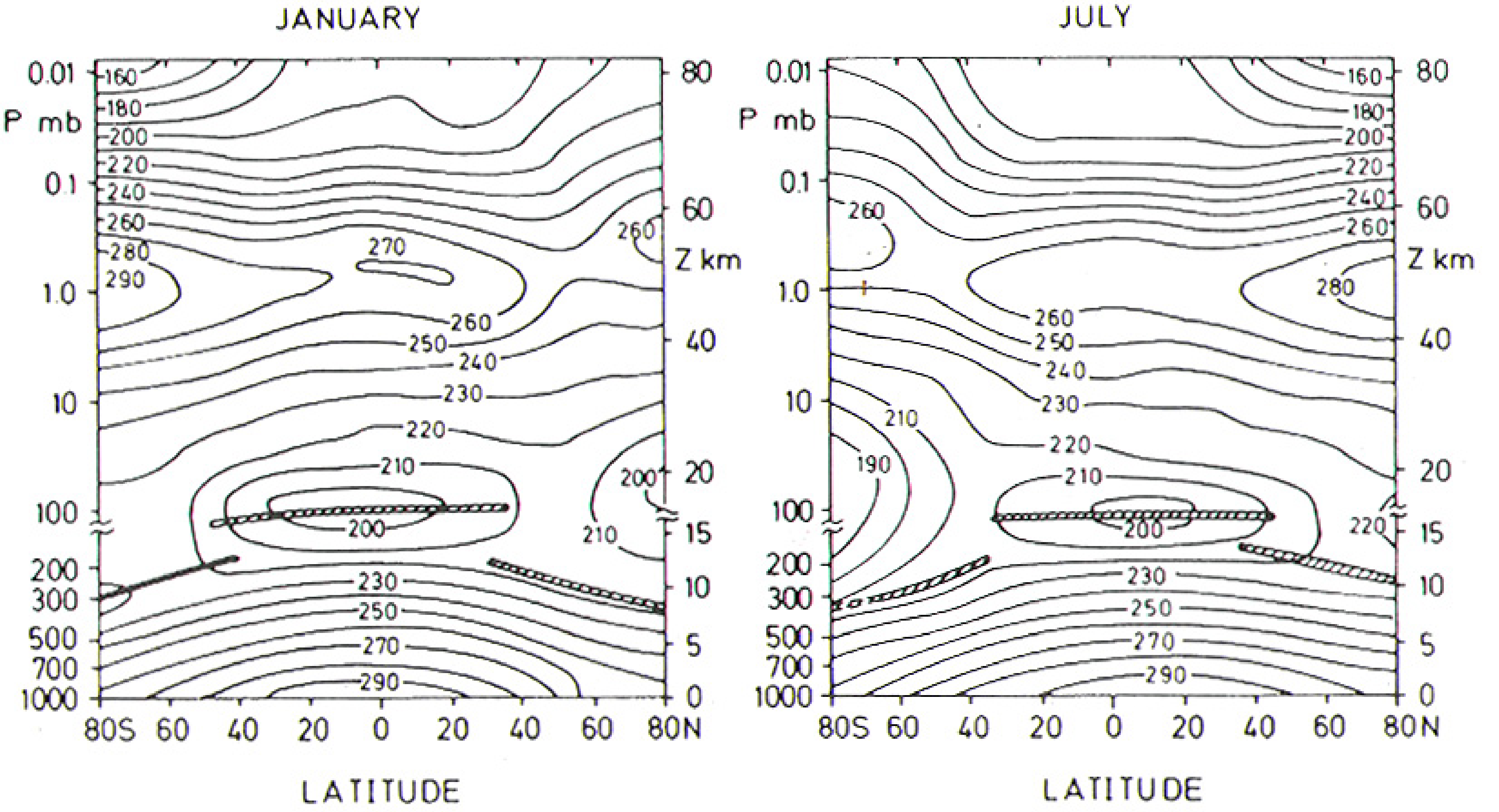


Fig. 1-4. Atmospheric distribution of zonal mean temperatures (in K) for January and July. [Data from Newell *et al.* (1972) for the lower 20 km and from Labitzke and Barnett (1979) for the upper atmosphere are combined.] The tropopause levels are indicated by shaded bars.

Formation and evolution of the atmosphere

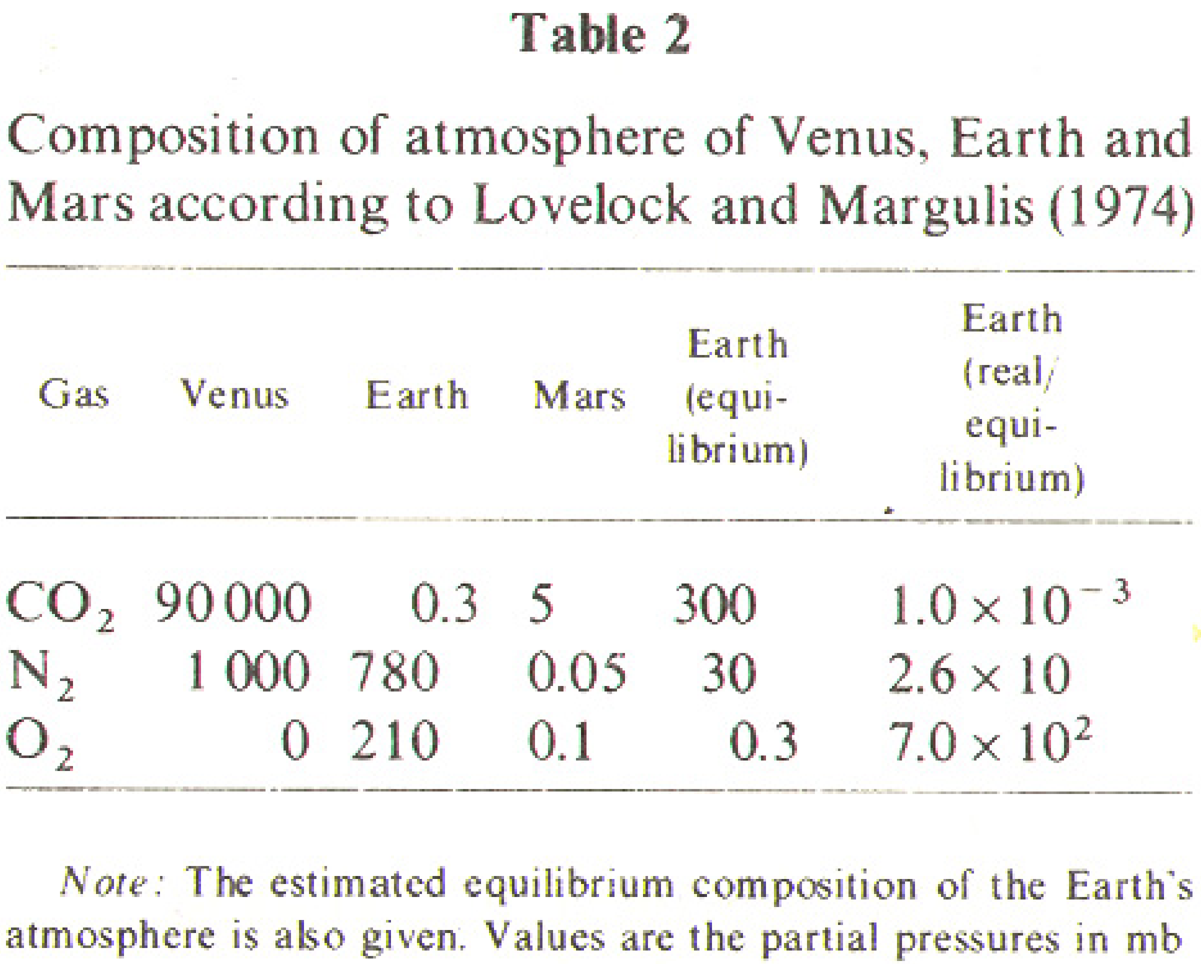


Table 2

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

Gas	Venus	Earth	Mars	Earth (equilibrium)	Earth (real/equilibrium)
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

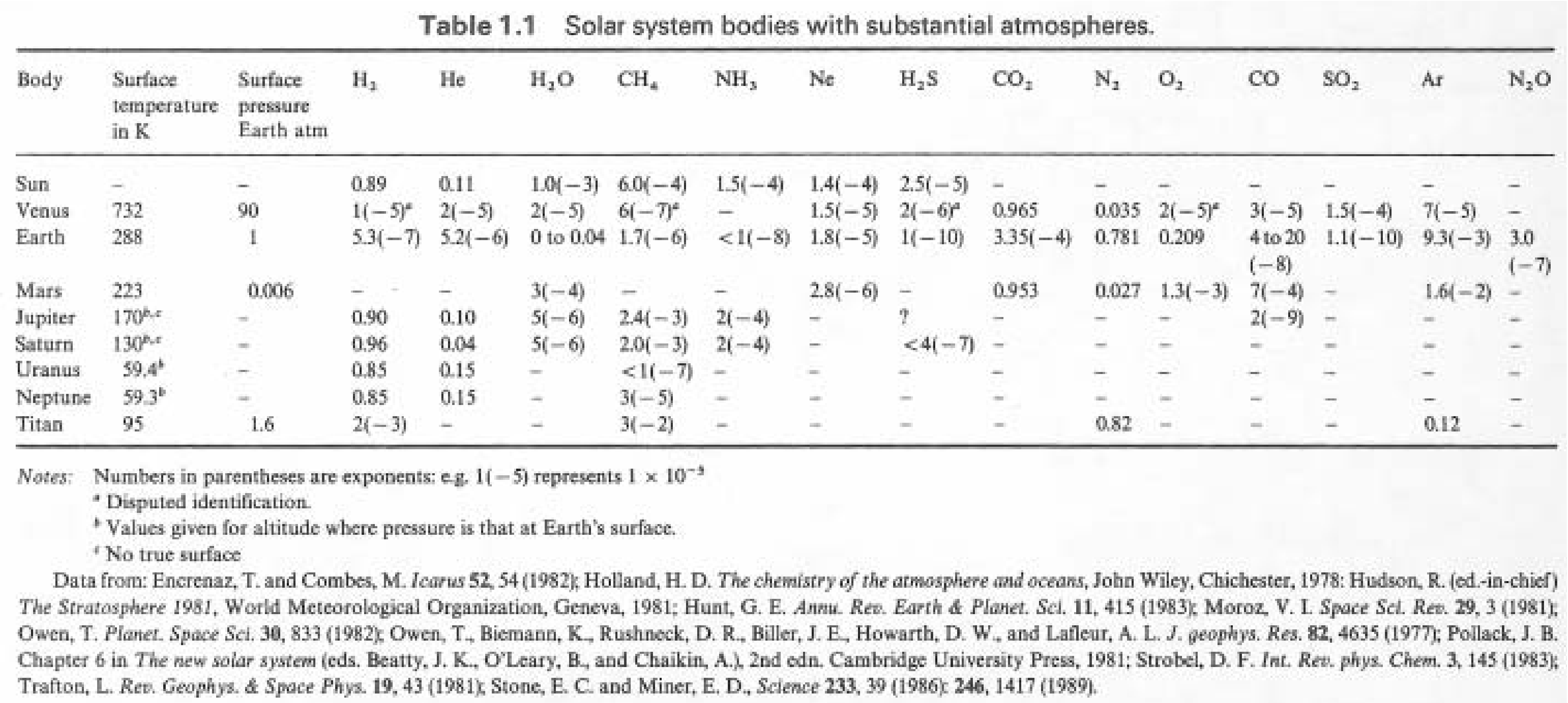


Table 1.1 Solar system bodies with substantial atmospheres.

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

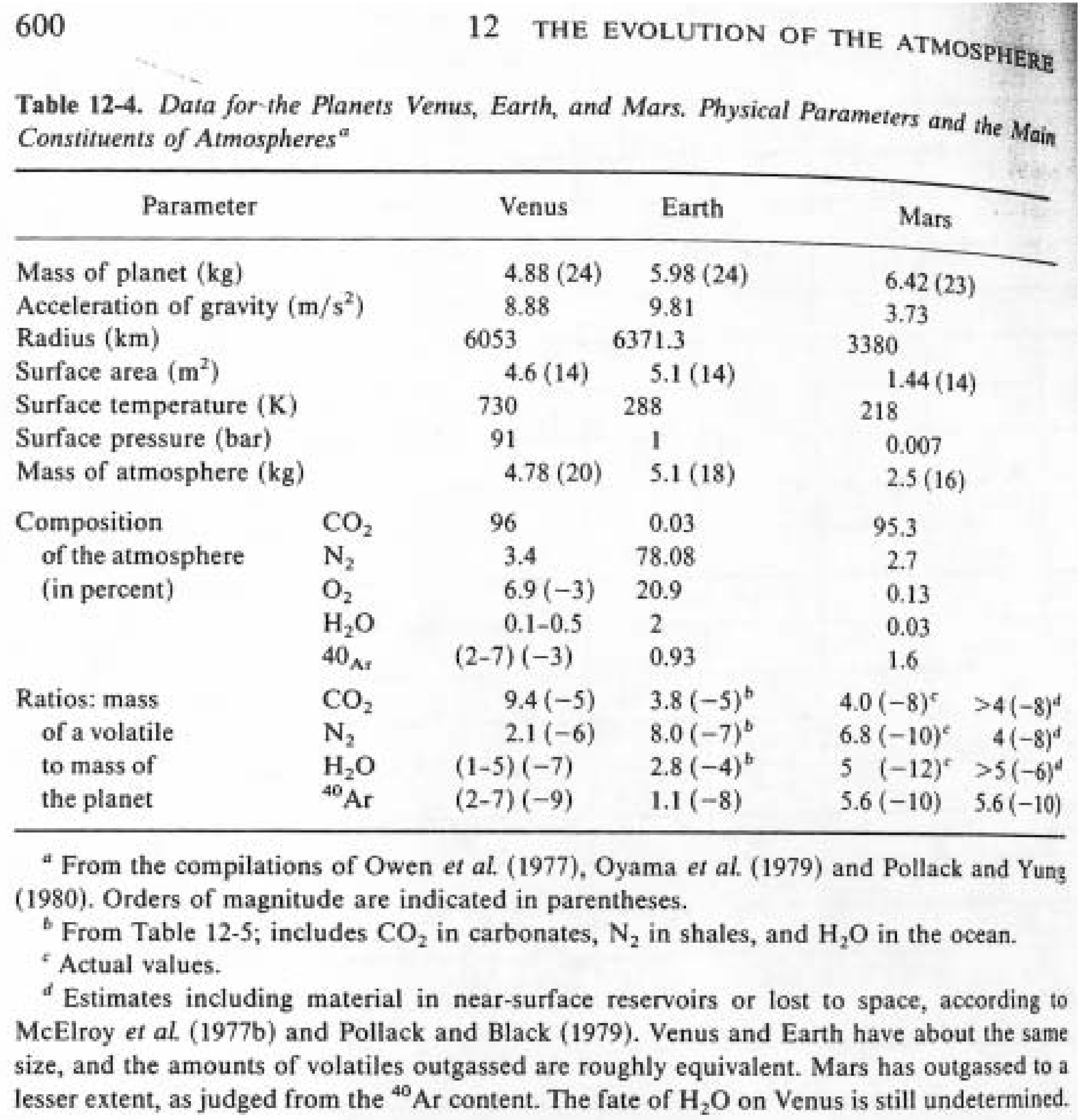


Table 12-4. *Data for the Planets Venus, Earth, and Mars. Physical Parameters and the Main Constituents of Atmospheres*[a]

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

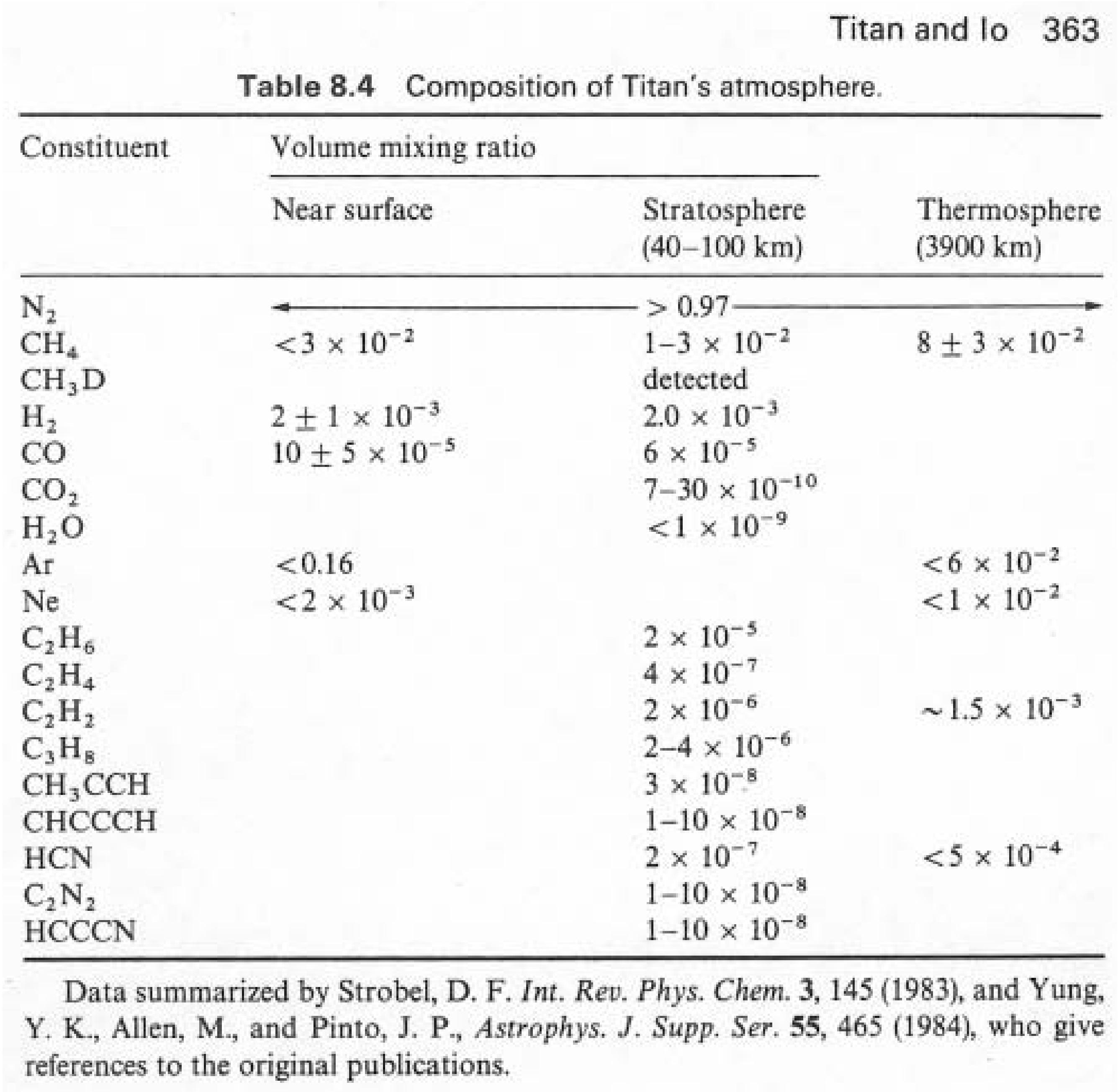


Table 8.4 Composition of Titan's atmosphere.

Constituent	Volume mixing ratio		
	Near surface	Stratosphere (40–100 km)	Thermosphere (3900 km)
N_2	← > 0.97 →		
CH_4	$<3 \times 10^{-2}$	$1–3 \times 10^{-2}$	$8 \pm 3 \times 10^{-2}$
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		$7–30 \times 10^{-10}$	
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		$2–4 \times 10^{-6}$	
CH_3CCH		3×10^{-8}	
CHCCCH		$1–10 \times 10^{-8}$	
HCN		2×10^{-7}	$<5 \times 10^{-4}$
C_2N_2		$1–10 \times 10^{-8}$	
HCCCN		$1–10 \times 10^{-8}$	

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.

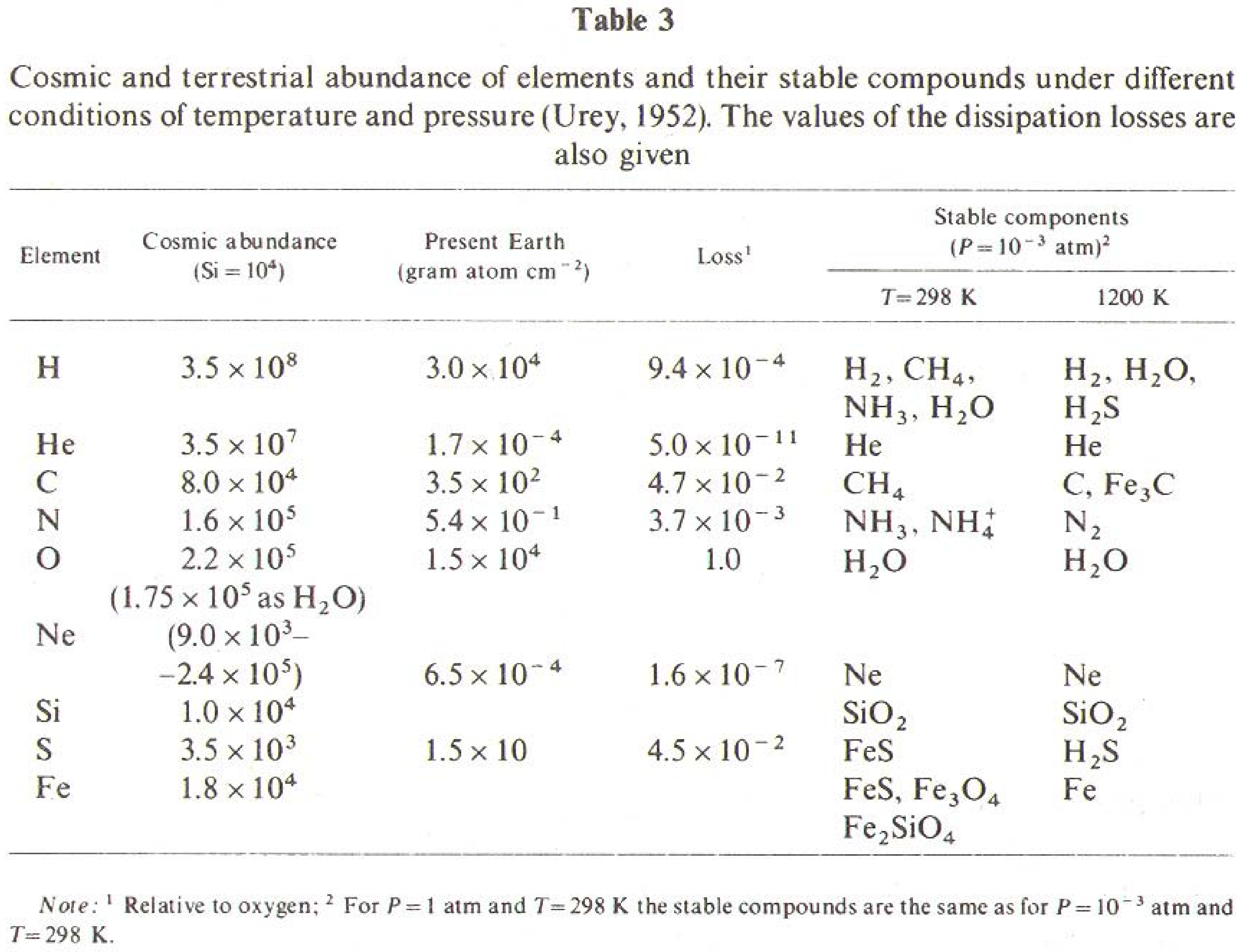


Table 3

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, an oxidising 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)

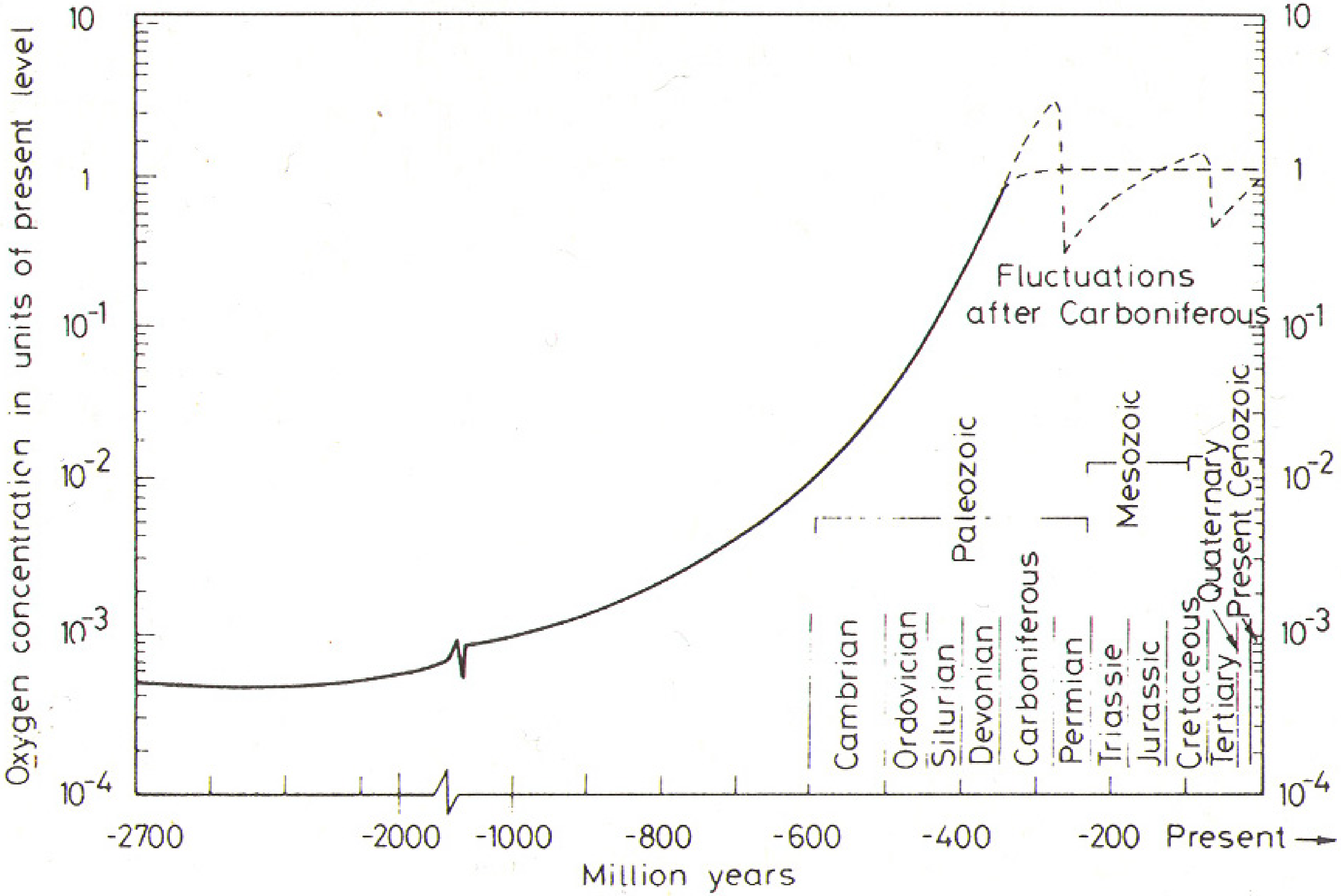
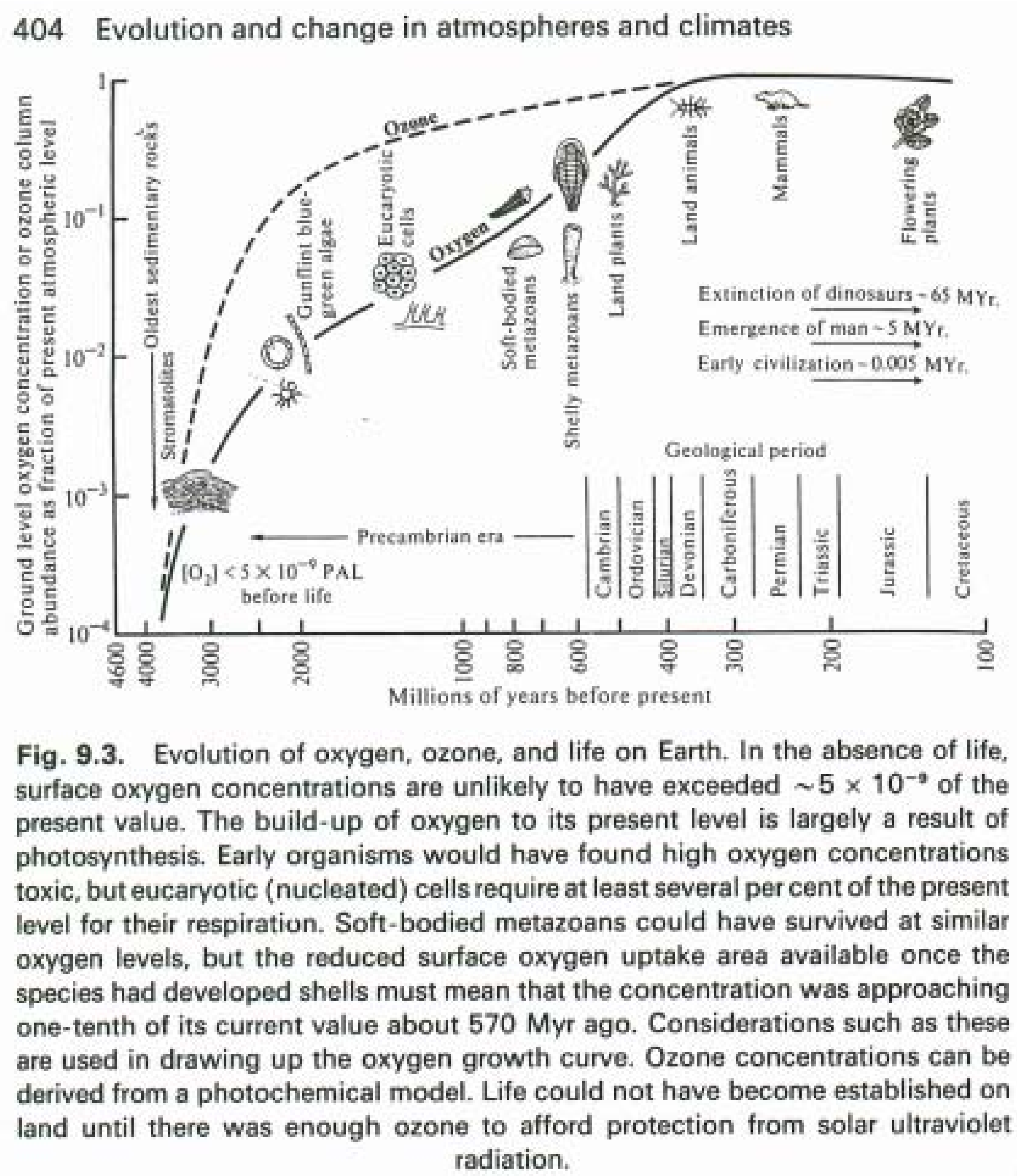


Fig. 3

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



404 Evolution and change in atmospheres and climates

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.

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

$O + O_2 \rightarrow O_3$

Mehr in Detail später

Live on earth started in a reduced atmosphere

Photosynthesis:

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

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

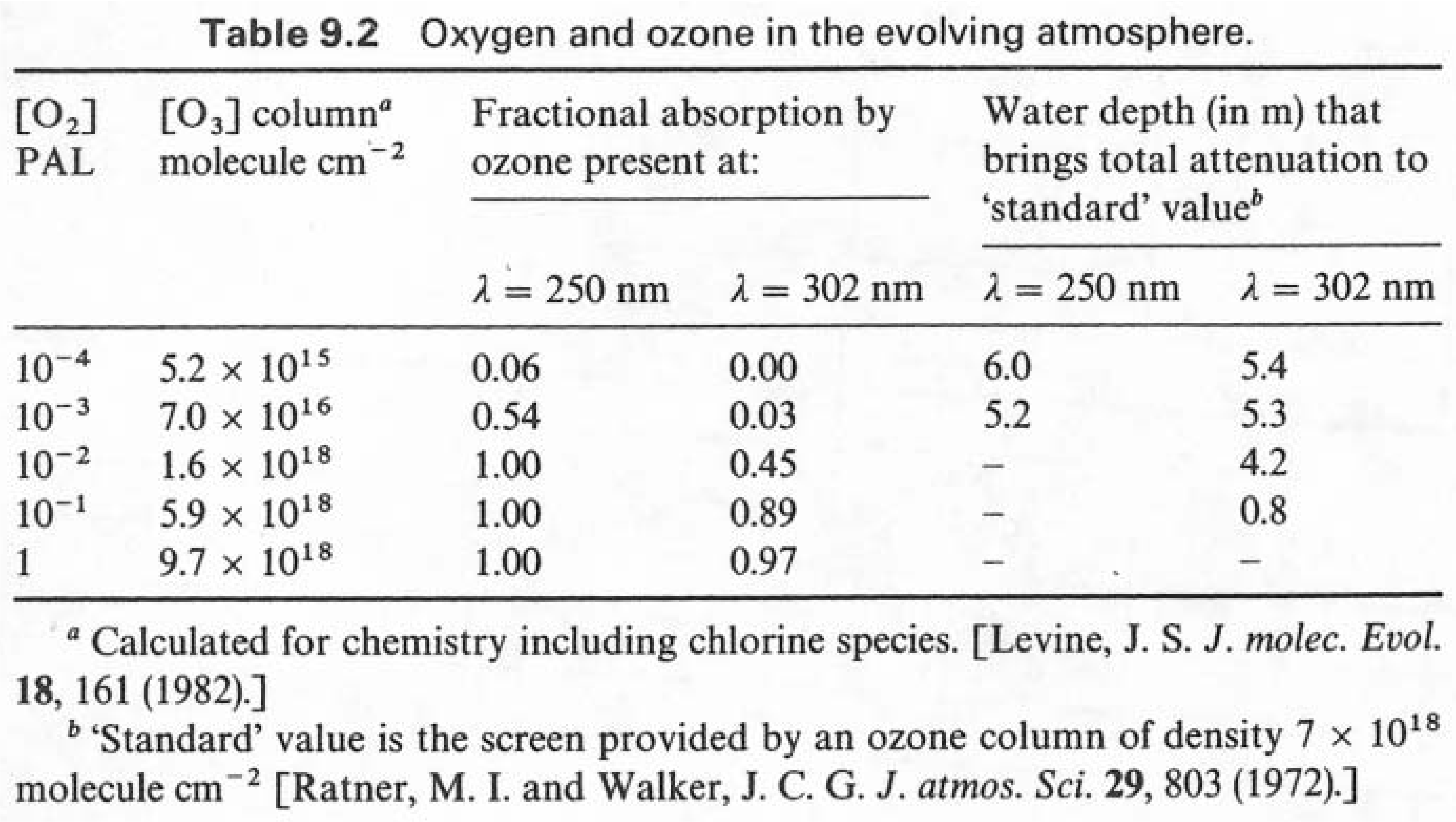


Table 9.2 Oxygen and ozone in the evolving atmosphere.

$[O_2]$ 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:

$C_nH_mO_p + O_2 \rightarrow H_2O + CO_2$ + energy
(more energy than by photosynthesis)

Fermentation:

$C_nH_mO_p \rightarrow C_2H_5OH + CO_2$ + 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

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

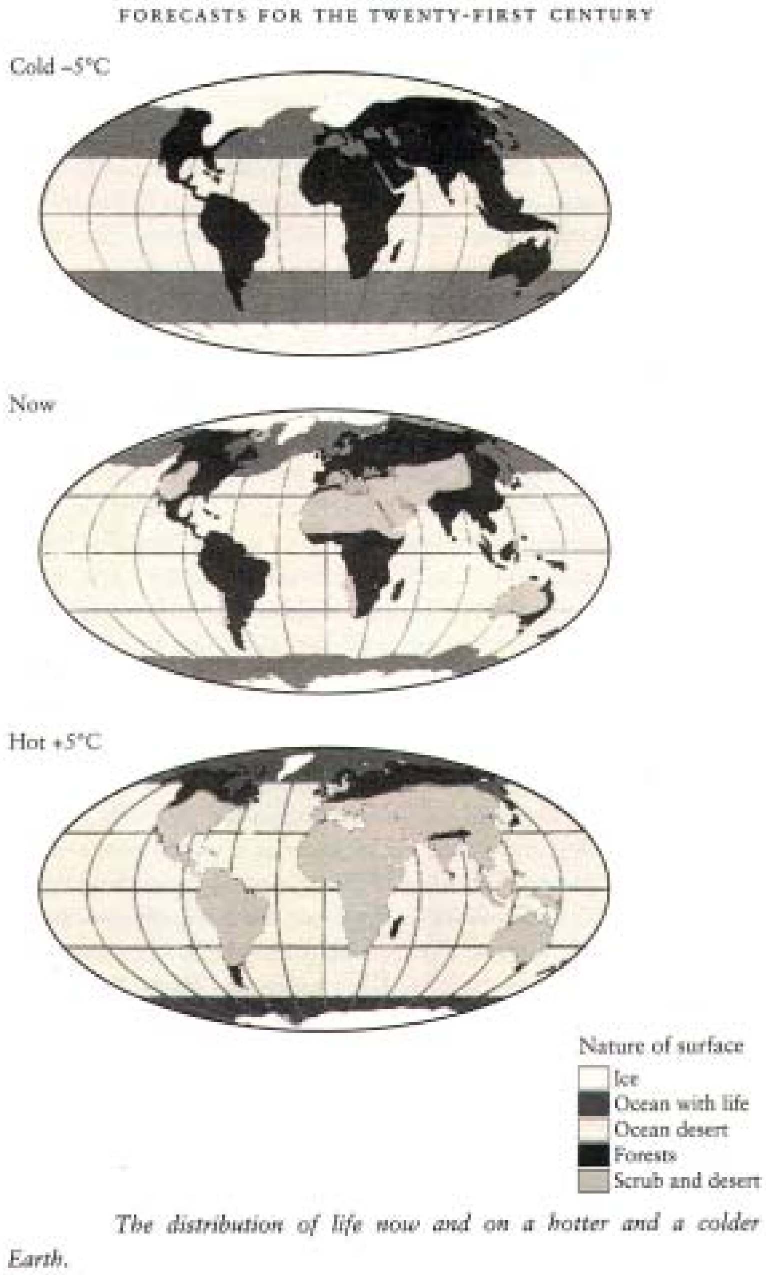
Gaia hypothesis	:	James Lovelock
Homeostasis	:	The eco-system creates the atmosphere, the environment, in which it feels well The system contains numerous (delicate) feed-back mechanisms to keep the balance

Capacity of control

Figures from:

- The revenge of Gaia James Lovelock Penguin Books 2006
- Question: What is the best temperature for life on earth?

Figure 1: Distribution of Life



FORECASTS FOR THE TWENTY-FIRST CENTURY

Cold −5°C

Now

Hot +5°C

Nature of surface

- ☐ Ice
- ▨ Ocean with life
- ☐ Ocean desert
- ■ Forests
- ▨ Scrub and desert

The distribution of life now and on a hotter and a colder Earth.

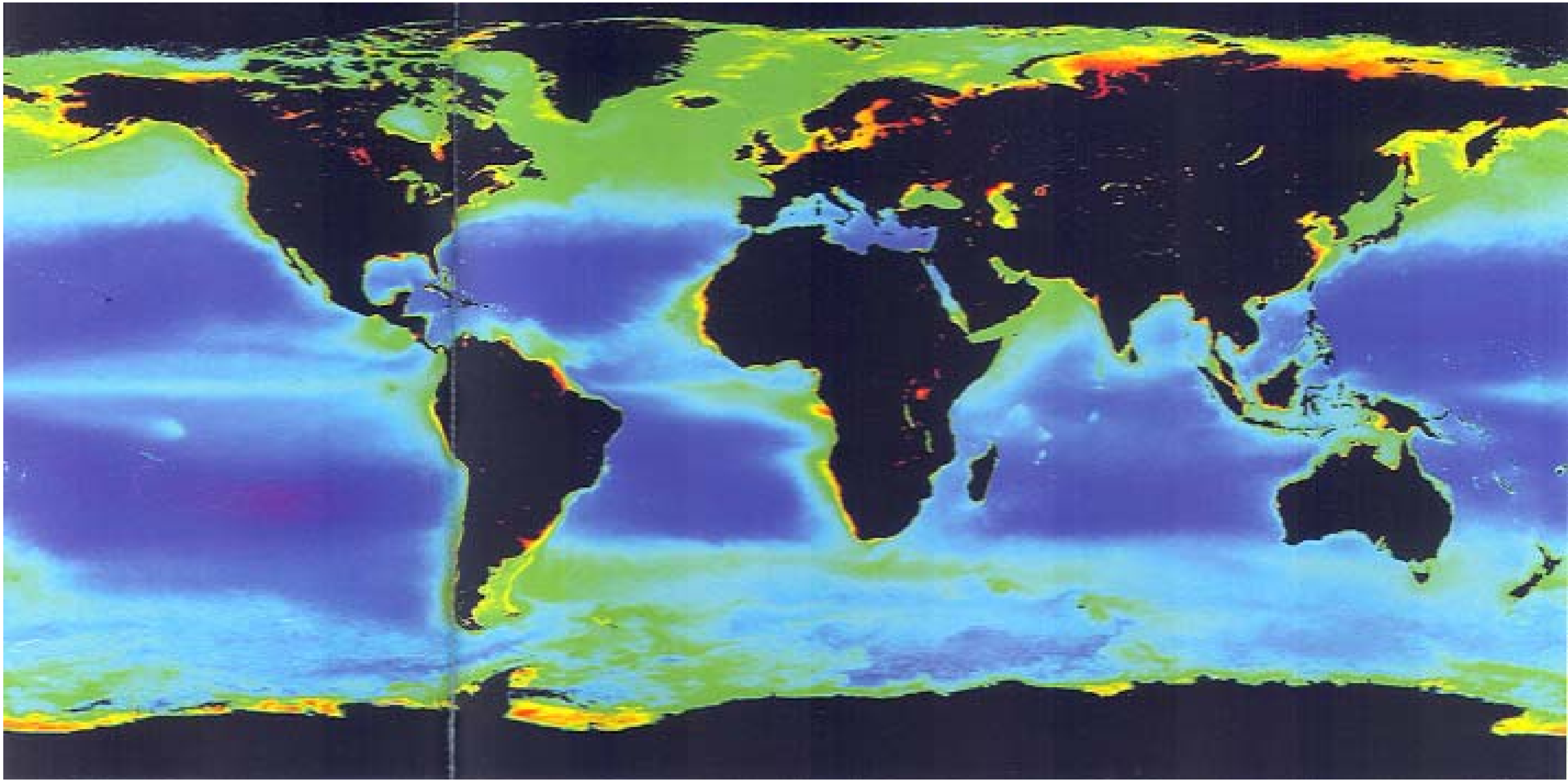


Figure 2: Algal life in the oceans: blue: ocean deserts

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	0.0038 %, equals 380 ppm, pre-industrial 270 ppm pre-industrial 270 ppm; increase 2 ppm/year
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

Wissenschaftliche Frage

- Wie wahr der Chemische Zusammensetzung von der natürliche Erdatmosphäre?
- Für CO_2 und CH_4: Eiskernbohren, zurück ca. 150.000 Jahr
- Was mit Aerosolen/Feinstaub??

Natural Aerosols

- Soil Dust
- Sea Spray
- Smoke from Wildfires
- Biological Particles
- Biogenic Dimethyl Sulfide
- Vulcano's

Aerosols and Cloud Condensation Nuclei-CCN

Paper Andreae “Aerosols before Pollution”

CCN: size 60-90 nm = 0.06-0.09 um

Cloud formation

Aerosols disappear mainly from the atmosphere by rain-out

Aerosols before pollution over the ocean and over land

about 100 particles/cm^3

about 5 µgr/m^3

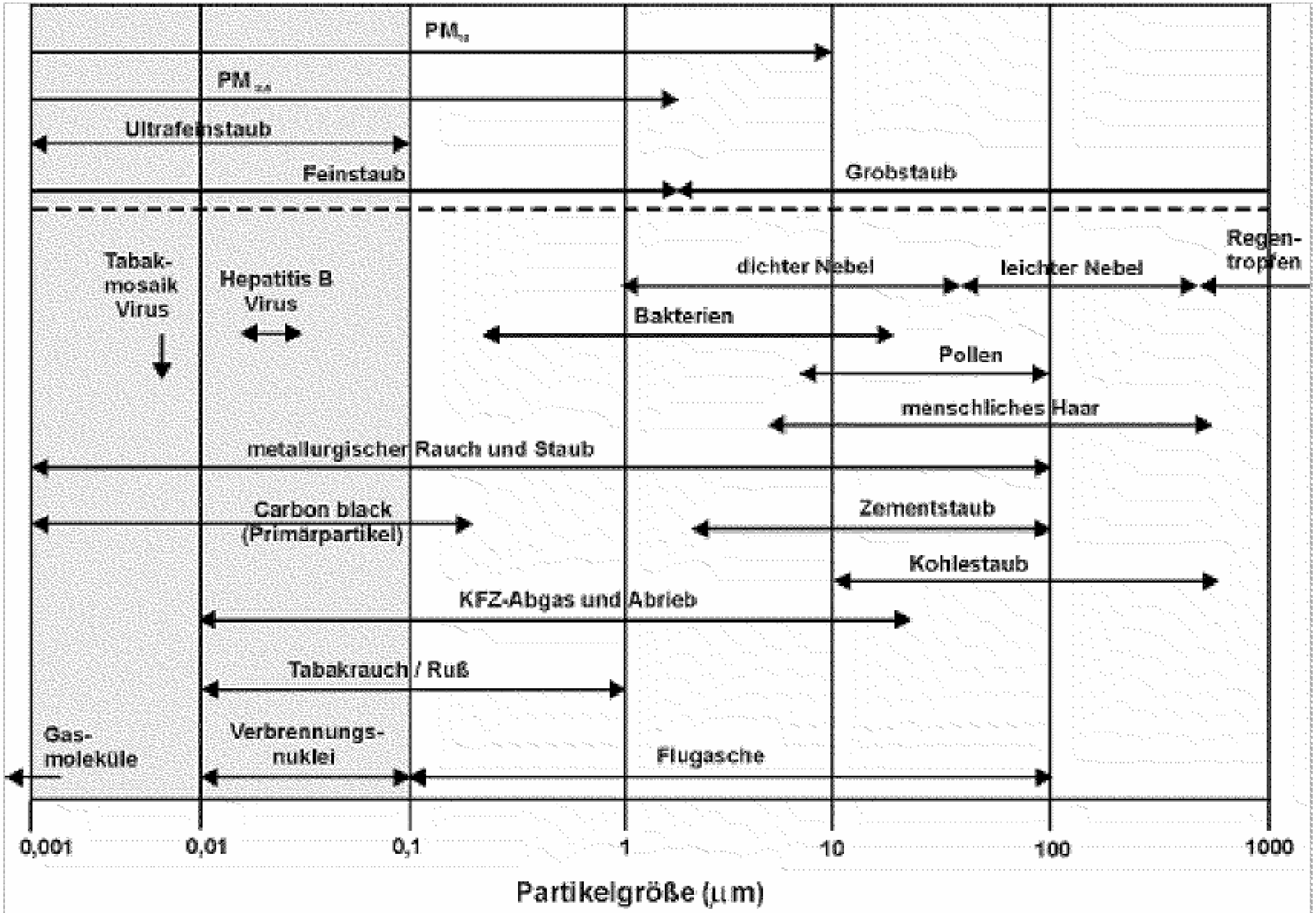


Abb.1: Partikeldefinitionen und Größenbereiche umweltrelevanter Partikel [Krug 2003

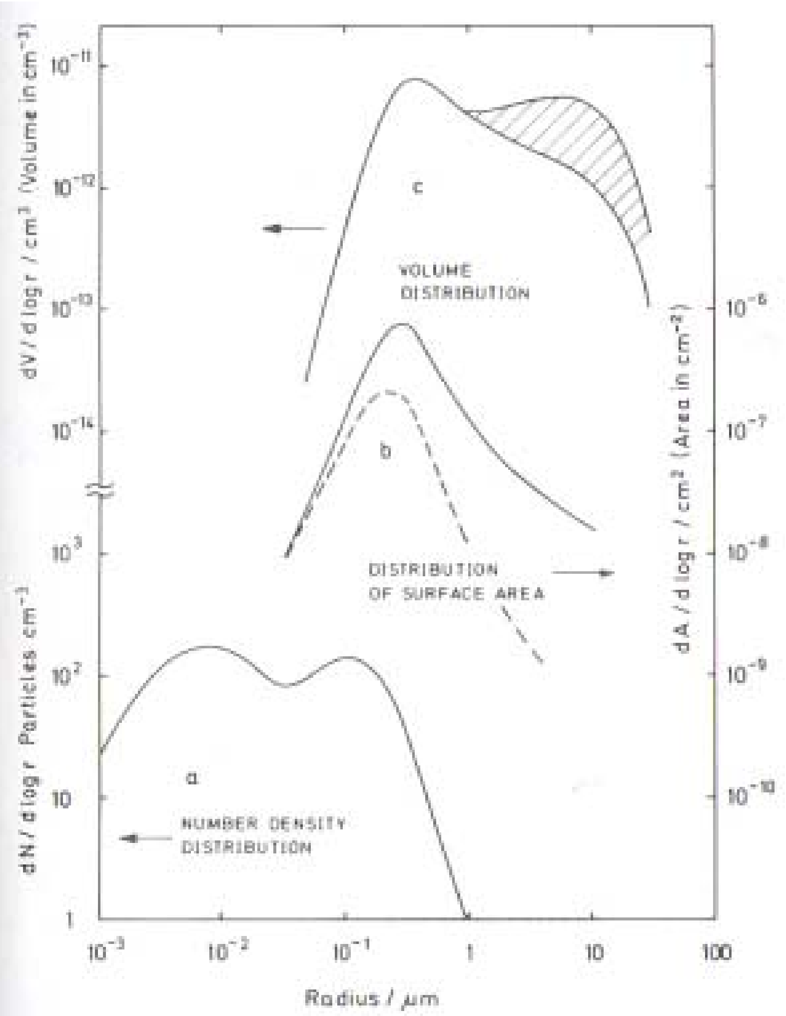


Fig. 7-2. Model size distributions of the marine background aerosol: (a) particle number density, (b) surface area, (c) volume. The contribution of sea salt to the volume distribution is indicated by the shaded area, and arrows indicate the appropriate scale. By integration one obtains a total number density $N = 290$ particles/cm³, a total surface area $A = 1.8 \times 10^{-7}$ 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.

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

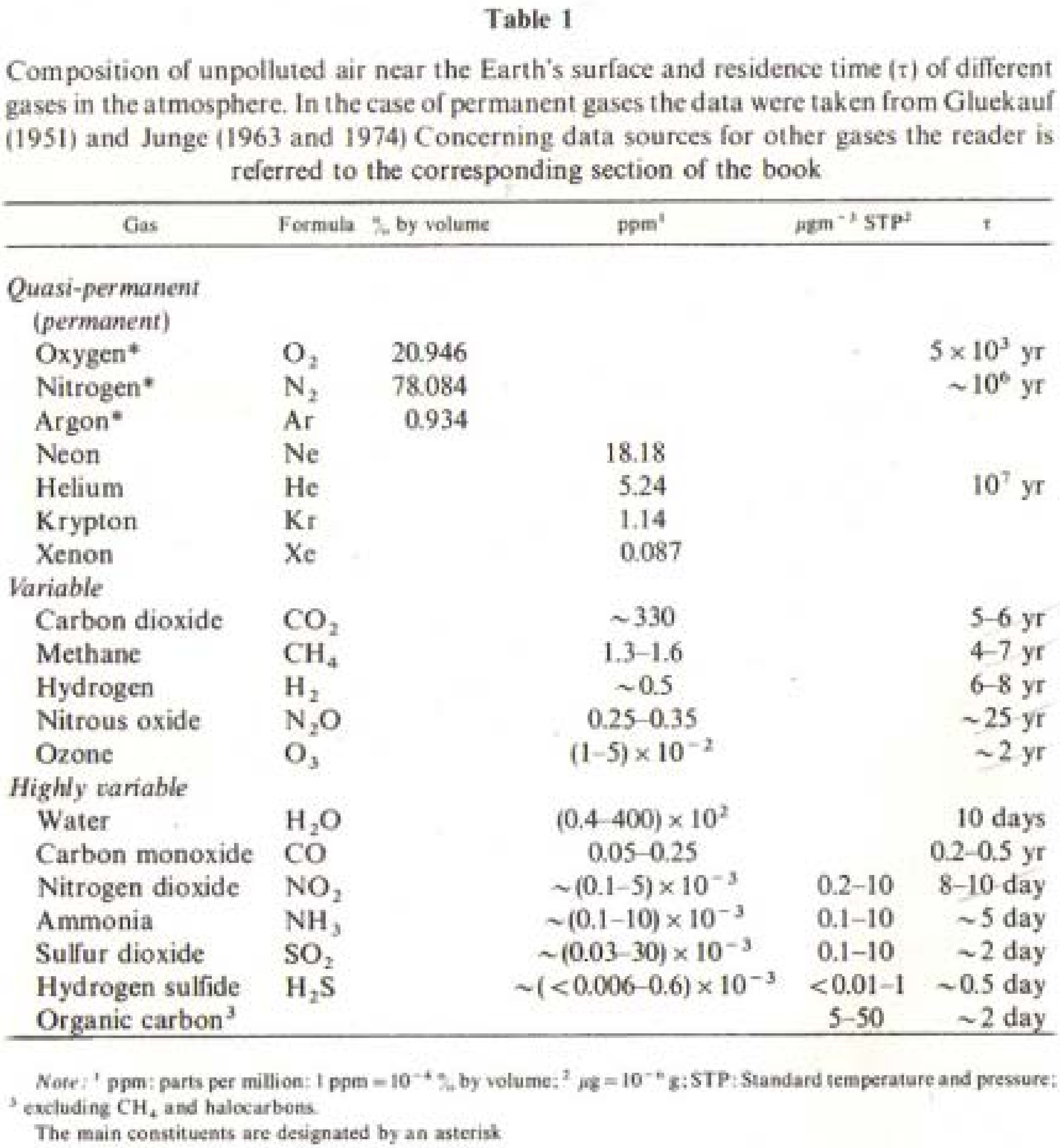


Table 1

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]	$\mu g m^{-3}$ 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

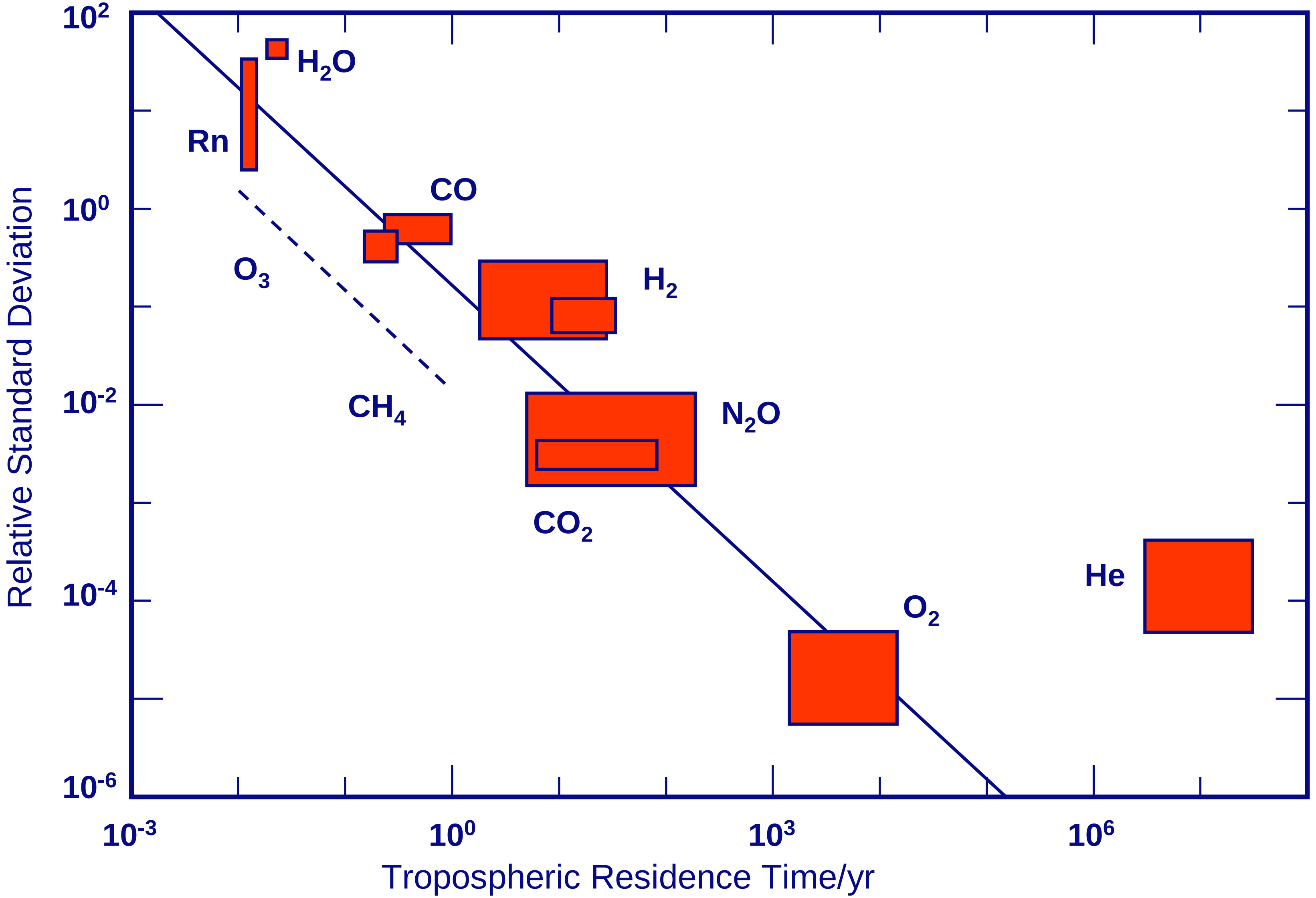
Junge's law

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

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

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

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



10^2
10^0
10^{-2}
10^{-4}
10^{-6}
Relative Standard Deviation
H_2O
Rn
CO
O_3
H_2
CH_4
N_2O
CO_2
He
O_2
10^{-3}
10^0
10^3
10^6
Tropospheric Residence Time/yr

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)

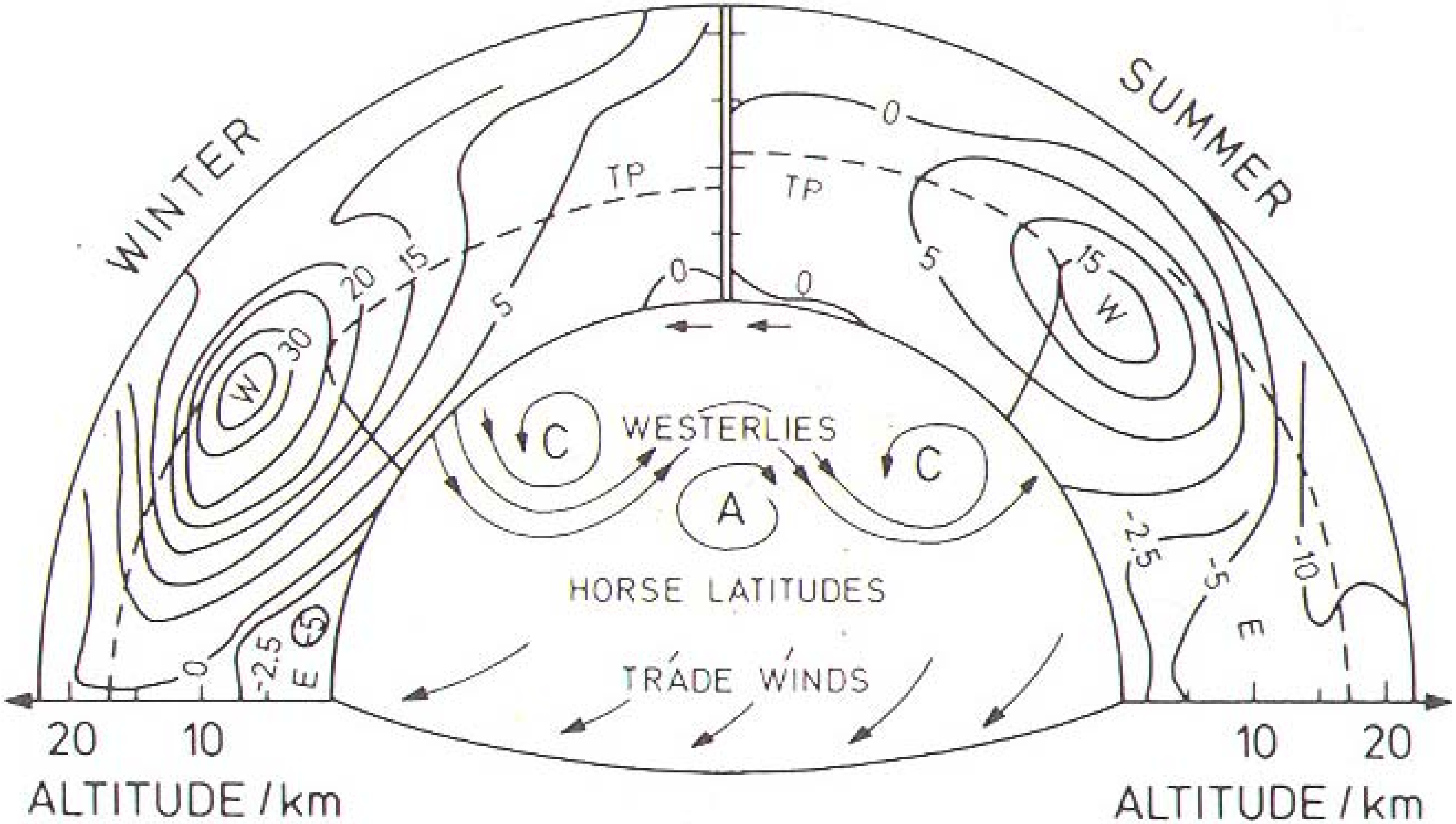
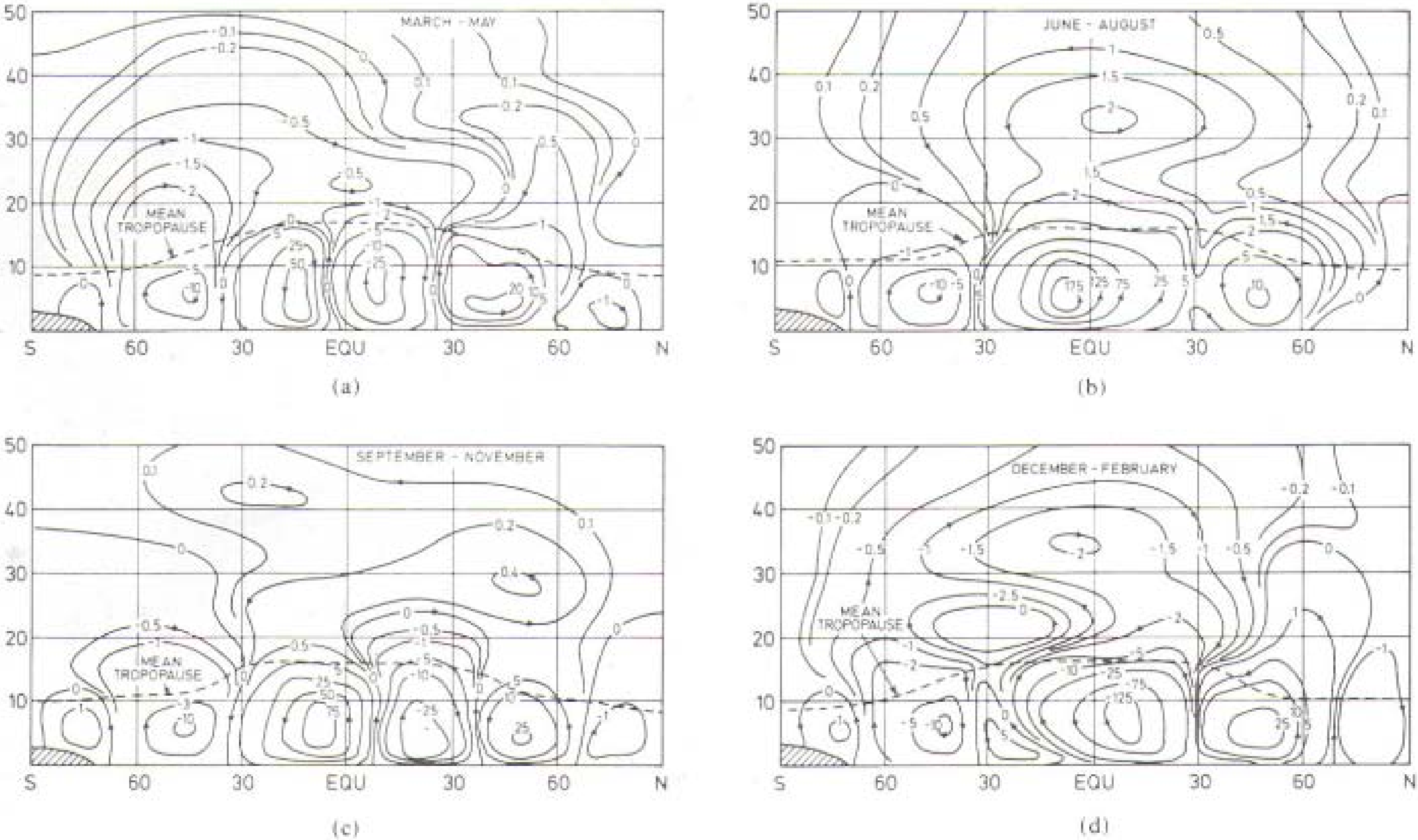


Fig. 1-6. Mean zonal circulation in the northern hemisphere, 0–20 km. Distribution of wind velocities (in units of m/s) was taken from Labitzke (1980). W, Mean winds from the west; E, mean winds from the east; the heavy lines indicate the approximate location of the polar front, the broken lines the 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.



(a) (b) (c) (d)

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

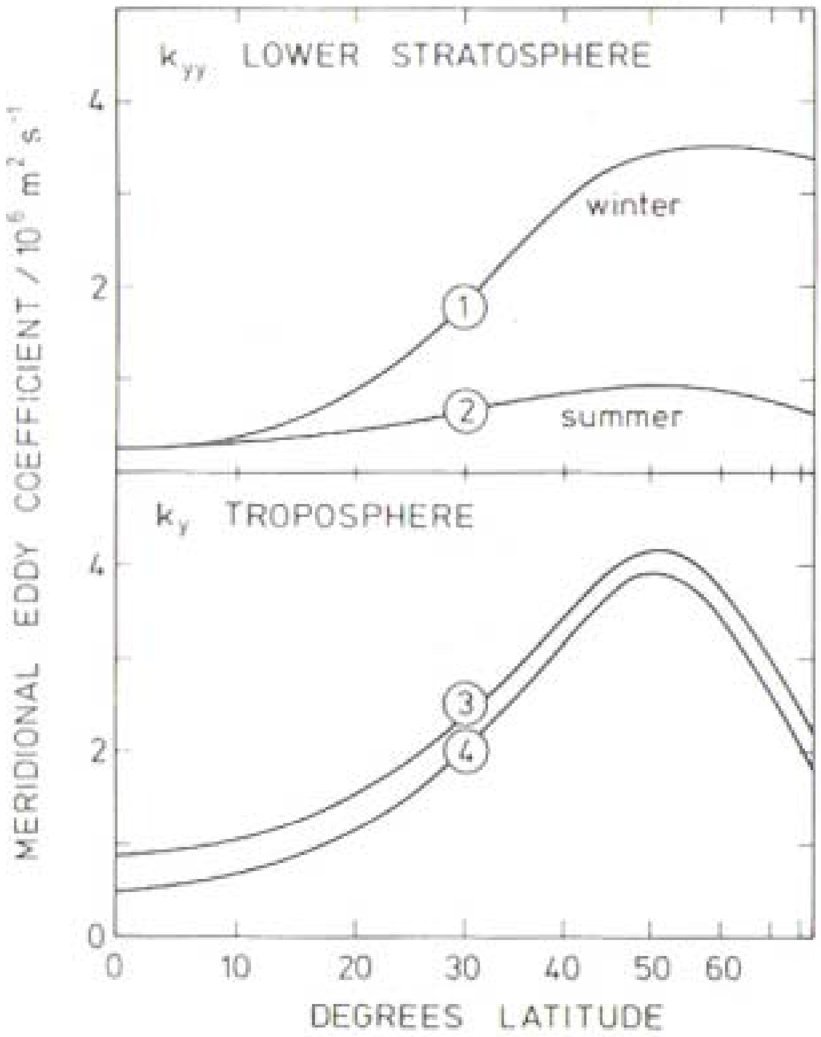


Fig. 1-8. Eddy diffusion coefficients in the northern hemisphere. Upper frame: Lower stratosphere (100 mbar, about 16 km altitude); curve 1 for December–January, curve 2 for June–August, approximated from Luther (1975) and Hidalgo and Crutzen (1977). Lower frame: One-dimensional K_y values for the troposphere 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.

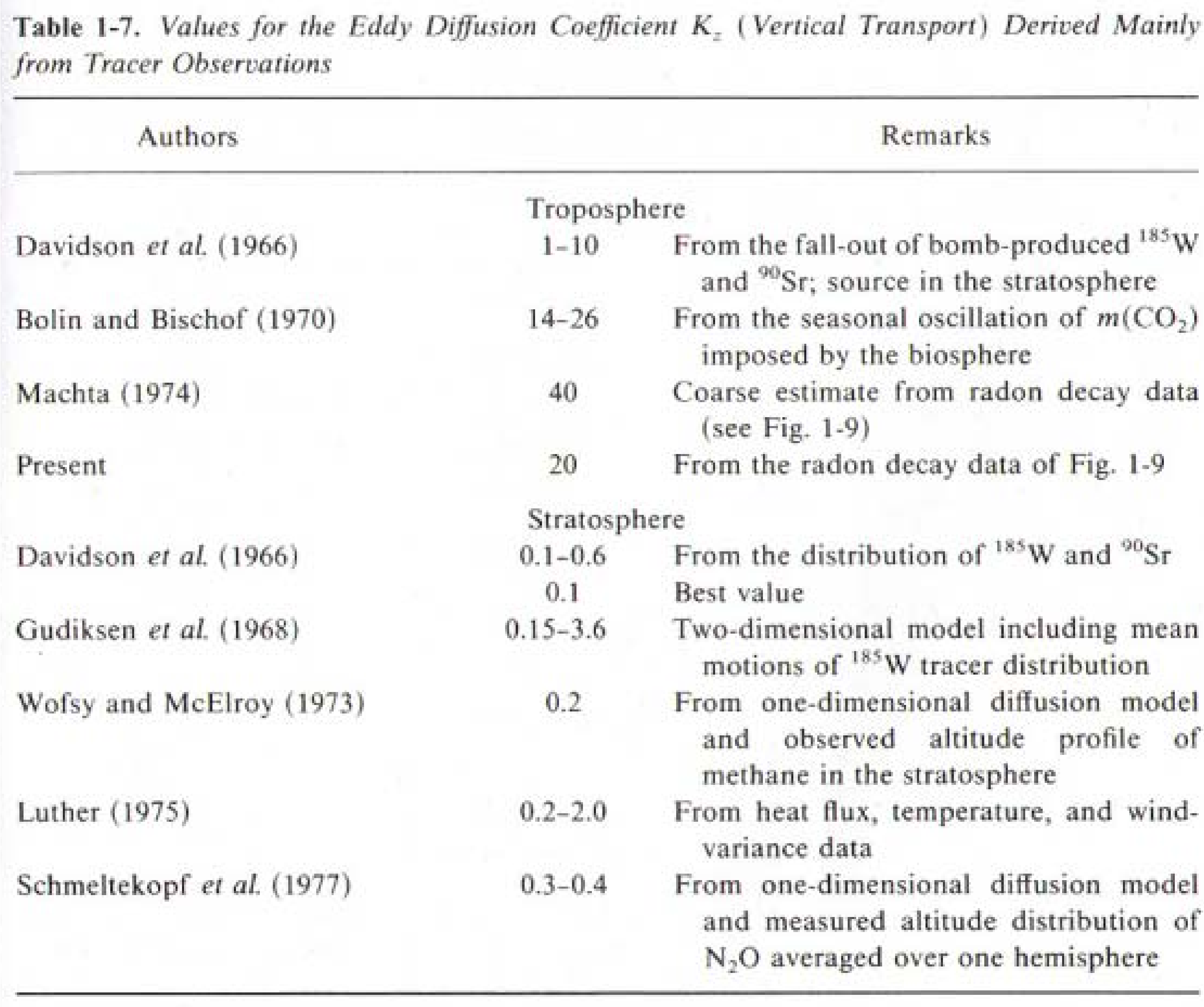


Table 1-7. *Values for the Eddy Diffusion Coefficient K_z (Vertical Transport) Derived Mainly from Tracer Observations*

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

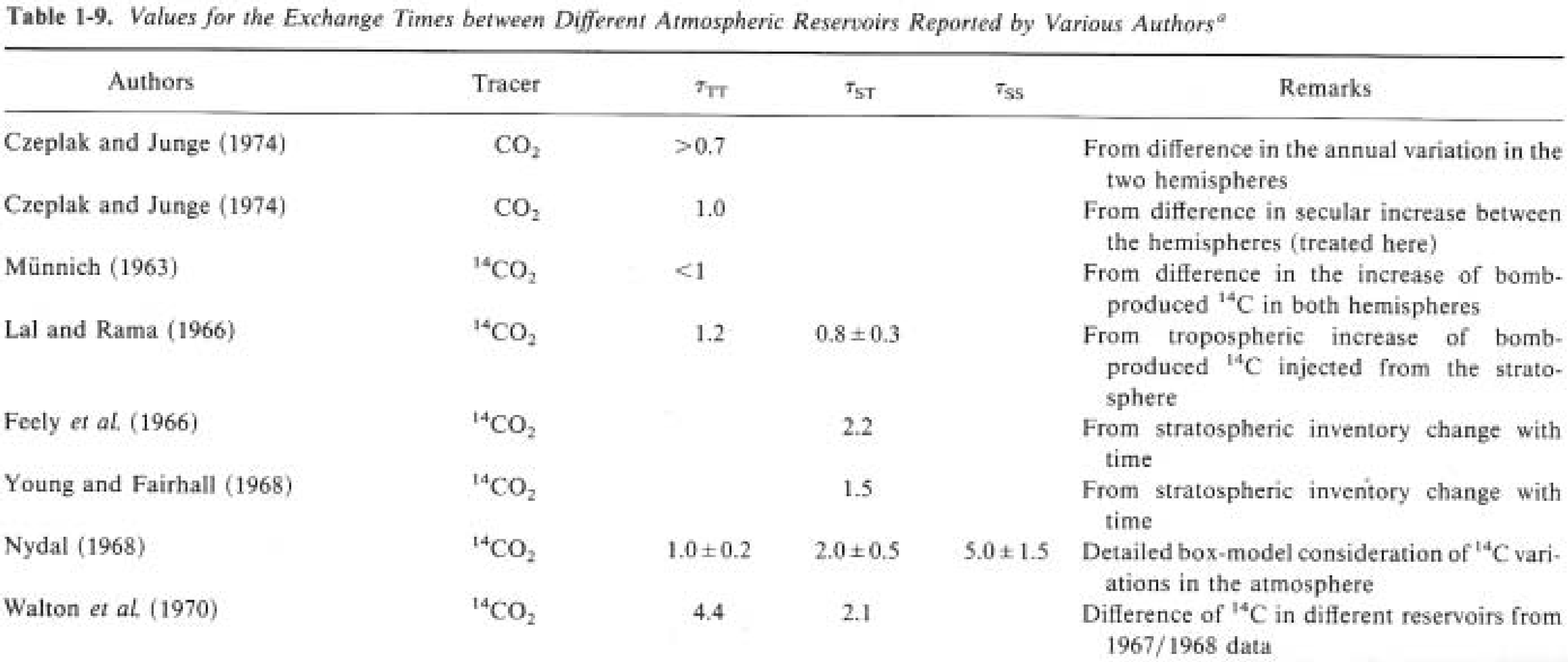
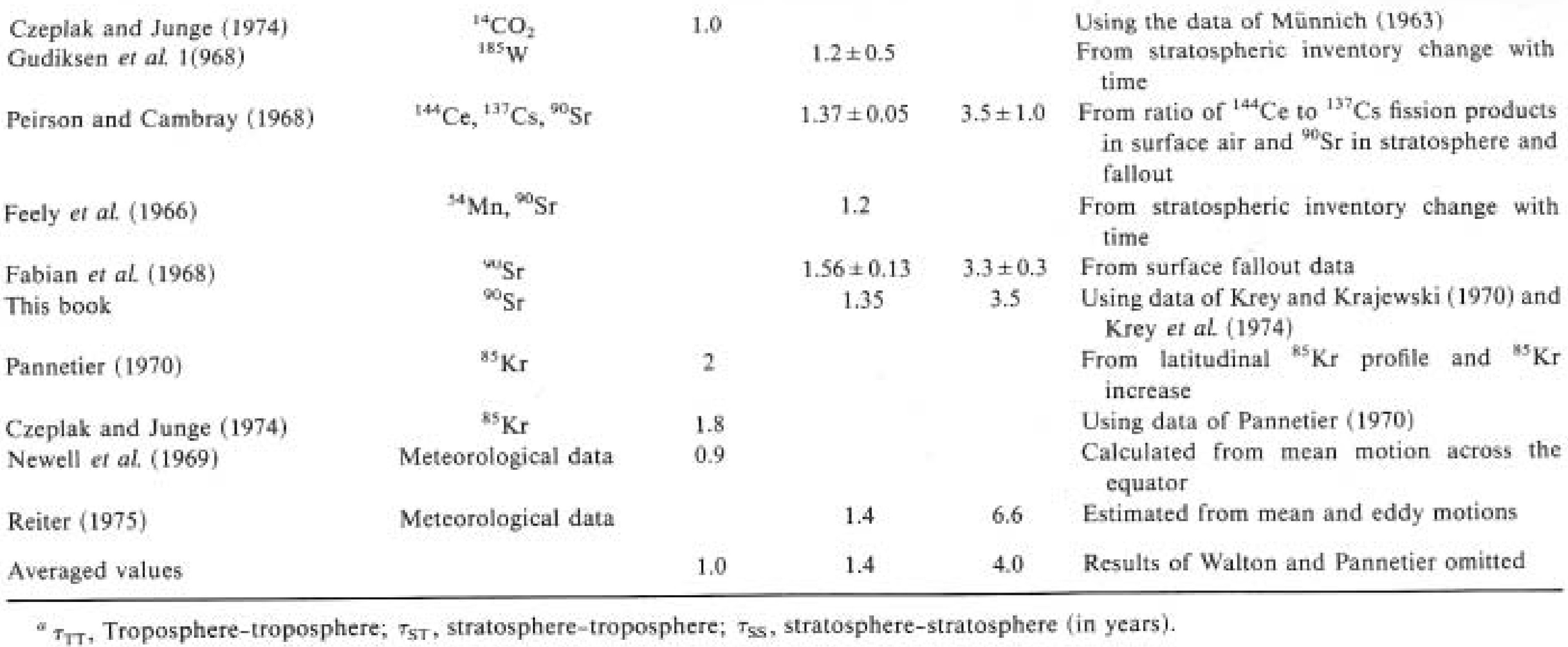


Table 1-9. *Values for the Exchange Times between Different Atmospheric Reservoirs Reported by Various Authors*[a]

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).

II) Basisprinzipen von Chemie und Strahlung

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

Chemical reaction rate k
$-dCH_4/dt = k\ CH_4$

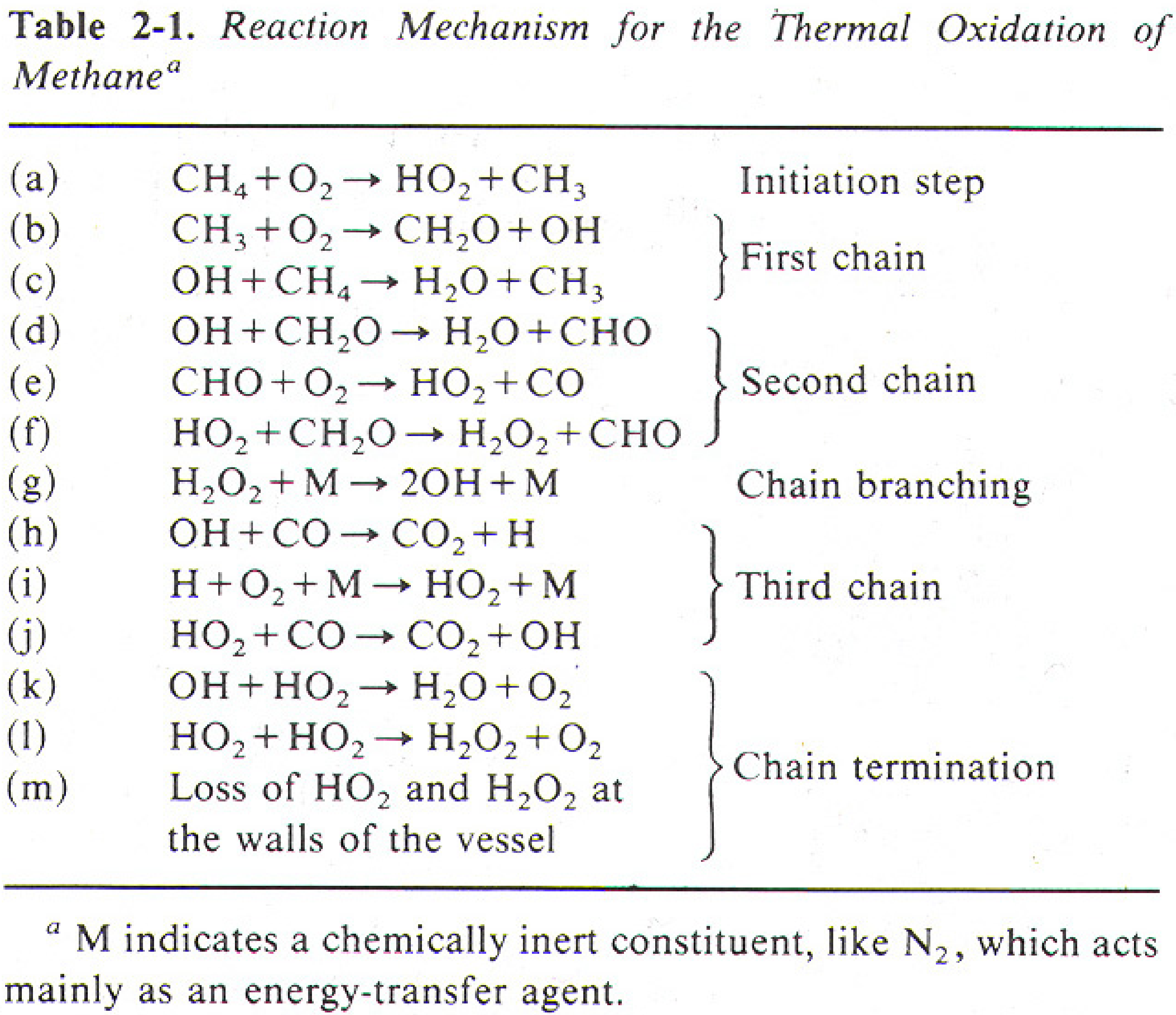


Table 2-1. *Reaction Mechanism for the Thermal Oxidation of Methane*[a]

(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.

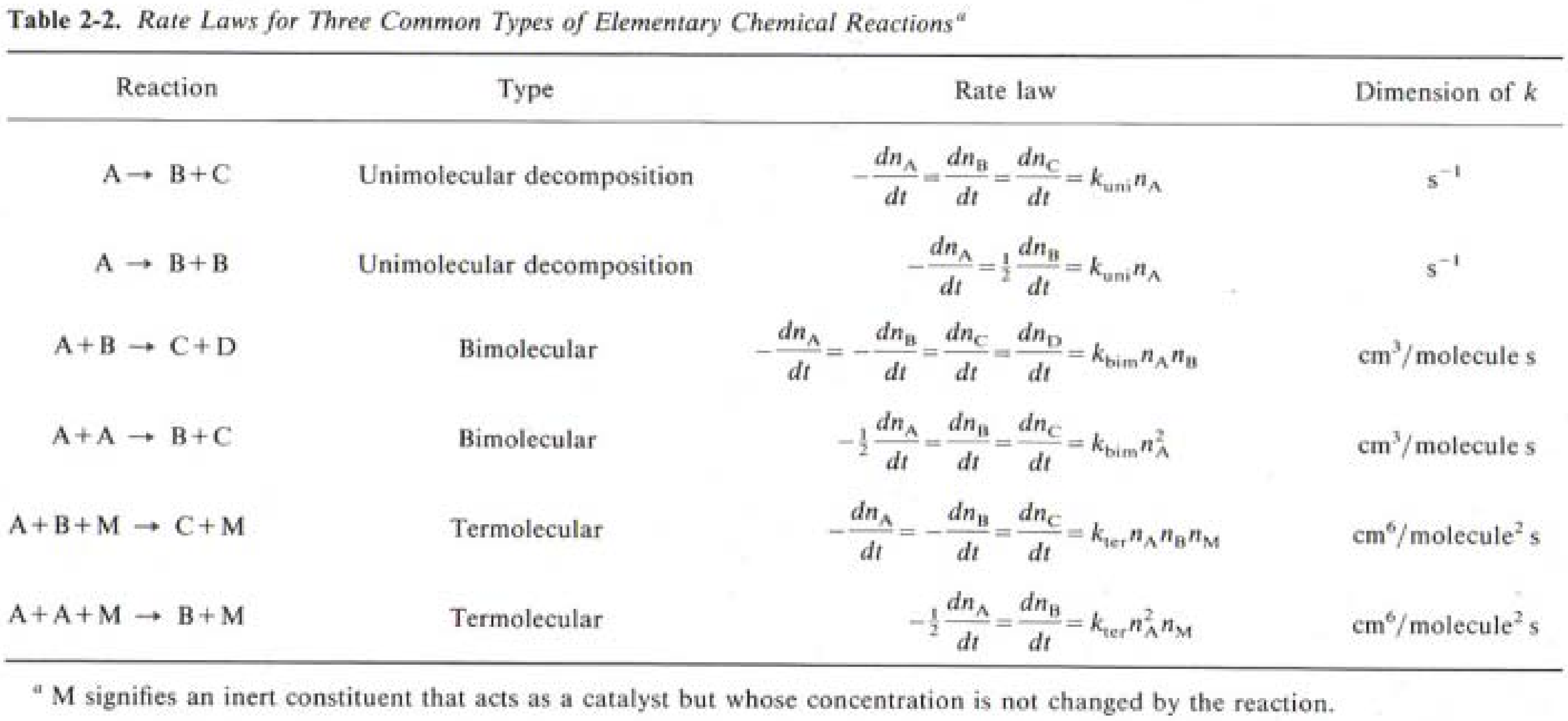
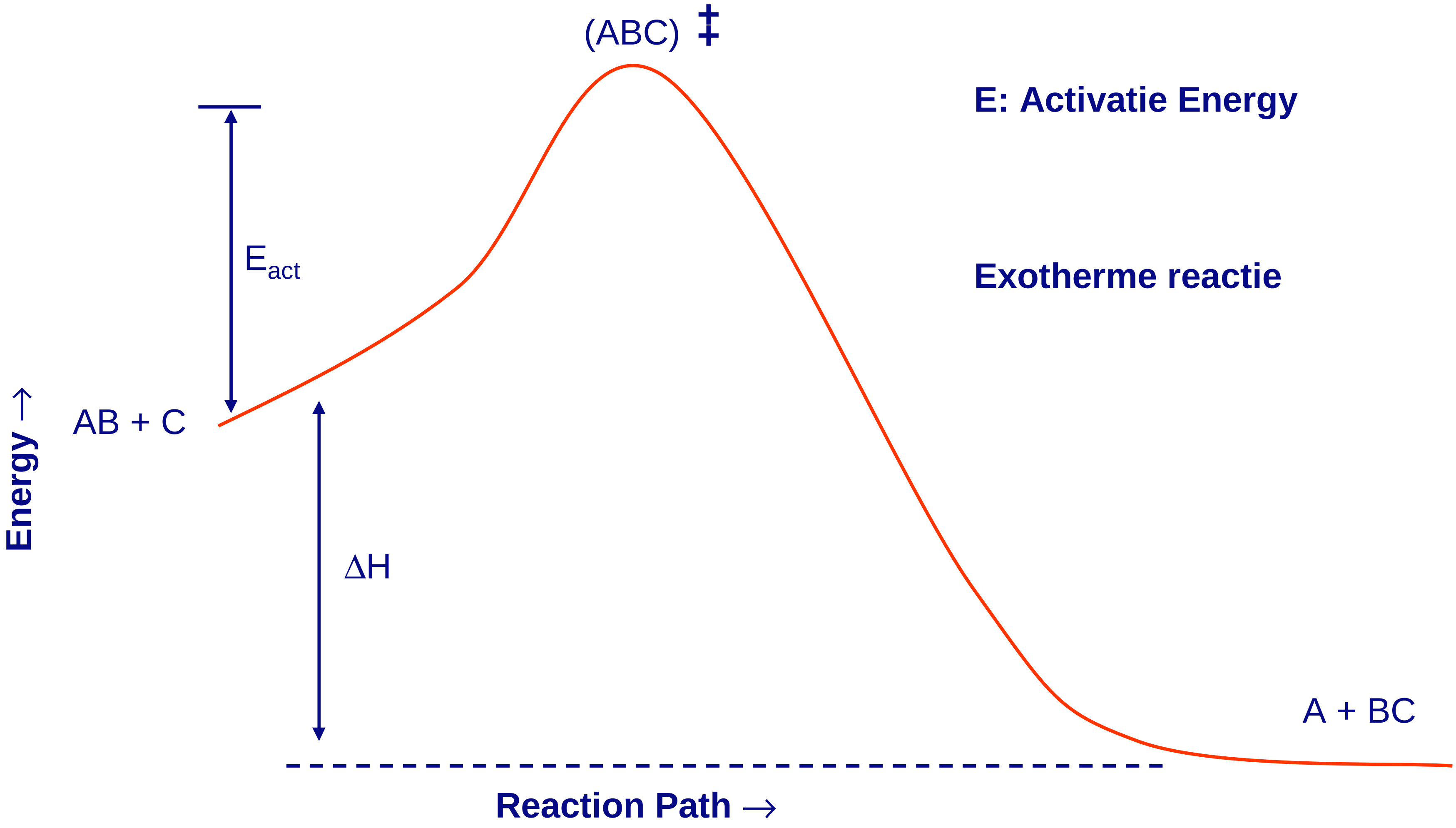


Table 2-2. *Rate Laws for Three Common Types of Elementary Chemical Reactions*[a]

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

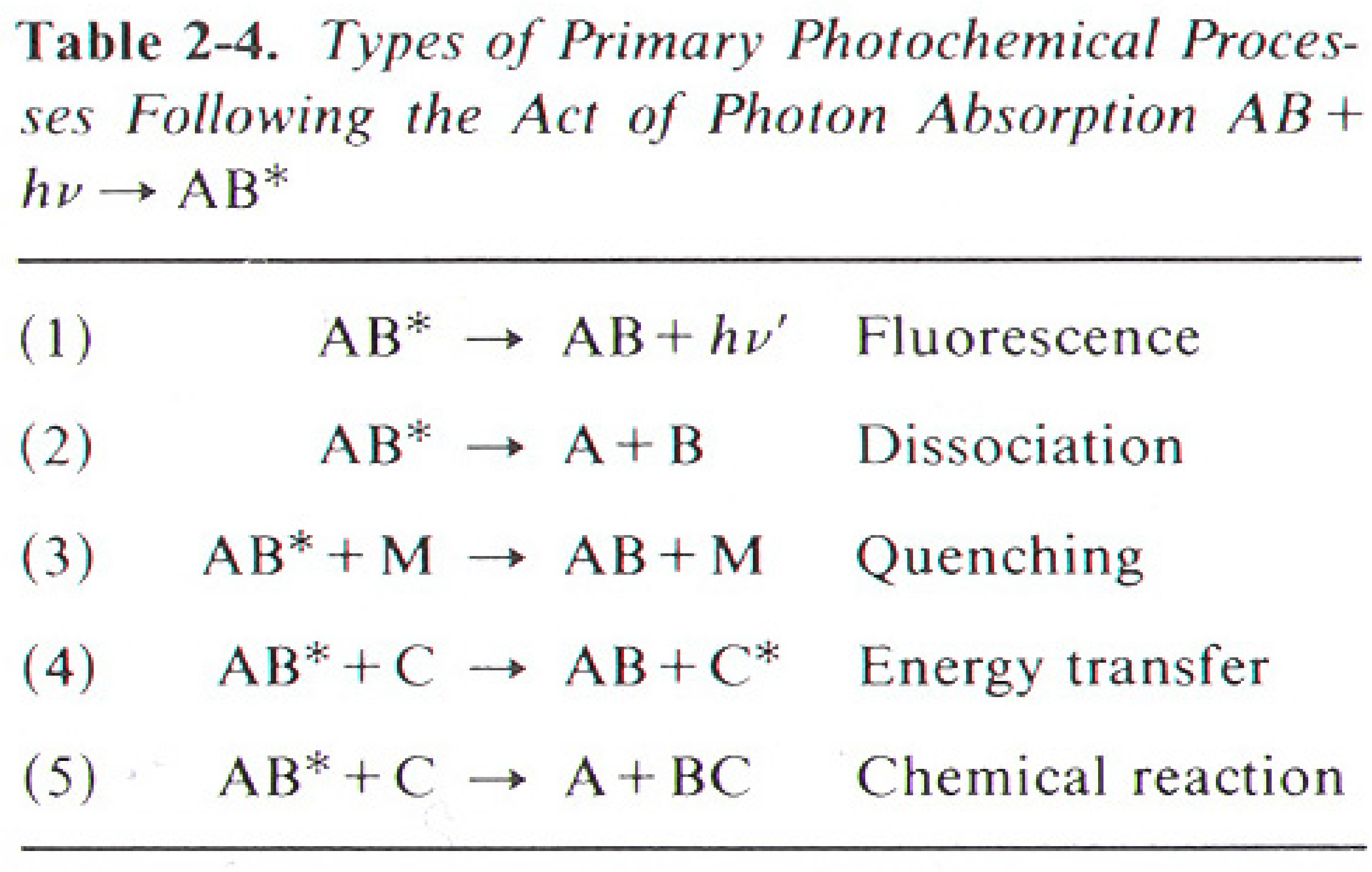


Table 2-4. *Types of Primary Photochemical Processes Following the Act of Photon Absorption* $AB + h\nu \rightarrow AB^*$

(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

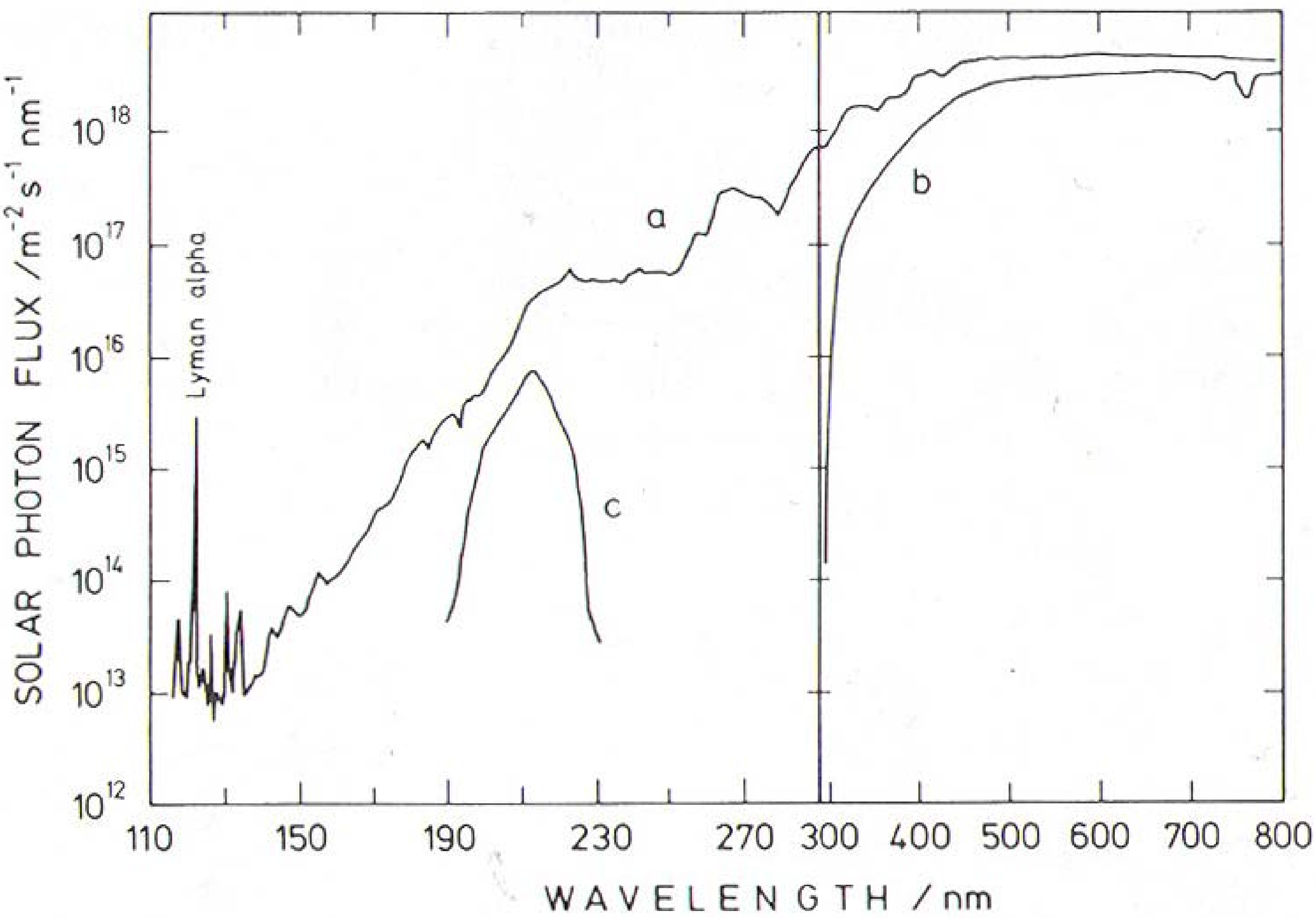


Fig. 2-5. The solar flux spectrum in the 120–800 nm wavelength region (a) outside the earth atmosphere, (b) at sea level, and (c) at about 30 km altitude to show the atmospheric window in the 185–215 nm wavelength region.

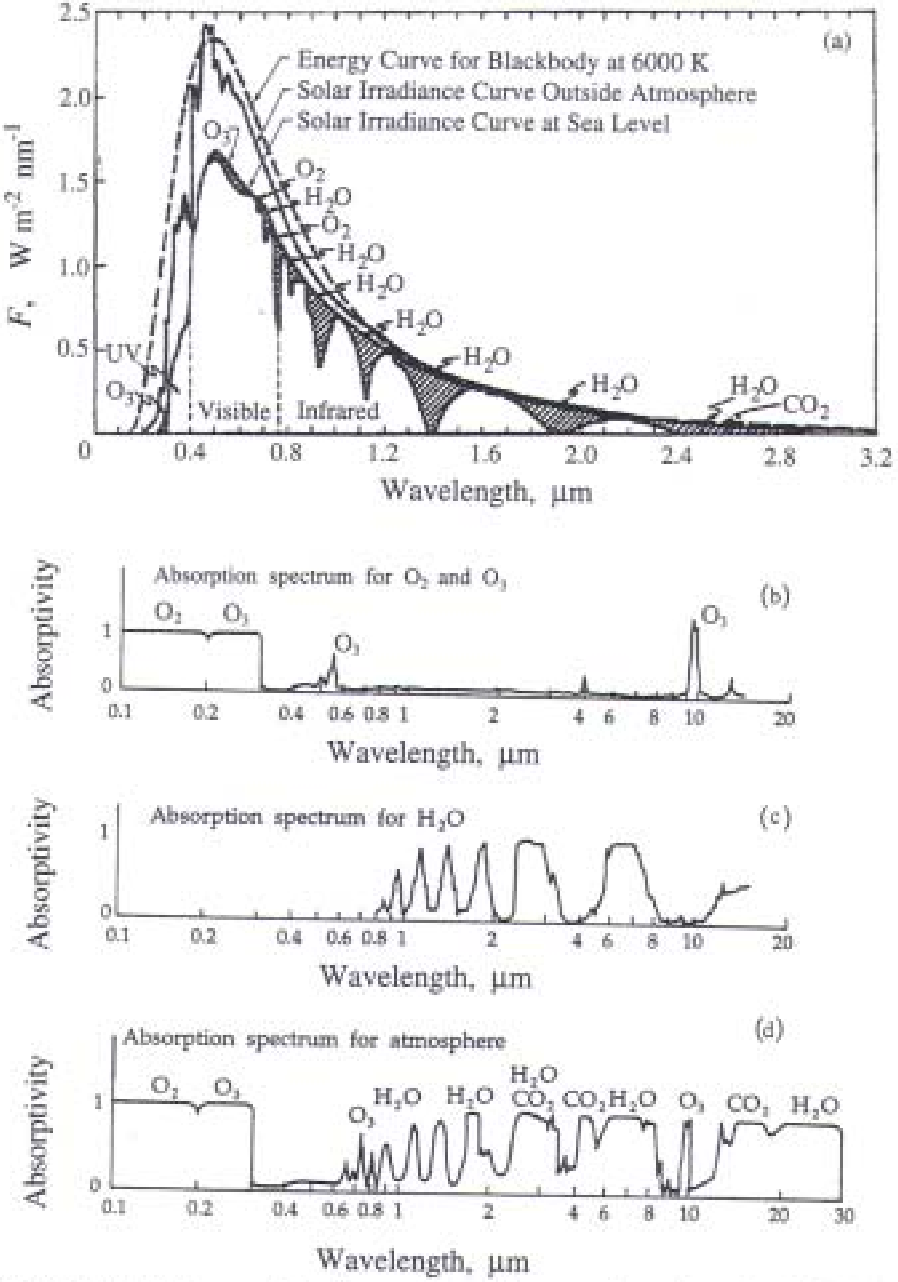


FIGURE 1.9 (a) Solar spectral irradiance at the top of the atmosphere and at sea level. Shaded regions indicate the molecules responsible for absorption. Absorption spectra for (b) molecular oxygen and ozone, (c) water vapor, and (d) the atmosphere, expressed on a scale of 0 to 1.

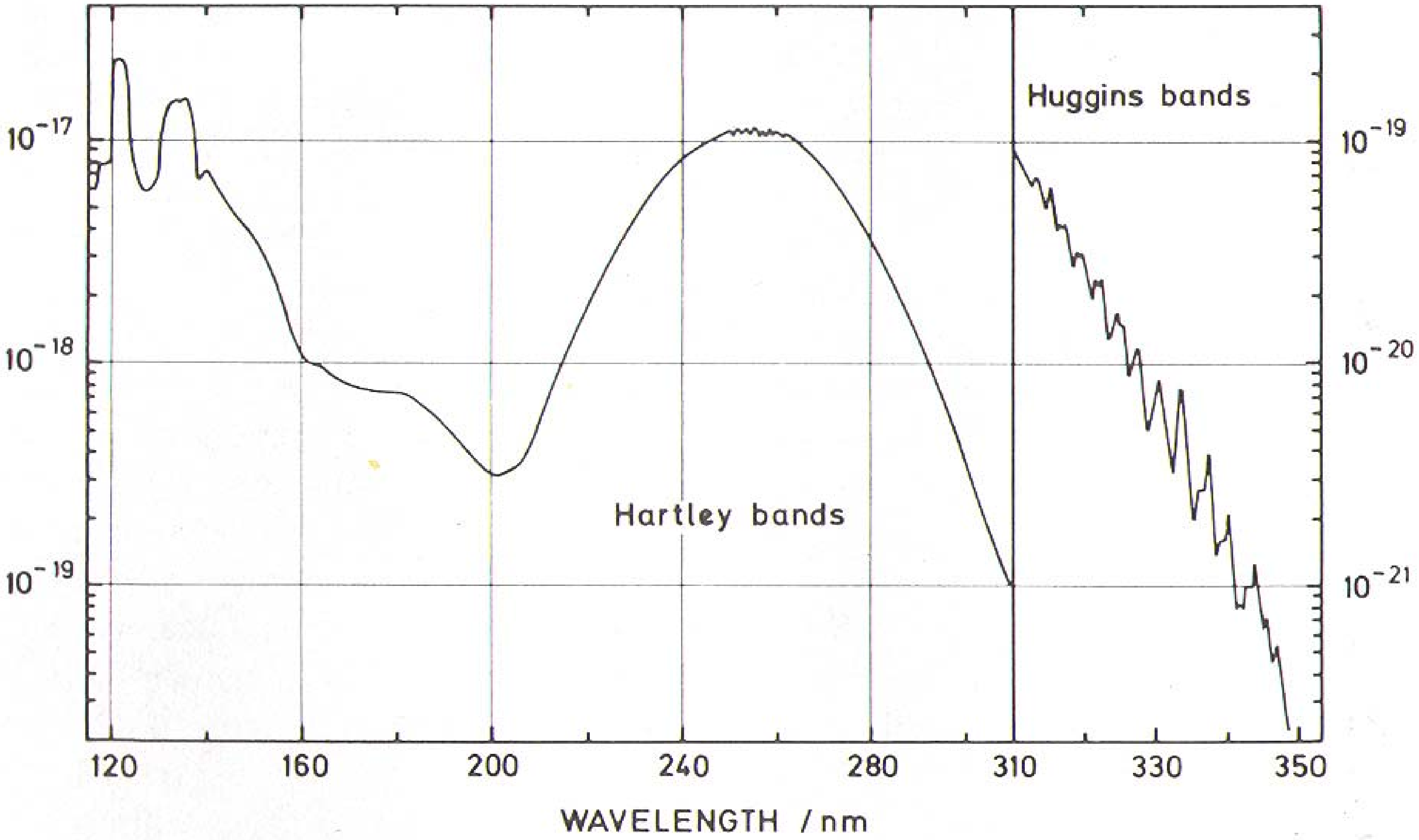


Fig. 2-8. Absorption spectrum of ozone in the wavelength region 115–350 nm, with cross sections given in units of cm^2/molecule. Data used are from Inn and Tanaka (1953), Tanaka *et al.* (1953), and Griggs (1968).

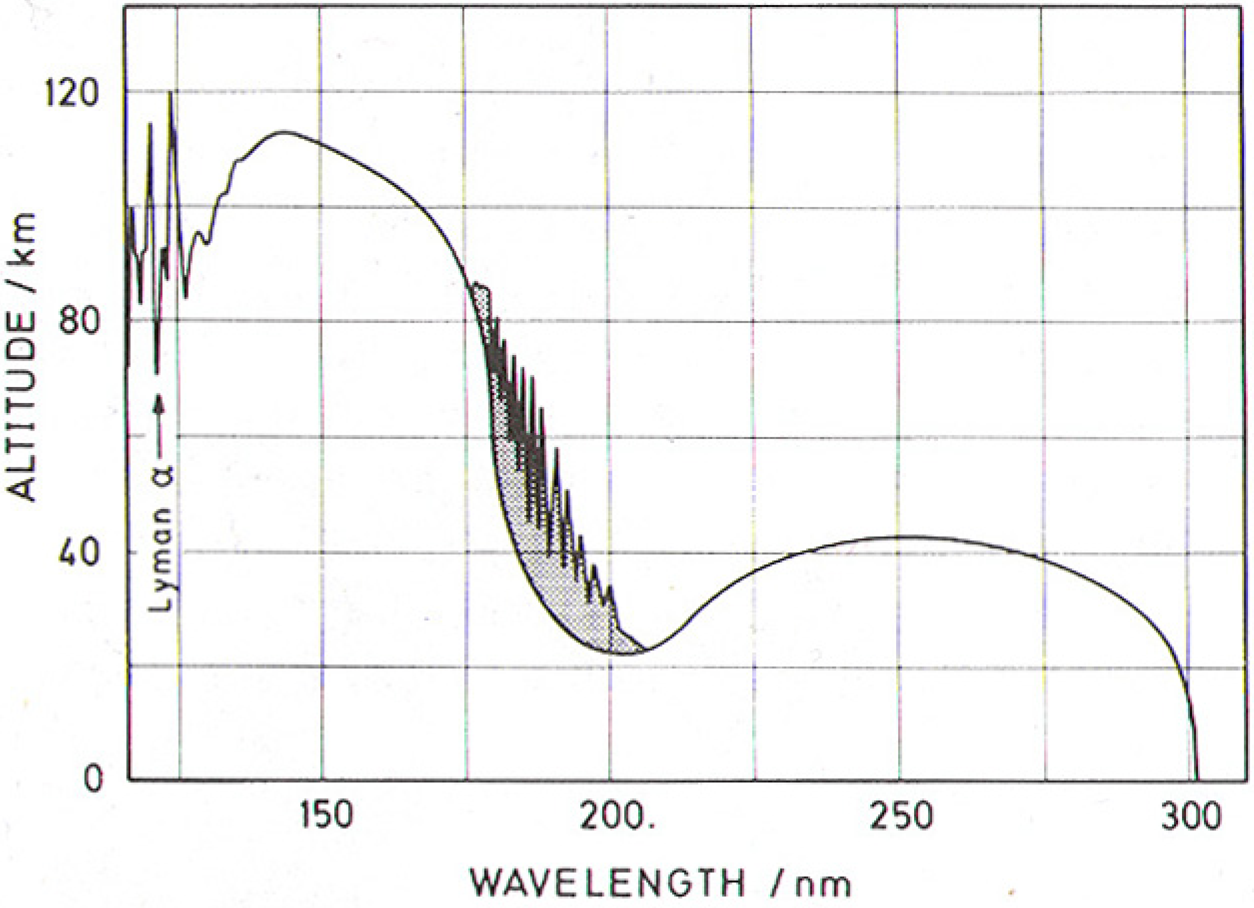


Fig. 2-9. Altitude at which incoming solar radiation from an overhead sun is attenuated to one-tenth the initial intensity.

III) Stratospheric chemistry and other trace gases

First, some observations

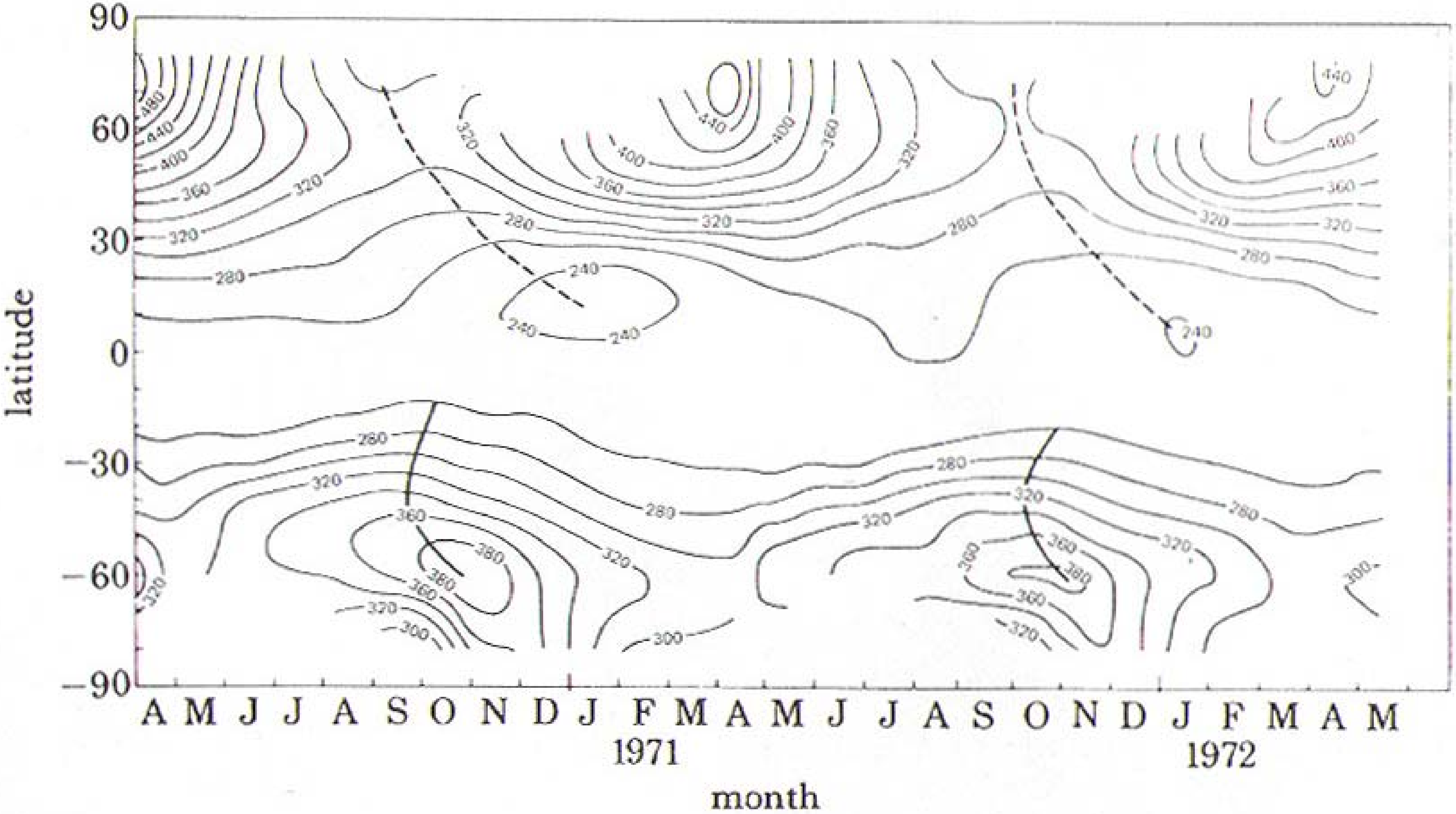


Fig. 3-1. Total ozone versus time and latitude as derived from 10° zonal means of *Nimbus* 4 satellite data. [From Hilsenrath *et al.* (1979), with permission.]

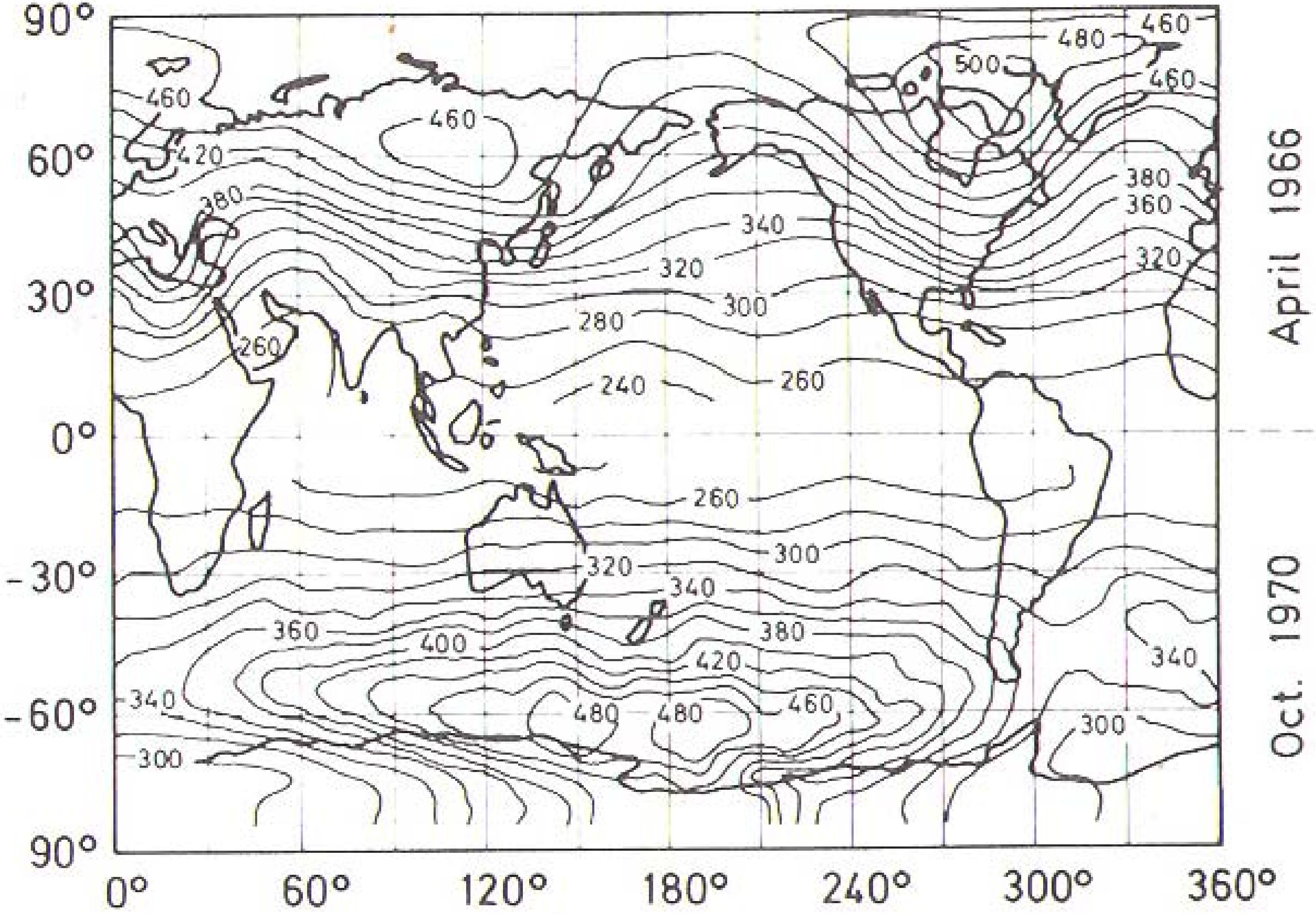


Fig. 3-2. Total ozone averaged versus latitude and longitude. [From Dütsch (1980), with permission.]

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

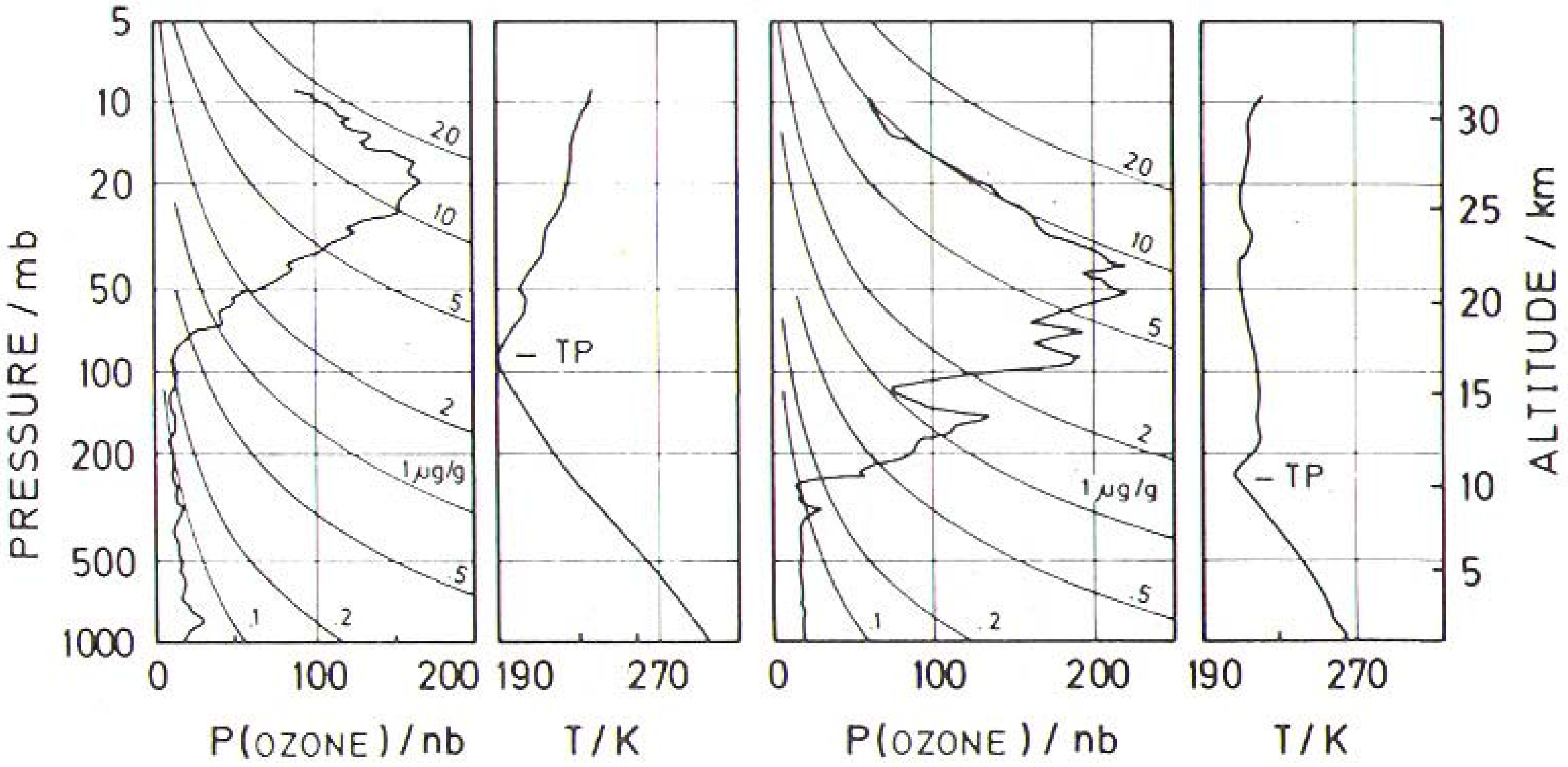


Fig. 3-3. Balloon soundings of ozone (in units of partial pressure). Left: Low latitude, Right: High latitude. Vertical temperature profiles are included to indicate the tropopause levels. [Adapted from Hering and Borden (1967).]

Formation of stratosphere O_3

$O_2 + h\nu$	➡	$O + O$	j_a
$O + O_2 + M$	➡	$O_3 + M$	k_b
$O_3 + h\nu$	➡	$O_2 + O$	j_c
$O + O_3$	➡	$O_2 + O_2$	k_d

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

O_2 + hV → 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 → O_2 + O ('D)   λ 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 → OH

Mehr Detail über Chemie

- O (‘D) usw: Angeregte Zustand: Spin, Verbotene Schale (shell)
- Energy levels, „Spin-forbidden Transitions“ etc.
- For example in Physical Chemistry, P.W.Atkins, 1994

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:

$$n_3\ (O_3) = \left(\frac{B}{A}\right)^{½} \frac{1 - \exp.\ [-2\ (AB)^{½}\ t]}{1 + \exp.\ [-2\ (AB)^{½}\ t]}$$

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

In equilibrium:

Theory of Chapman (1932)

From the 4 reactions follows:

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

(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!

Other stratospheric trace gases

N_2O, H_2O, CH_4, (CH_3Cl etc.)

Origin: the troposphere

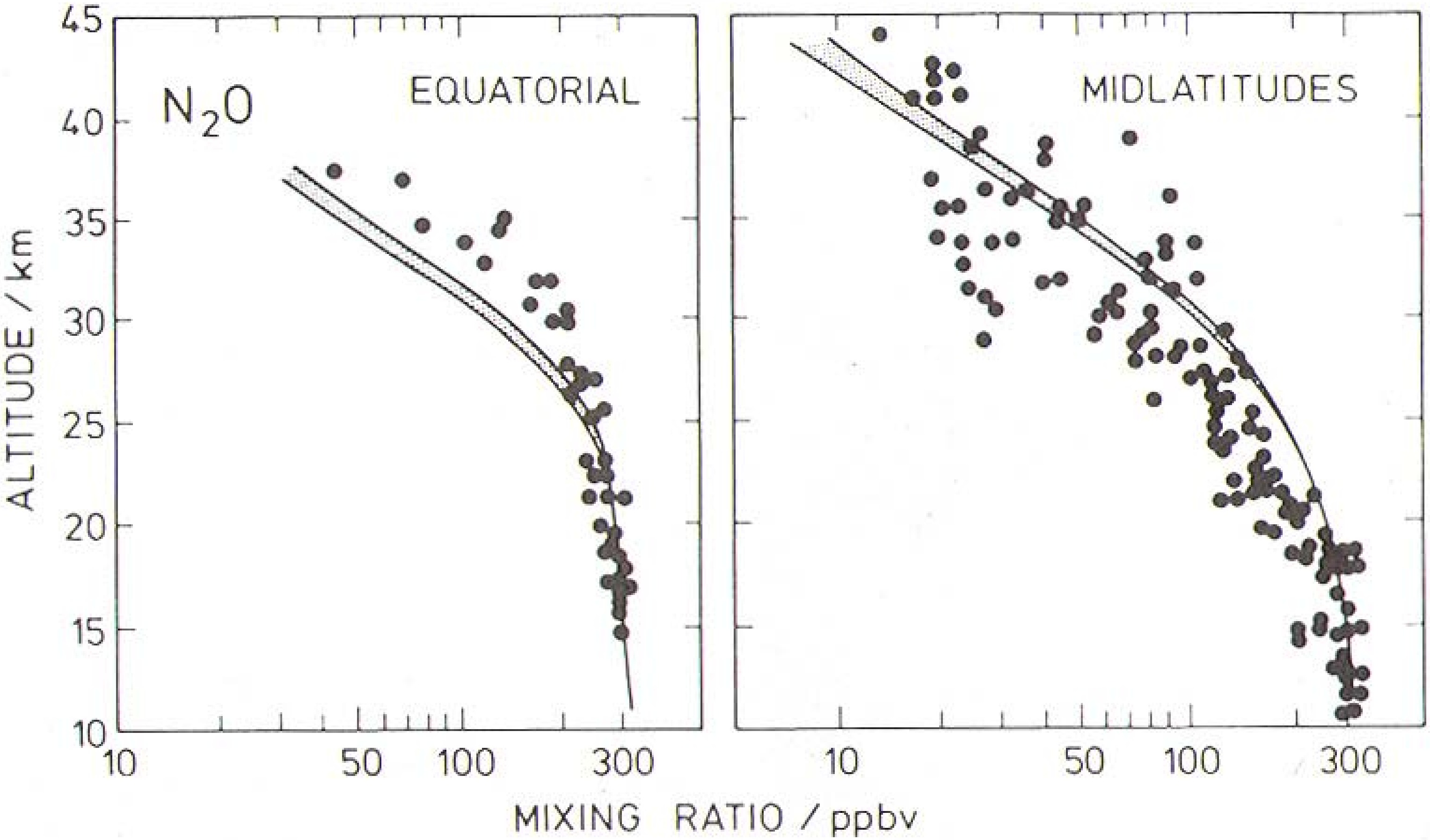


Fig. 3-6. Vertical profiles of the N$_2$O mixing ratio at low and high latitudes. From measurements of Heidt *et al.* (1980), Tyson *et al.* (1978), Vedder *et al.* (1978, 1981), Fabian *et al.* (1979b, 1981), Goldan *et al.* (1980, 1981). The solid lines were calculated by Gidel *et al.* (1983) with a two-dimensional model.

N_2O (ca. 90 % of biogenic origin)

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

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

$\rightarrow 2NO$

↑

from O_3-photo-dissociation

Followed by:

$$\begin{aligned}
&NO + O_3 &&\rightarrow &&NO_2 + O_2\\
&NO_2 + hV &&\rightarrow &&NO + O\\
&O + O_2 \quad + M &&\rightarrow &&O_3 + M\\
&(NO + NO_2 = \text{constant}) && && \\
&O + NO_2 &&\rightarrow &&NO + O_2\\
&(O + O_3 &&\rightarrow &&2O_2)
\end{aligned}$$

Leading to:

$$\begin{aligned}
&O_3 + hV &&\rightarrow &&O + O_2\\
&O + NO_2 &&\rightarrow &&O_2 + NO\\
&NO + O_3 &&\rightarrow &&NO_2 + O_2\\
\hline
\end{aligned}$$

Netto:

$$O_3 + O_3 \rightarrow 3O_2$$

With $NO_x = NO + NO_2$ as catalyst

Paul Crutzen: 1970

“The influence of nitrogen oxides on the atmospheric ozone content”
Quart. J.R.Met.Soc. (1970), 320-325

The paper by Paul Crutzen shows:

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 $N_2O + O \rightarrow 2NO$

Nobel Prize for Chemistry in 1995 with Molina and Rowland

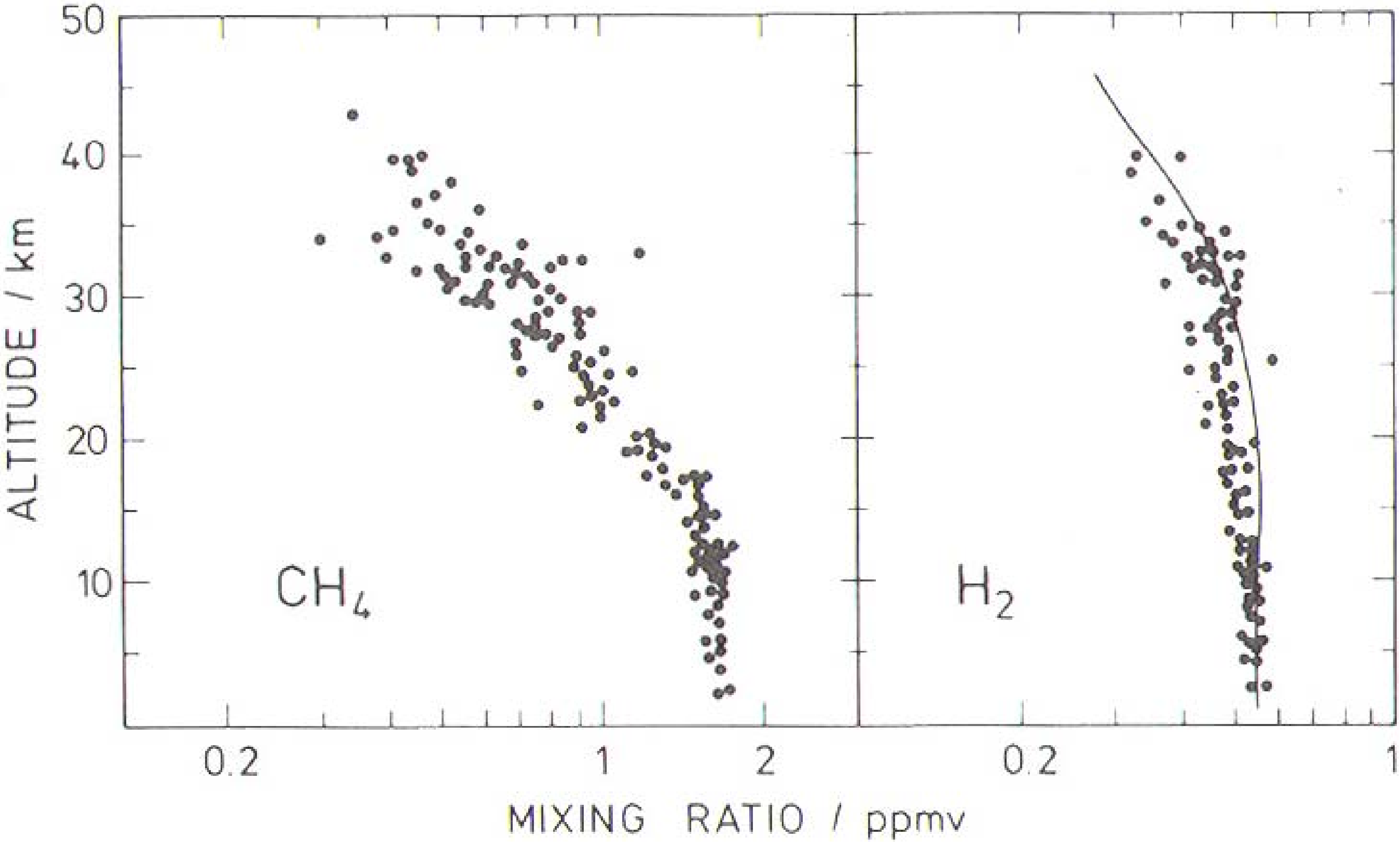


Fig. 3-10. Vertical distribution of methane and hydrogen in the stratosphere at midlatitudes (40–60° N). [From observations of Bush *et al.* (1978), Ehhalt and Heidt (1973), Ehhalt *et al.* (1974, 1975), Pollock *et al.* (1980), Heidt and Ehhalt (1980), Fabian *et al.* (1979, 1981b), and Volz *et al.*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

H_2O troposphere: 0.02 - 4%
stratosphere: 2 - 7 ppm

O ('D) + H_2O → 2OH

CH_4 in the stratosphere

CH_4 + OH → H_2O + CH_3 (lower stratosphere)

CH_4 + O ('D) → OH + CH_3 (higher stratosphere)

CH_4 + Cl → HCl + CH_3

- $O + H_2O \rightarrow 2\ OH$
- OH in Stratosphäre und Troposphäre
- OH reagiert mit sehr viel Komponenten, nur nicht mit N_2, O_2 und CO_2
- OH ist "cleansing agent", und bestimmt der Oxidation Capacity von der Atmosphäre
- Is the cleansing capacity of the atmosphere changing?
  Guy Brasseur and Ron Prinn

Für viele Spezies bestimmt OH die “Chemical Lifetime” in der Atmosphäre

In der Troposphäre:

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

$O + H_2O \rightarrow OH$

Und $CH_4 + OH$

$CO + OH$

Frage : Ändert sich OH ??

Die gestörte O_3-Schicht

Freonen, F11, F12 usw

$CF2CL2$: F12

$CFCL3$:F11

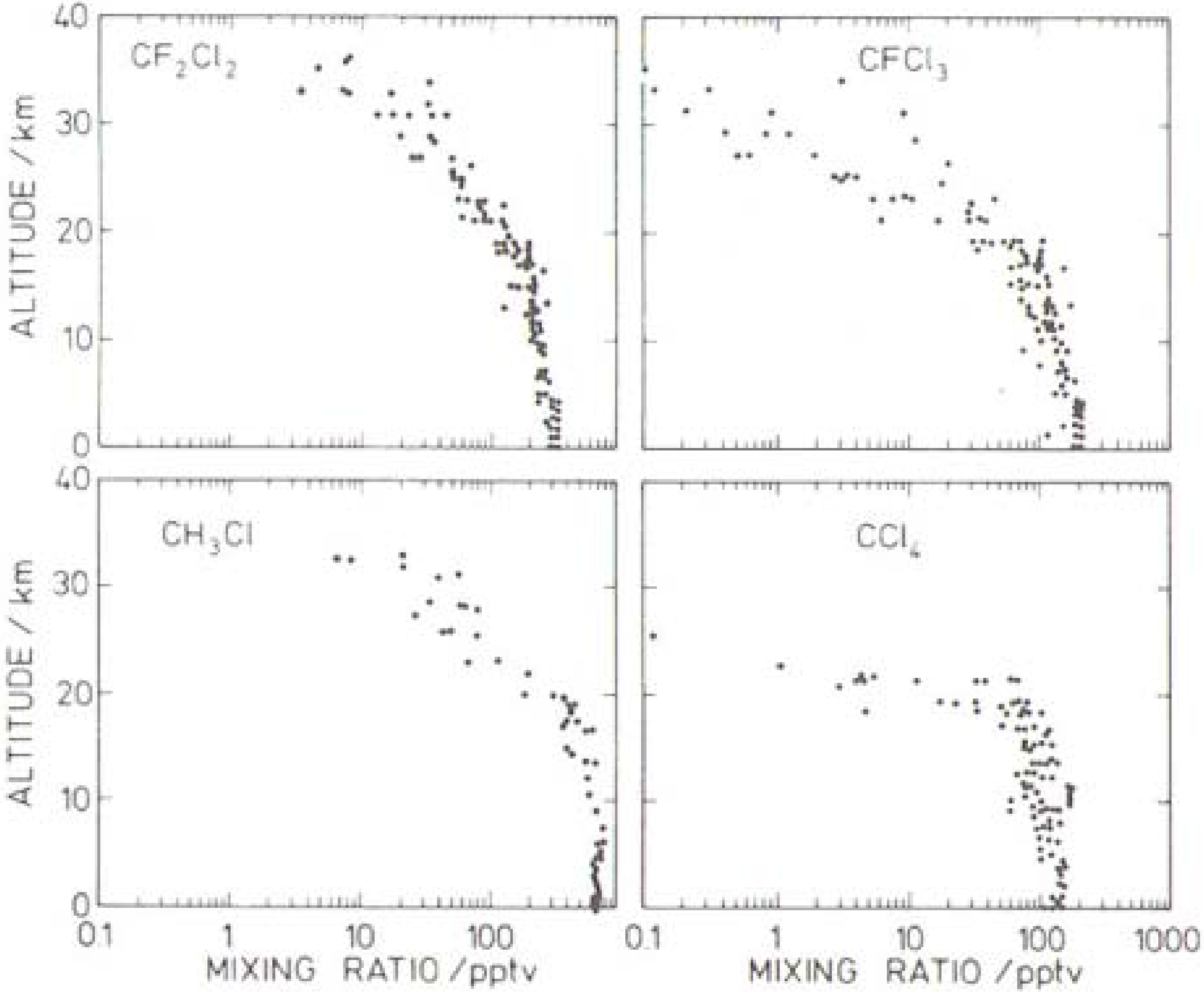


Fig. 3-11. Vertical distribution of CF_2Cl_2, $CFCl_3$, CH_3Cl, and CCl_4 in the stratosphere. [Data compiled by Fabian (1986) from Lovelock (1974a), Heidt *et al.* (1975), Schmeltekopf *et al.* (1975), Krey *et al.* (1977), Robinson *et al.* (1977), Seiler *et al.* (1978b), Tyson *et al.* (1978), Vedder *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:

$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2}$
$\mathrm{O} + \mathrm{ClO} \rightarrow \mathrm{Cl} + \mathrm{O_2}$
$\mathrm{O_3} + \mathrm{hV} \rightarrow \mathrm{O} + \mathrm{O_2}$

Netto: $\mathrm{O_3} + \mathrm{O_3} \rightarrow 3\mathrm{O_2}$

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

Nobel Preis zusammen mit Paul Crutzen

O_3 “residence time”

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

Residence time is the time needed to replace O_3 when stratospheric O_3 is taken away/destroyed.

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

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

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + NO_2 \rightarrow ClONO_2$

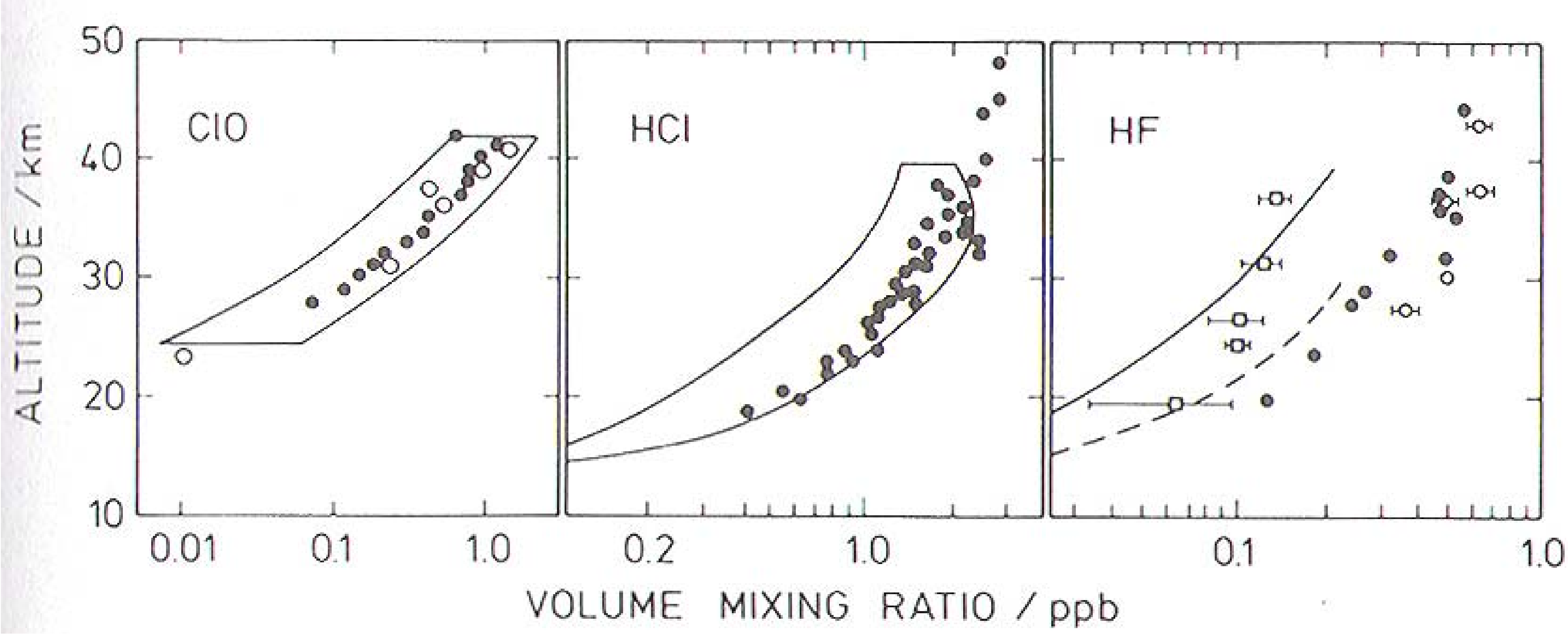


Fig. 3-12. Vertical distribution of ClO, HCl, and HF in the stratosphere. Left: Filled circles give the averages of eight altitude profiles for ClO measured in 1976–1979 by *in situ* resonance fluorescence; the envelope indicates the range of values (Weinstock *et al.*, 1981); two additional high-mixing-ratio 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

$X + O_3 \rightarrow XO + O_2$

$XO + O_{2n+1} \rightarrow X + (n+1)\, O_2$

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

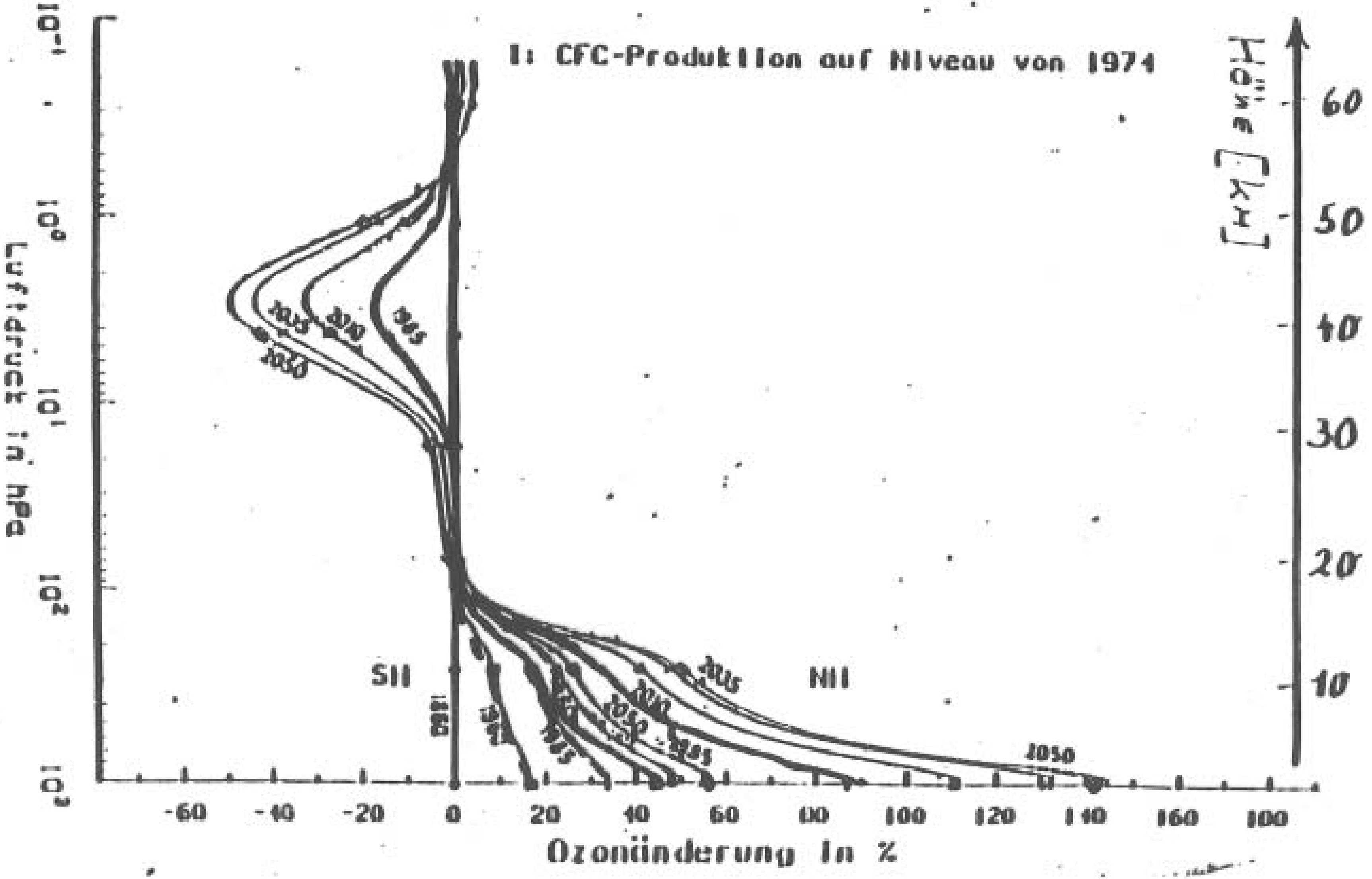
$O + O_3 \rightarrow 2O_2$ 20%

$NO + O_3 \rightarrow NO_2 + O_2$ 30%

$H + O_3 \rightarrow OH + O_2$ 30%

$Cl + O_3 \rightarrow ClO + O_2$ 20% ← anthropogenic

Also: $ClO + NO_2 \rightarrow ClONO_2$


I: CFC-Produktion auf Niveau von 1974
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
Luftdruck in hPa
Höhe [km]
60
50
40
30
20
10
2035
2010
1985
2050
SH
NH
1980
1985
2035
2010
2050
1985
2035
2050
-60
-40
-20
0
20
40
60
80
100
120
140
160
180
Ozonänderung in %

Erste synthese CFC’s 1929 Thomas Midgley, General Motors

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

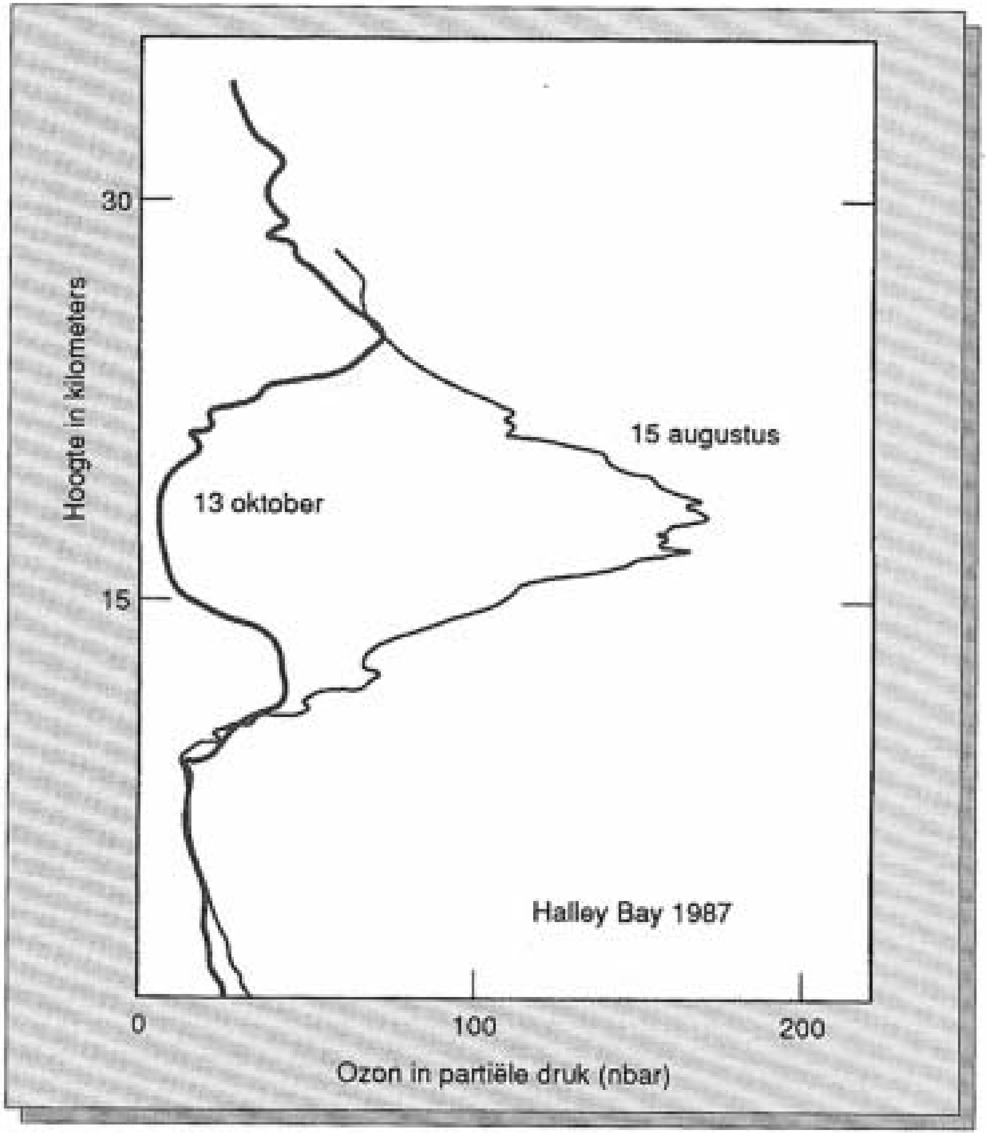
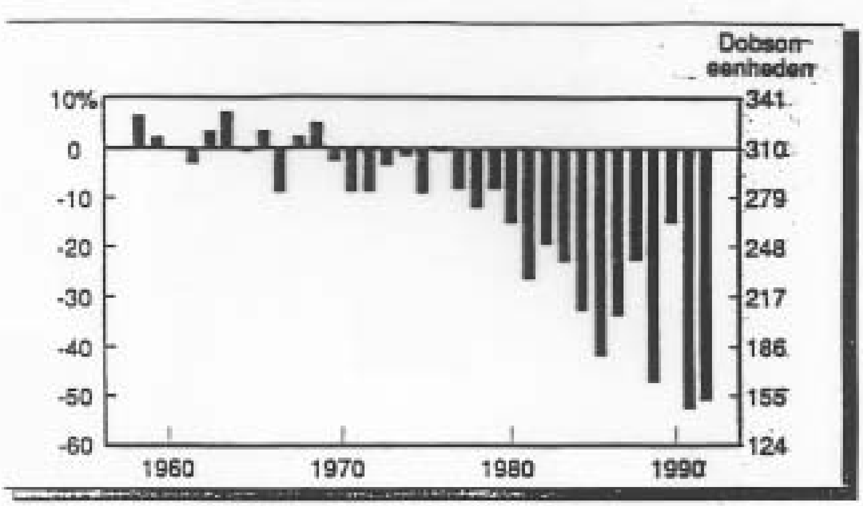
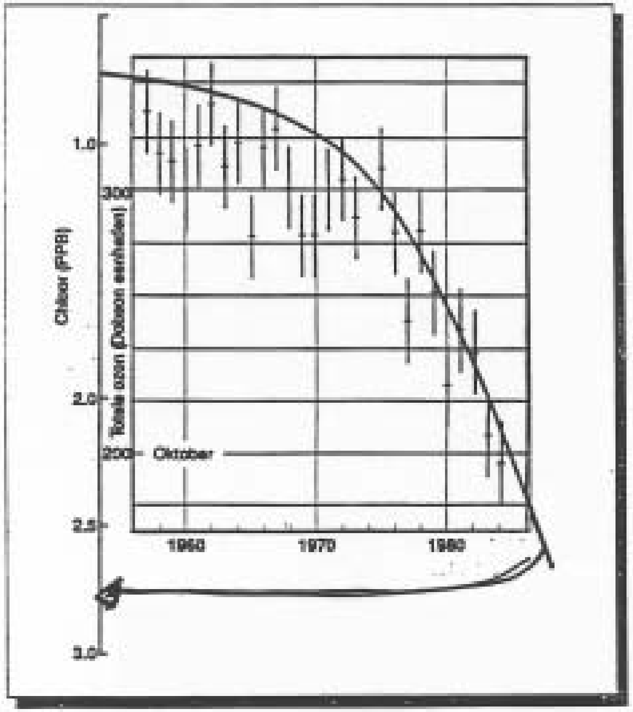
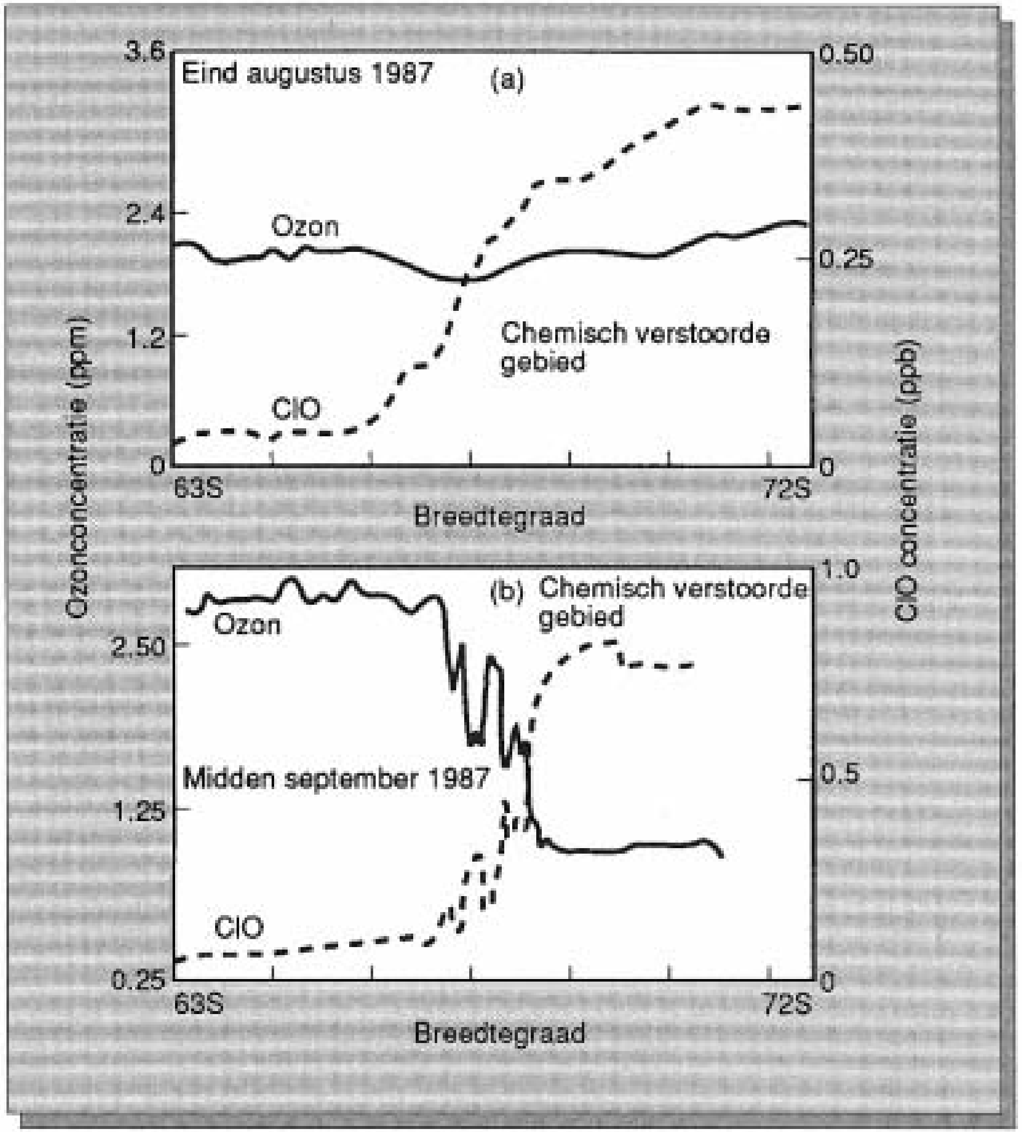


Fig. 9 Het ozongat
(Bron: 'Menschliche Einflüsse auf die Chemie der globalen Atmosphäre', Paul J. Crutzen, 1989)





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



Der Zusammenhang zwischen Ozon und ClO in das Chemisch Zerstörte Gebiet

Situation

Polar night: polar vortex ≈ 60 °S
temperature: < -83 °C
$HNO_3 + H_2O$ ➡ 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

$Cl_2 + h\nu$ ➡ 2Cl

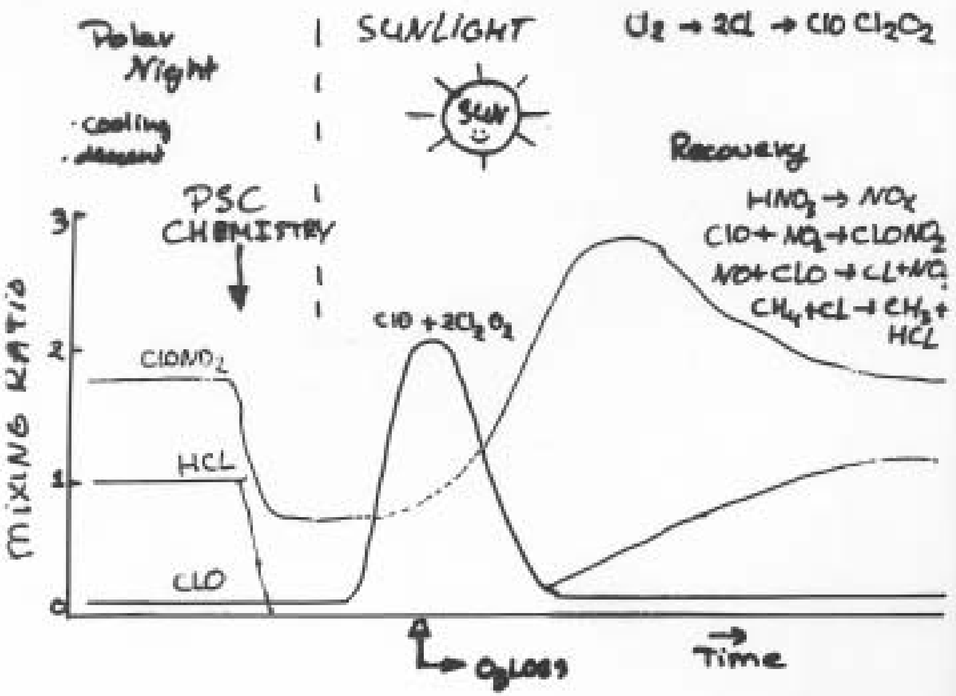
$HOCl + h\nu$ ➡ OH + Cl

O_3 increase after October:

breaking of polar vortex ➡ mixing

T > - 83 °C, no polar clouds

PSC: Polar Stratospheric Clouds
Key Role

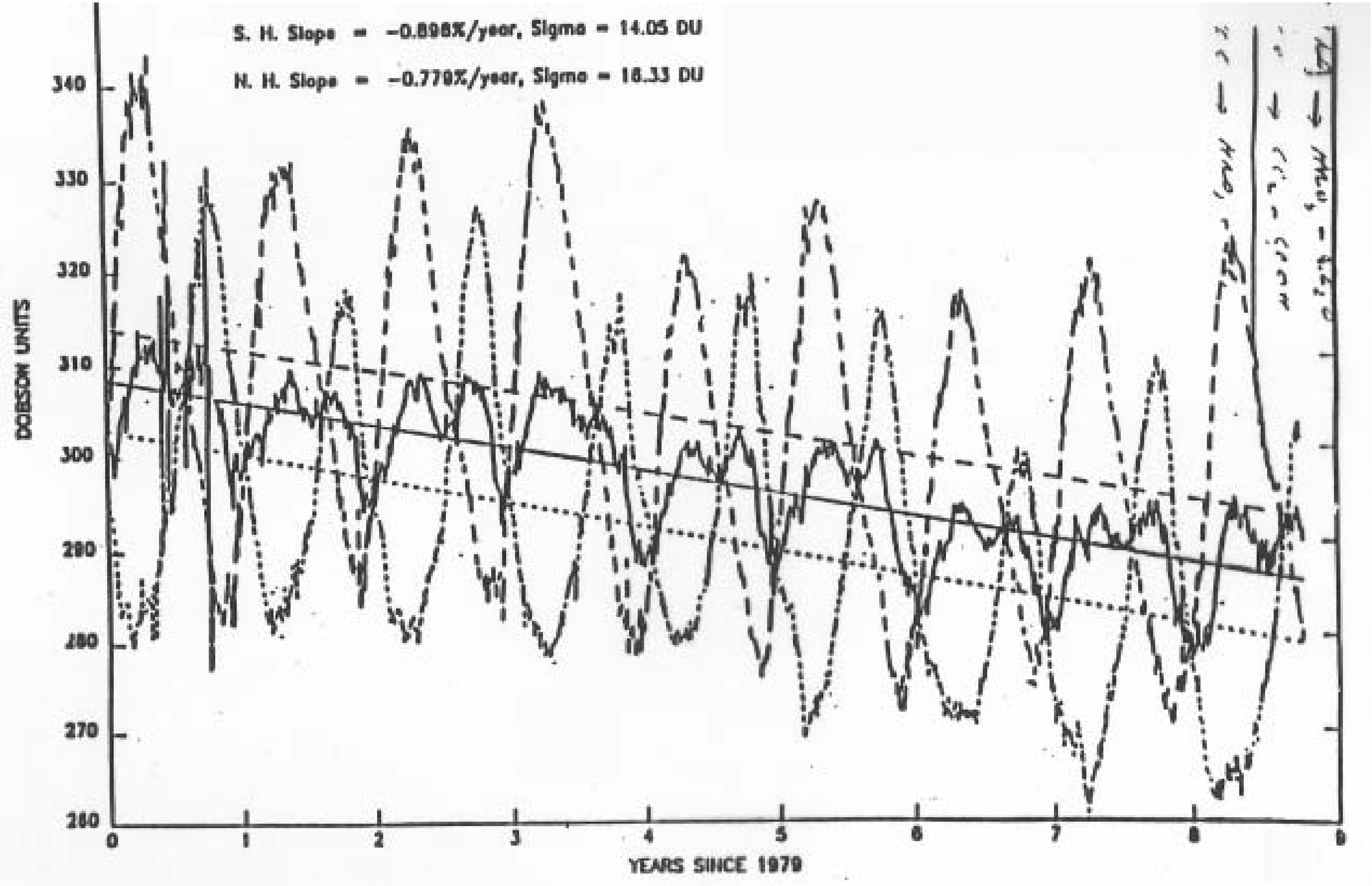


Perturbed

PSC: Heterogeneous chemistry:

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

Fig 19 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 ≈ ...

Weniger O_3 in der Stratosphäre gibt weniger Absorption von UV-B (280-315 nm) in der Stratosphäre

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

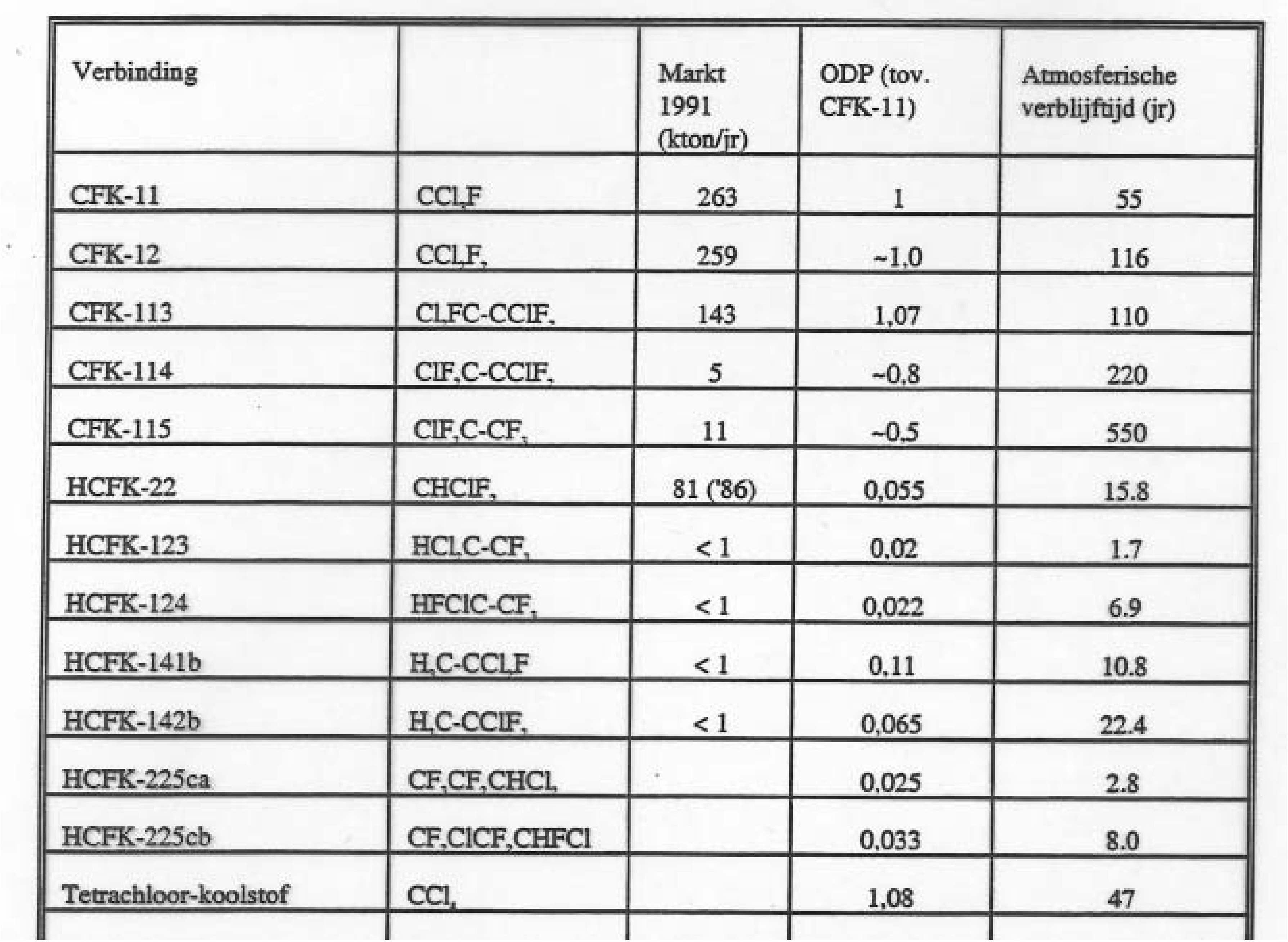
1) Ozone depletion potential-ODP

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



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

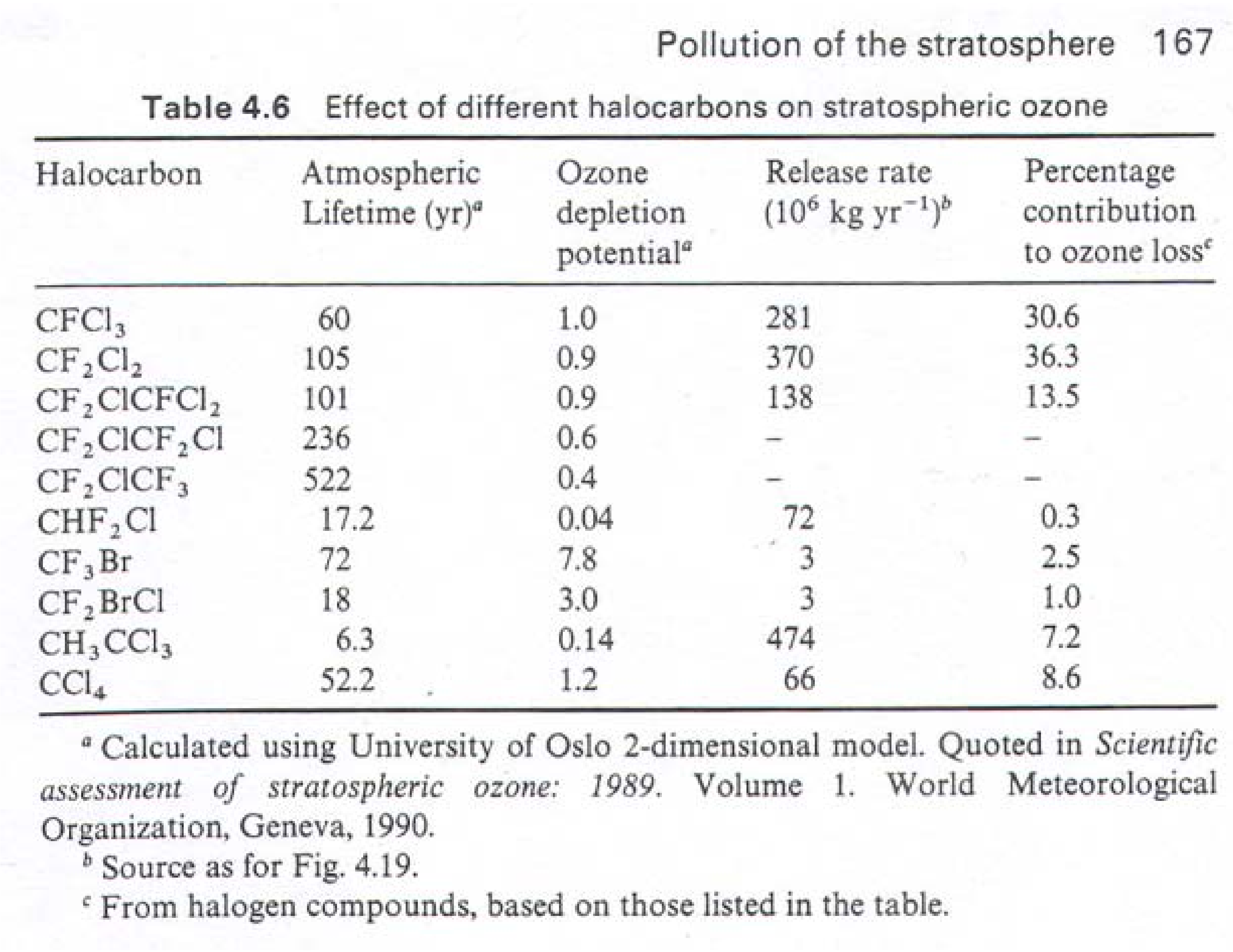


Table 4.6 Effect of different halocarbons on stratospheric ozone

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.

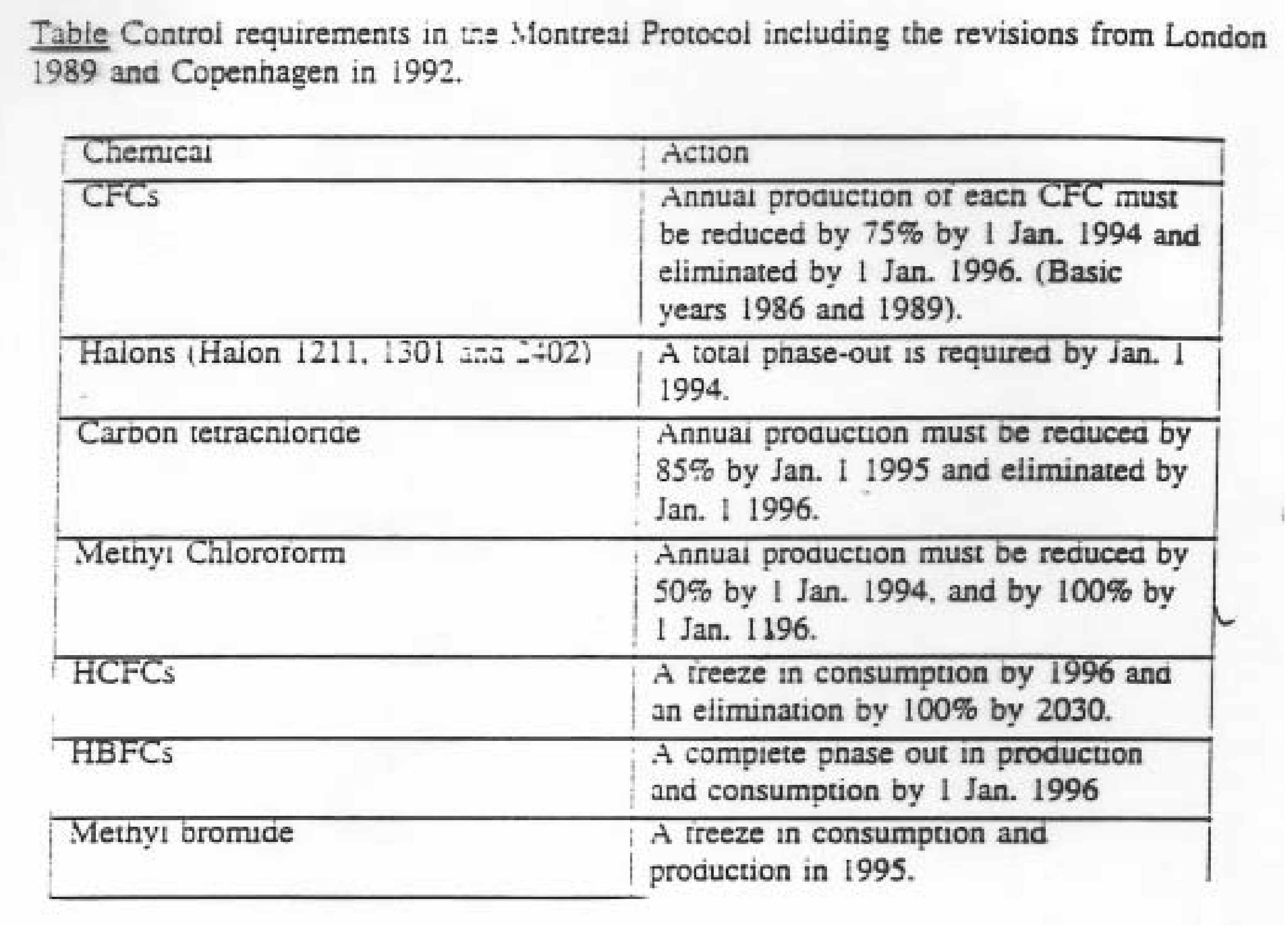
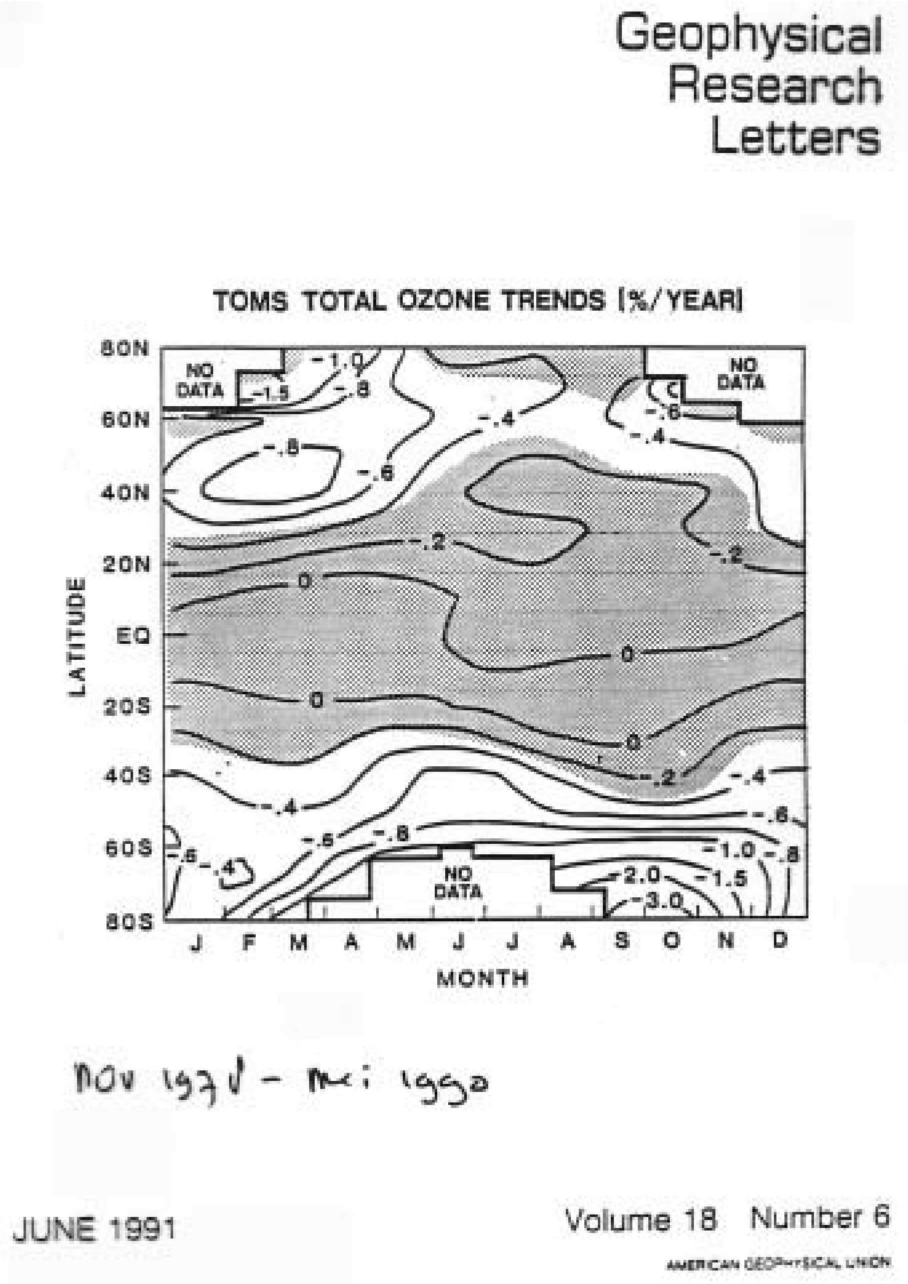


Table Control requirements in the Montreal Protocol including the revisions from London 1989 and Copenhagen in 1992.

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.



Geophysical
Research
Letters

TOMS TOTAL OZONE TRENDS [%/YEAR]

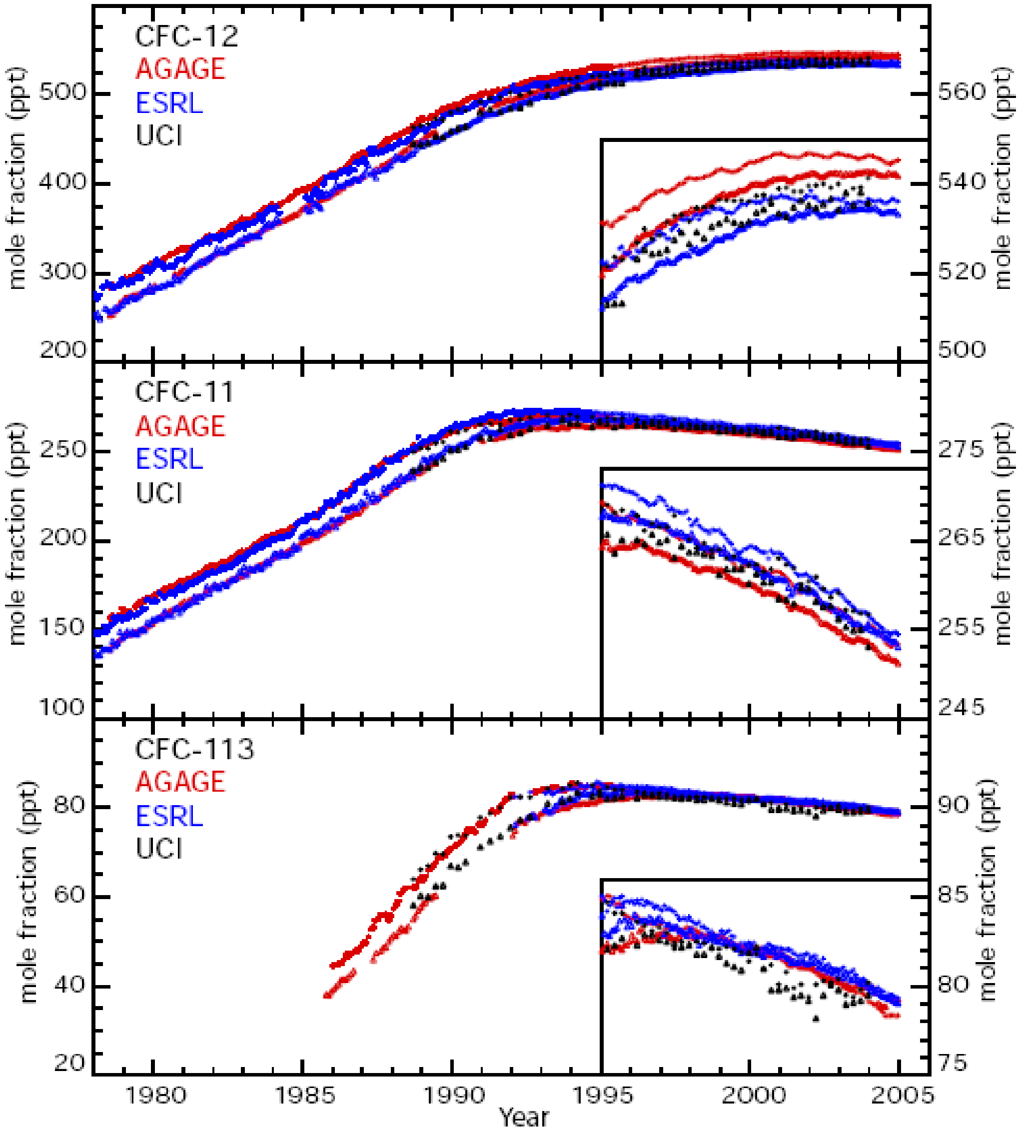
nov 1978 – mai 1990

JUNE 1991

Volume 18 Number 6

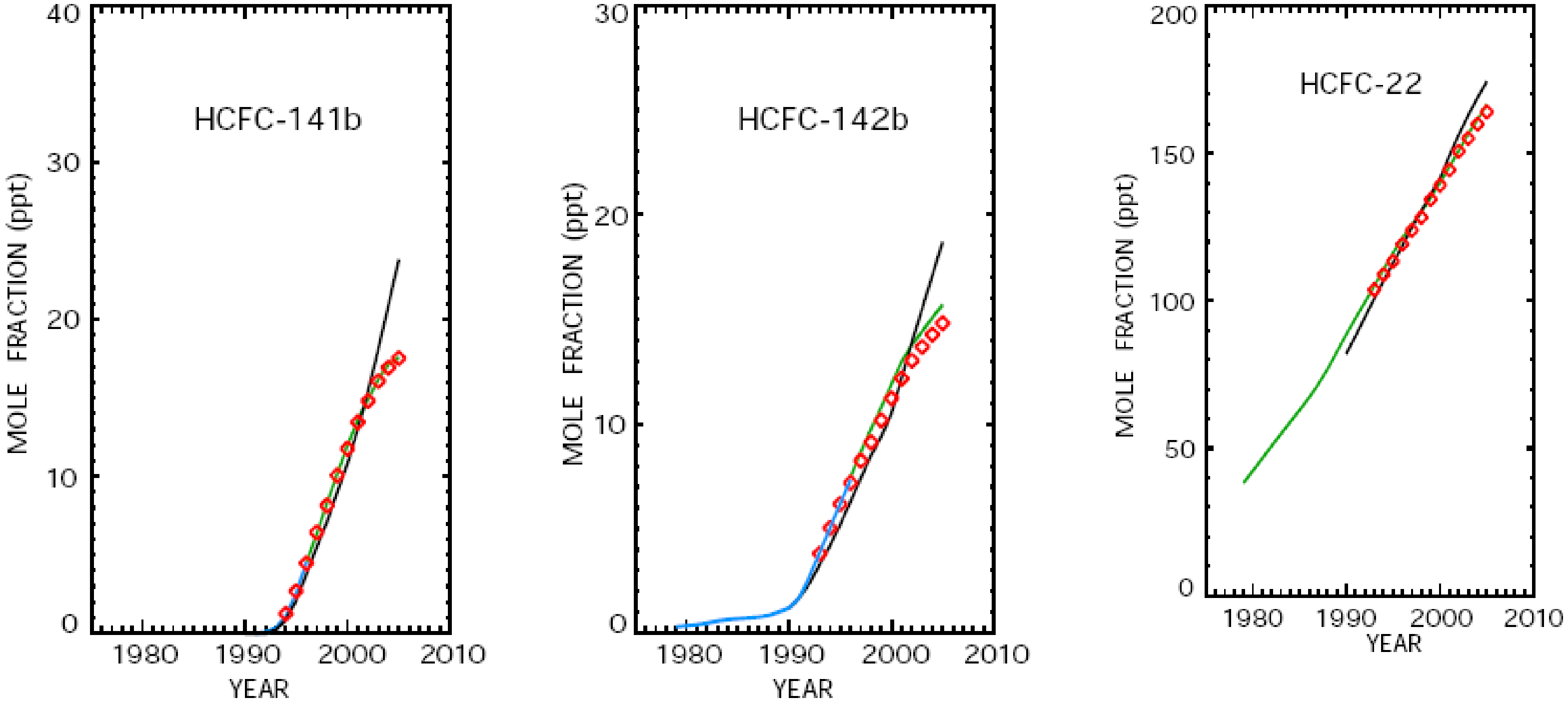
AMERICAN GEOPHYSICAL UNION

CFC Trends 1978 - 2006



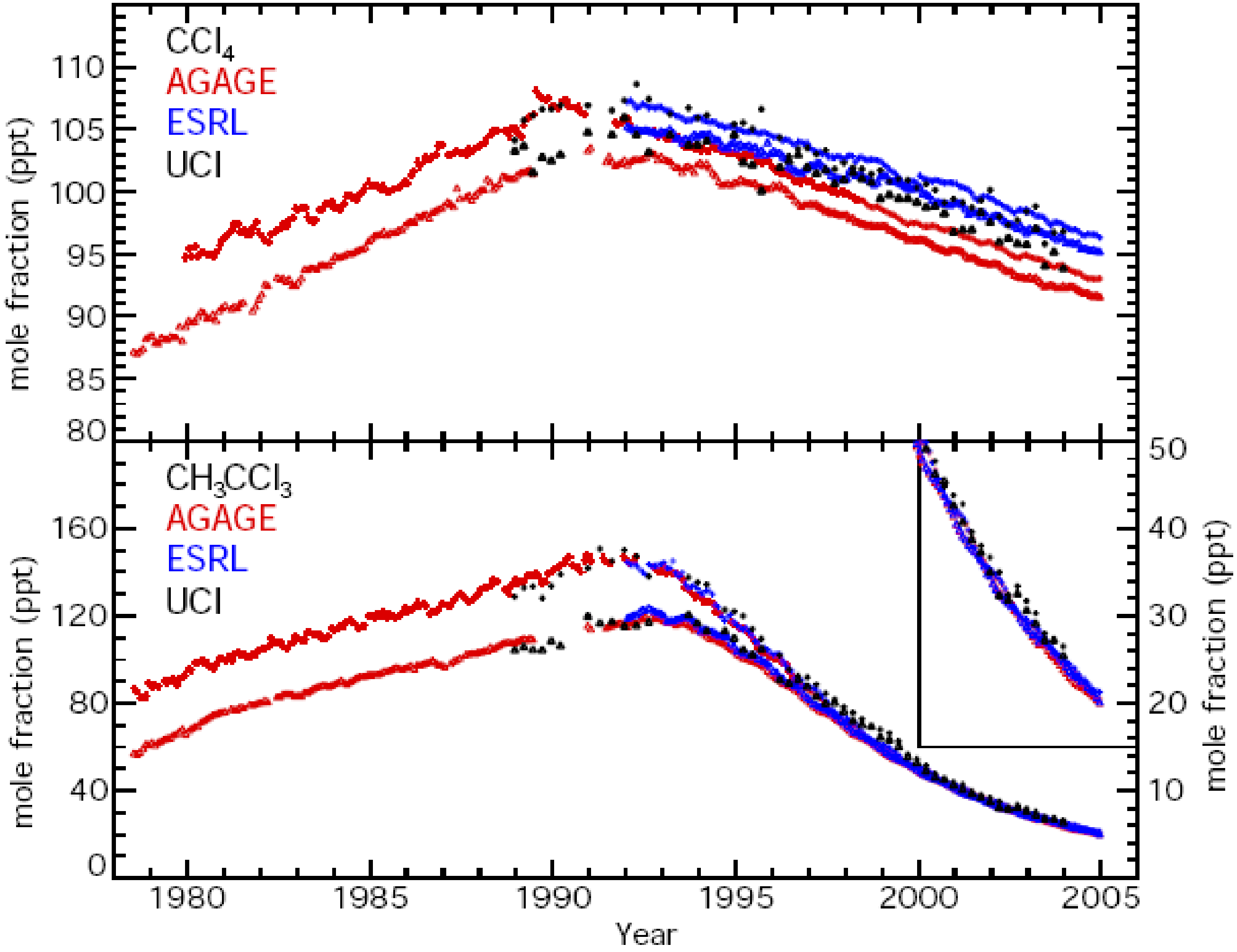
(WMO, 2007)

Trends HCFC



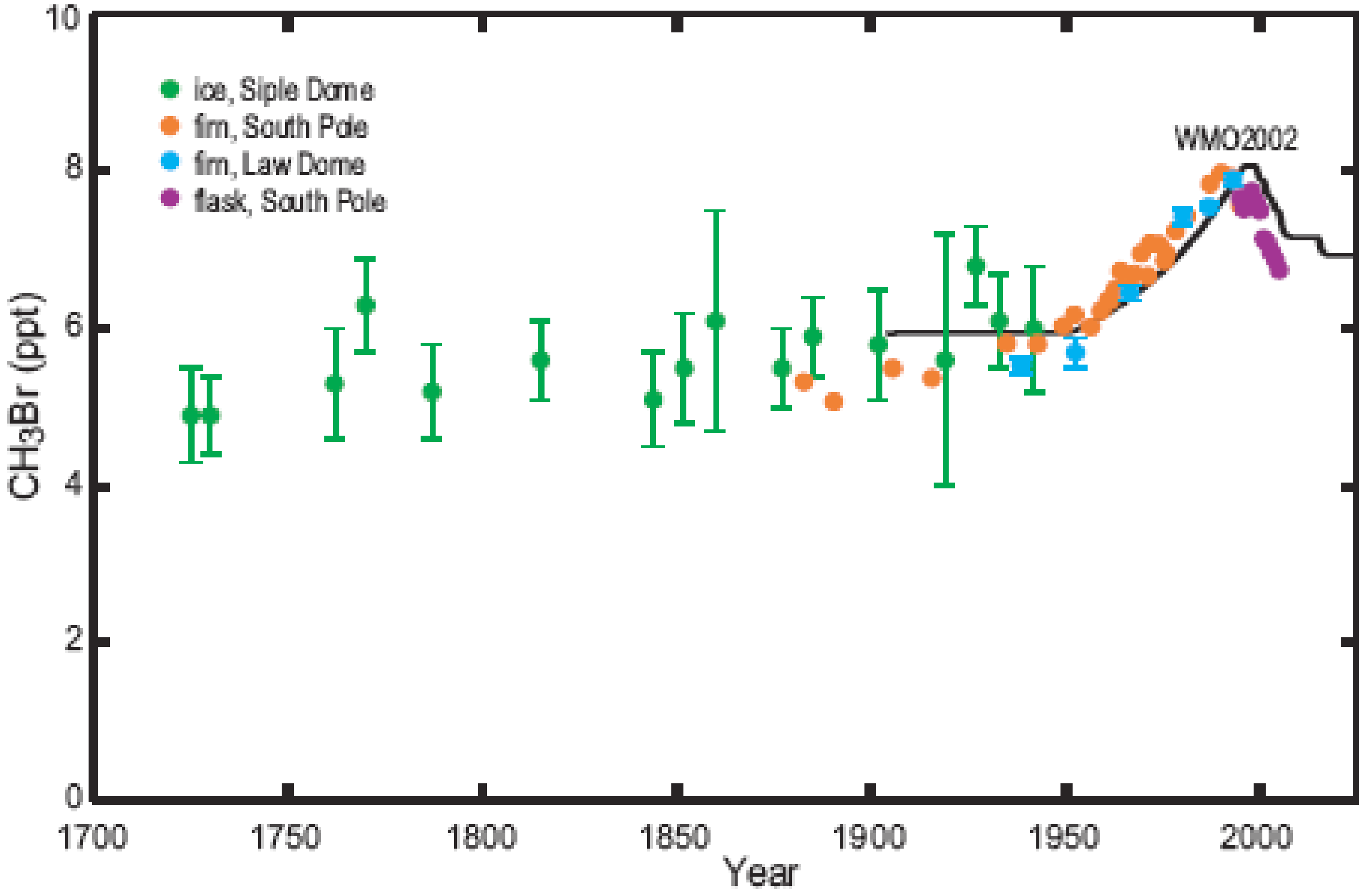
(WMO, 2007)

Trends CH_3ClCH_3 and CCl_4



(WMO, 2007)

Trend CH_3Br



(WMO, 2007)

ODP and GWP of different CFC’s

Fig 15a

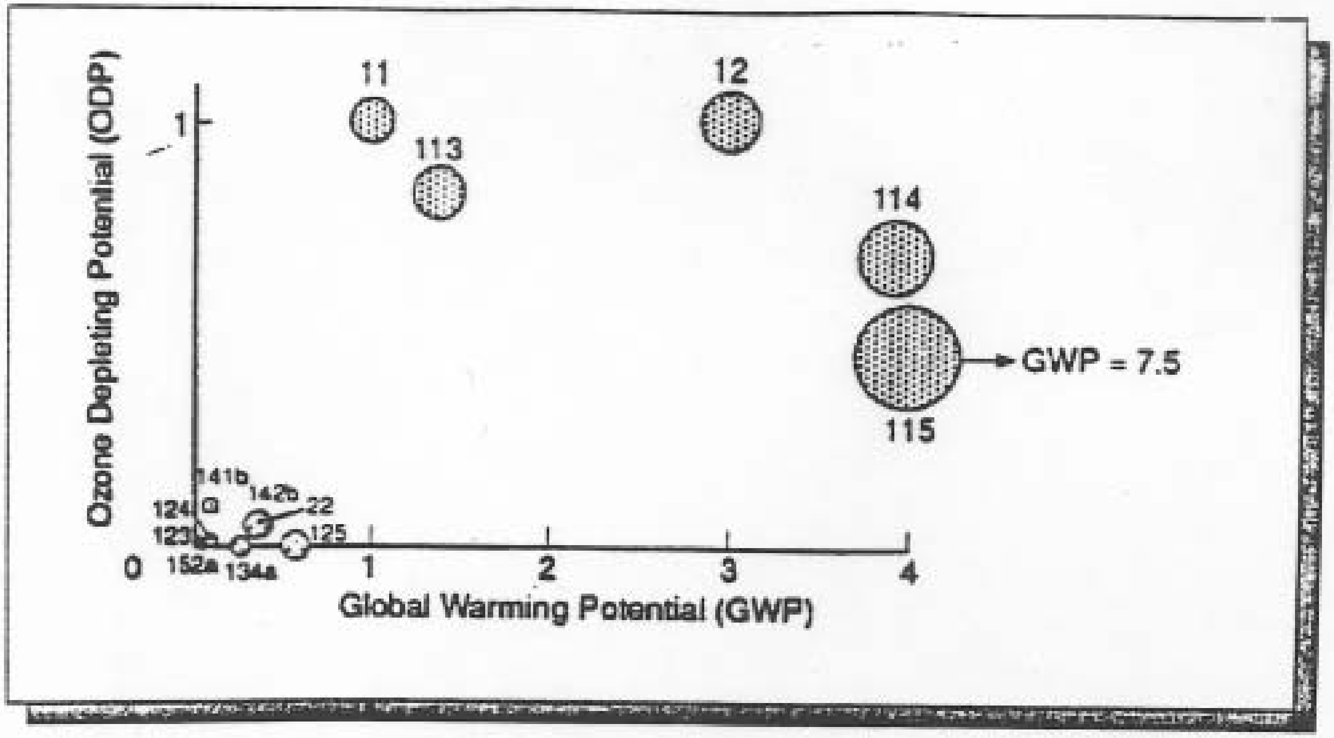


Fig. 15 Ozone Depletion Potential en Global Warming Potential van verschillende CFK’
(beide t.o.v. CFK-11).
(Bron: WMO Globale Ozone Research and Monitoring Project - Report No. 20 “Scientific Assessment of Stratospheric Ozone: 1989)

Effects of the emission reduction of CFC’s

Fig 15-b

Cl-verandering t.o.v. 1985 →

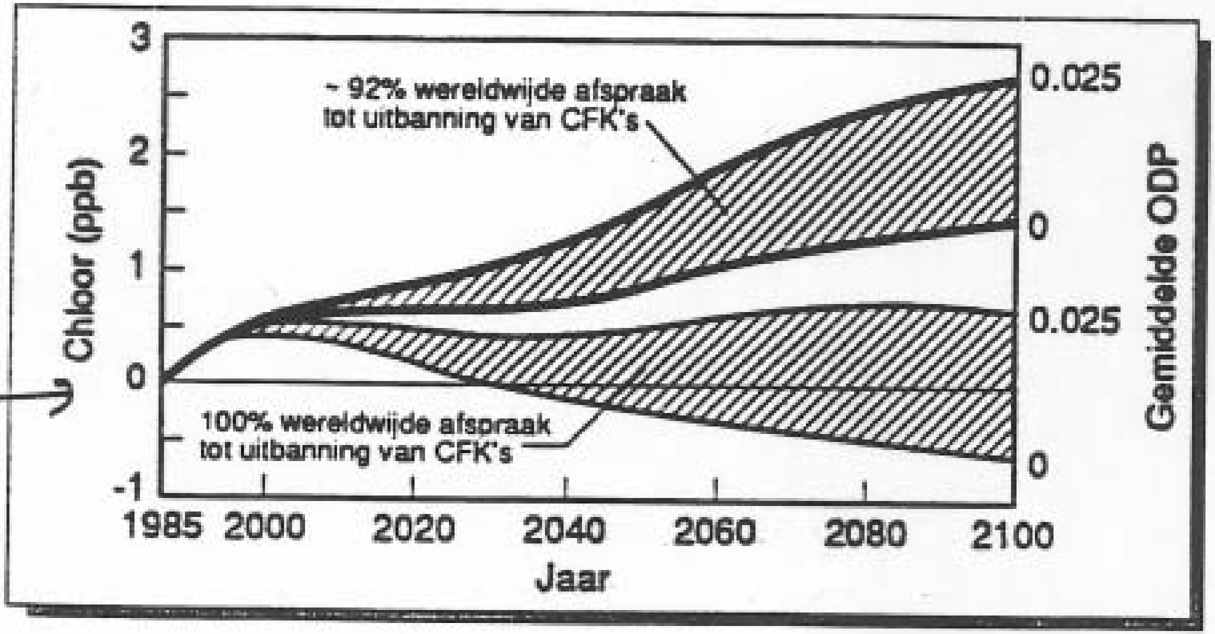


Fig. 16 Effecten van naleving van afspraken voor CFK's emissiereductie. De bandbreedte wordt veroorzaakt door substitutie met verschillende alternatieve CFK’s.
(Bron: Future concentrations of stratospheric chlorine and bromine, EPA page 400/I-88/005, J.S. Hoffman en M.J. Gibbs, 1988)

Ozone in Earth’s stratosphere

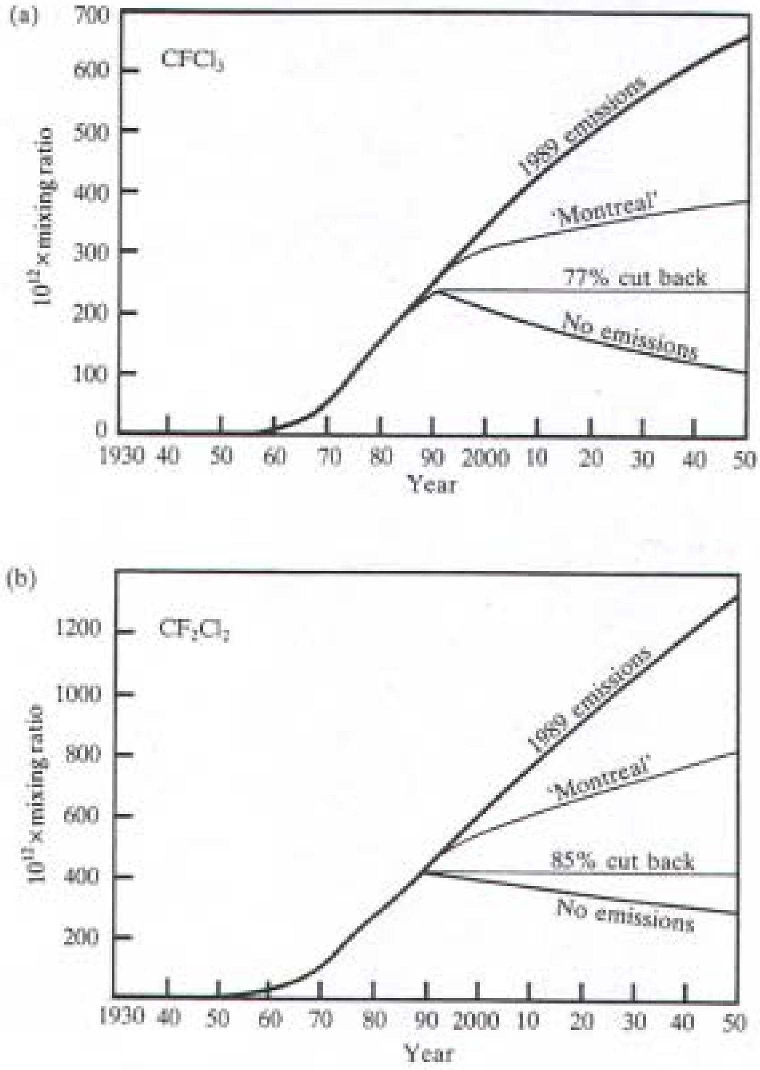


Fig. 4.21. Model predictions of the average concentrations of CFC11 and CFC12 in the atmosphere resulting from four different emission scenarios. Source: as for Fig. 4.19.

Pollution of the stratosphere

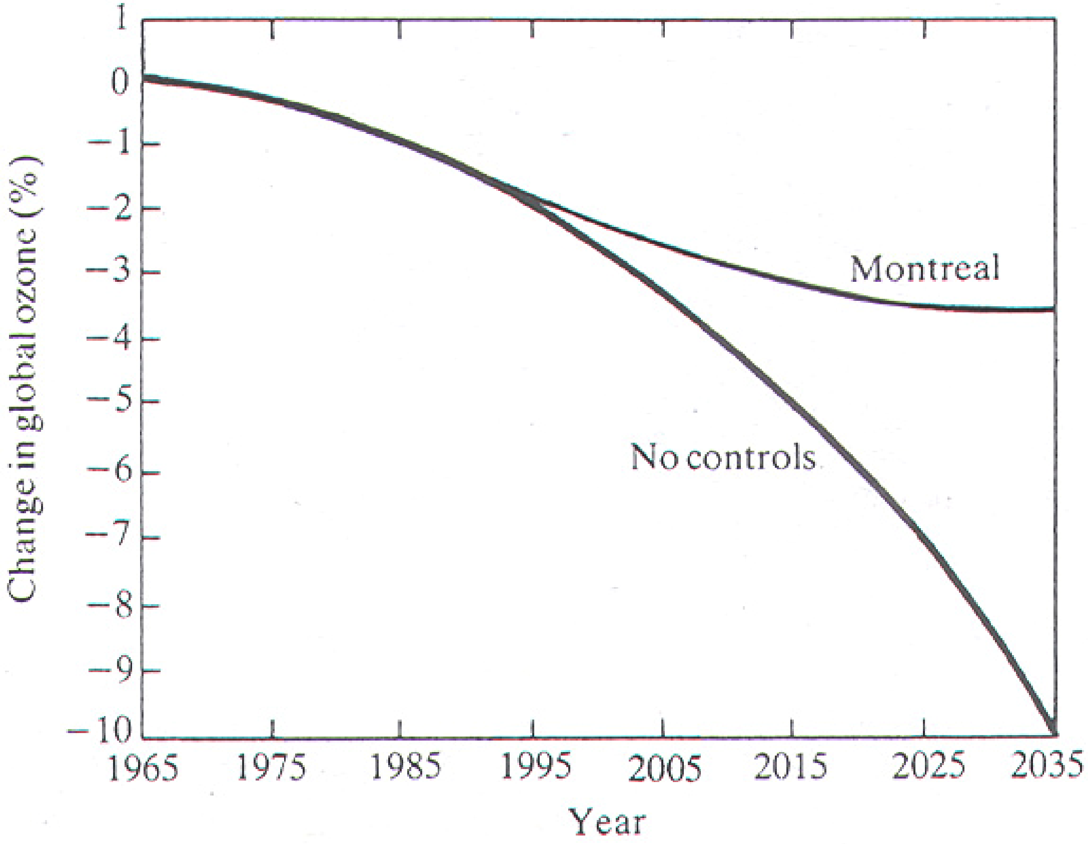


Fig. 4.23. Change in global mean column ozone predicted by the Oslo model. Allowance is made for growth of CO_2, N_2O and CH_4 (at annual rates of ca. 0.6%, 0.2%, and 1.0%, respectively). Source as for Fig. 4.19.

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

Modelberechnungen mit ein 3-D Nord-Hemisphärisch Circulations Modell, UK Met-Office

- Present Day CO_2 level
- Present Day CO_2 level+ calculated O_3-concentrations
- Double CO_2-level + climatological O_3-concentrations
- Double CO2-level + calculated O_3-concentrations

Look to areas with < 195 K

Koplung Klima-änderung und Luftqualität

Aerosolen/Feinstaub

“On avoiding dangerous anthropogenic interference with the climate system”.
V.Ramanathan and Y.Feng, PNAS, vol 105, 38, 14245-14250, Sept. 23, 2008

- Aerosols lead to cooling, accept Black Carbon
- Green House Gases and Atmospheric Brown Clouds
- Committed Equilibrium Warming, without, and with aerosols
- Coal, Oil, Gas

IV 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

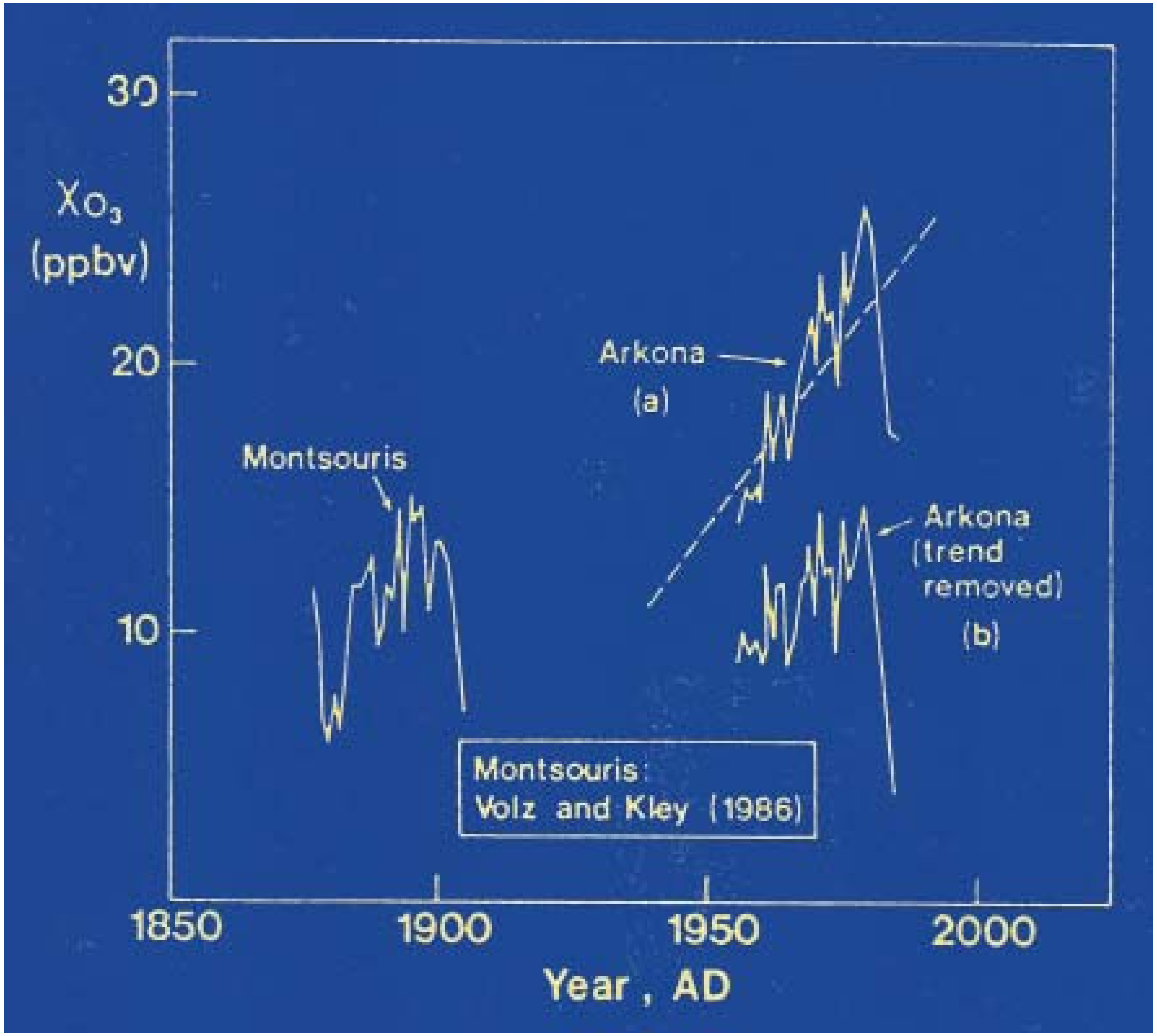
Photochemical smog : (smoke + fog = smog) in summer

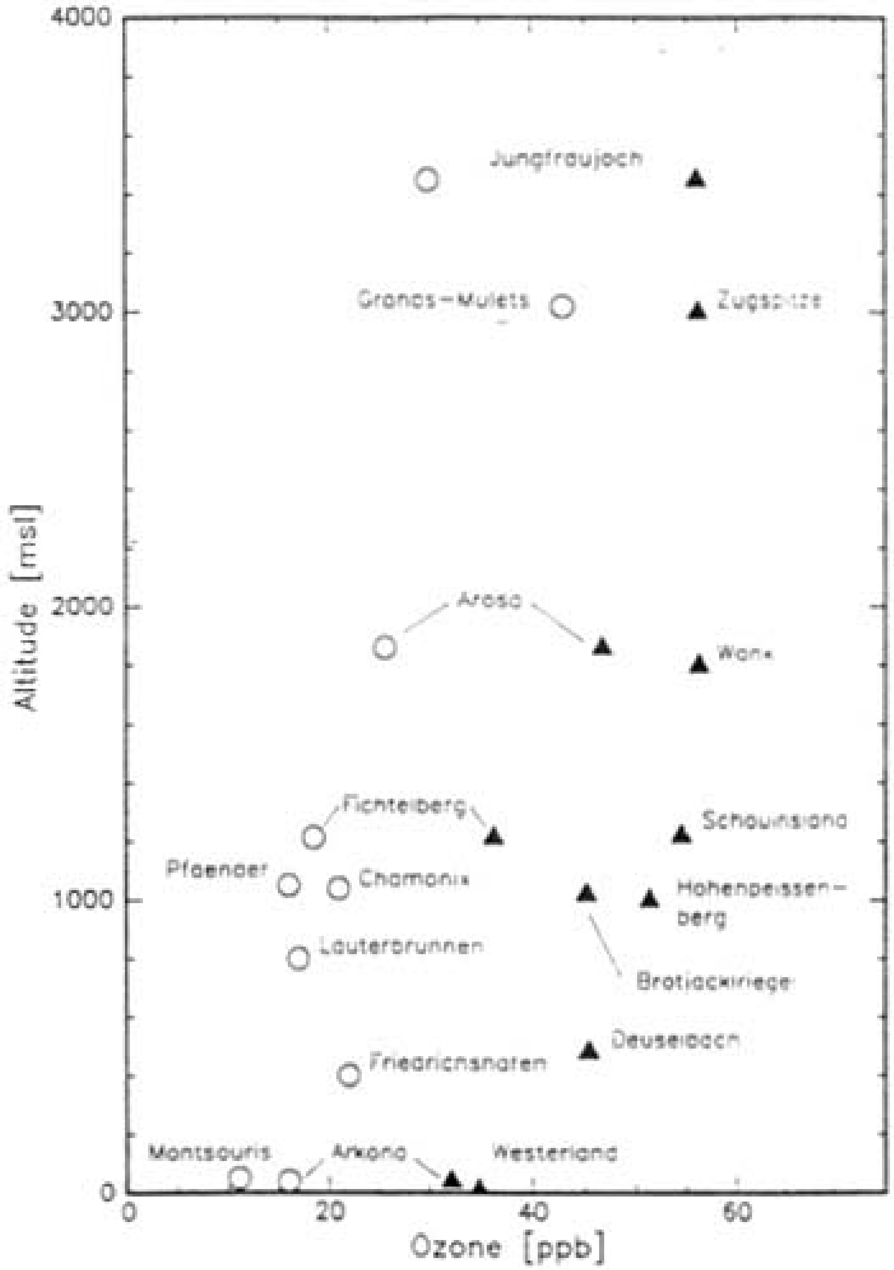
Wintersmog : London ‘fog’ 1940-1950: SO_2 and Sulfate-aerosols

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





Open symbols : Before 1950

Closed symbols : After 1990

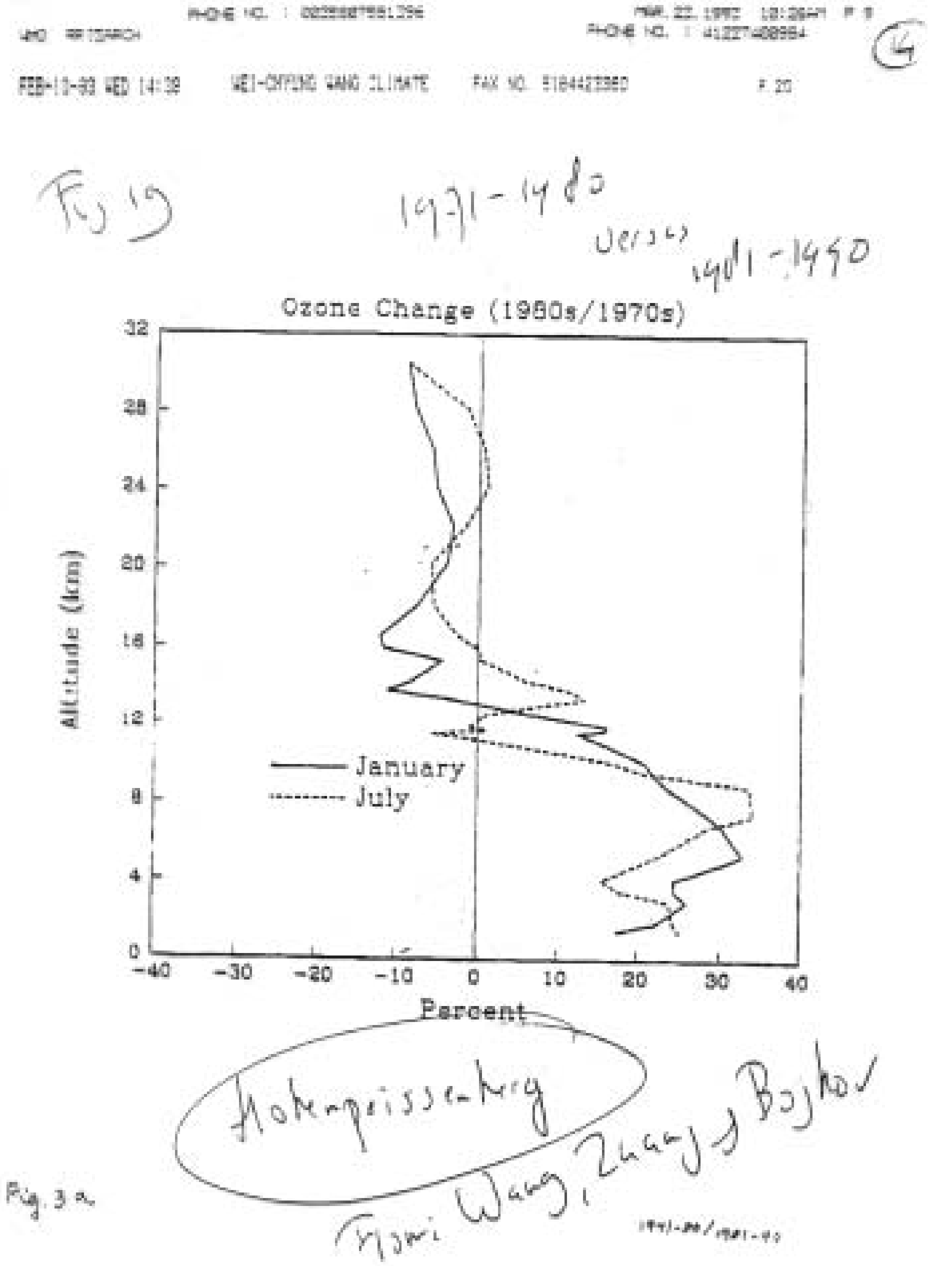


Fig 19

1971-1980

versus 1981-1990

Ozone Change (1980s/1970s)

Hohenpeissenberg

From: Wang, Zhang, Bojkov

Fig. 3a

1971-80/1981-90

Tropospheric chemistry

Stratospheric chemistry: mostly gasphase
Tropospheric chemistry: gasphase, aquous phase, aerosols

$NO_2 + hV \rightarrow NO + O \quad \lambda < 410\ \text{nm}$

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

$O_3 + NO \rightarrow NO_2 + O_2$

$NO_2 + O_2 \rightleftarrows NO + O_3$

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

$H_2O + NO \rightarrow NO_2 + OH$

Aldehydes Beispiele: Formaldehyde: HCHO
Acetaldehyde: CH_3CHO

$CH_3CHO+OH \rightarrow$ PAN: Peroxyacethylnitrate

Example

$CH_4 + OH \rightarrow H_2O + CH_3$

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

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow HCHO + HO_2$

↑

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:

$$P\ (O_3) = k_1\ [NO]\ [RO_2] + k_2\ [NO]\ [HO_2]$$

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

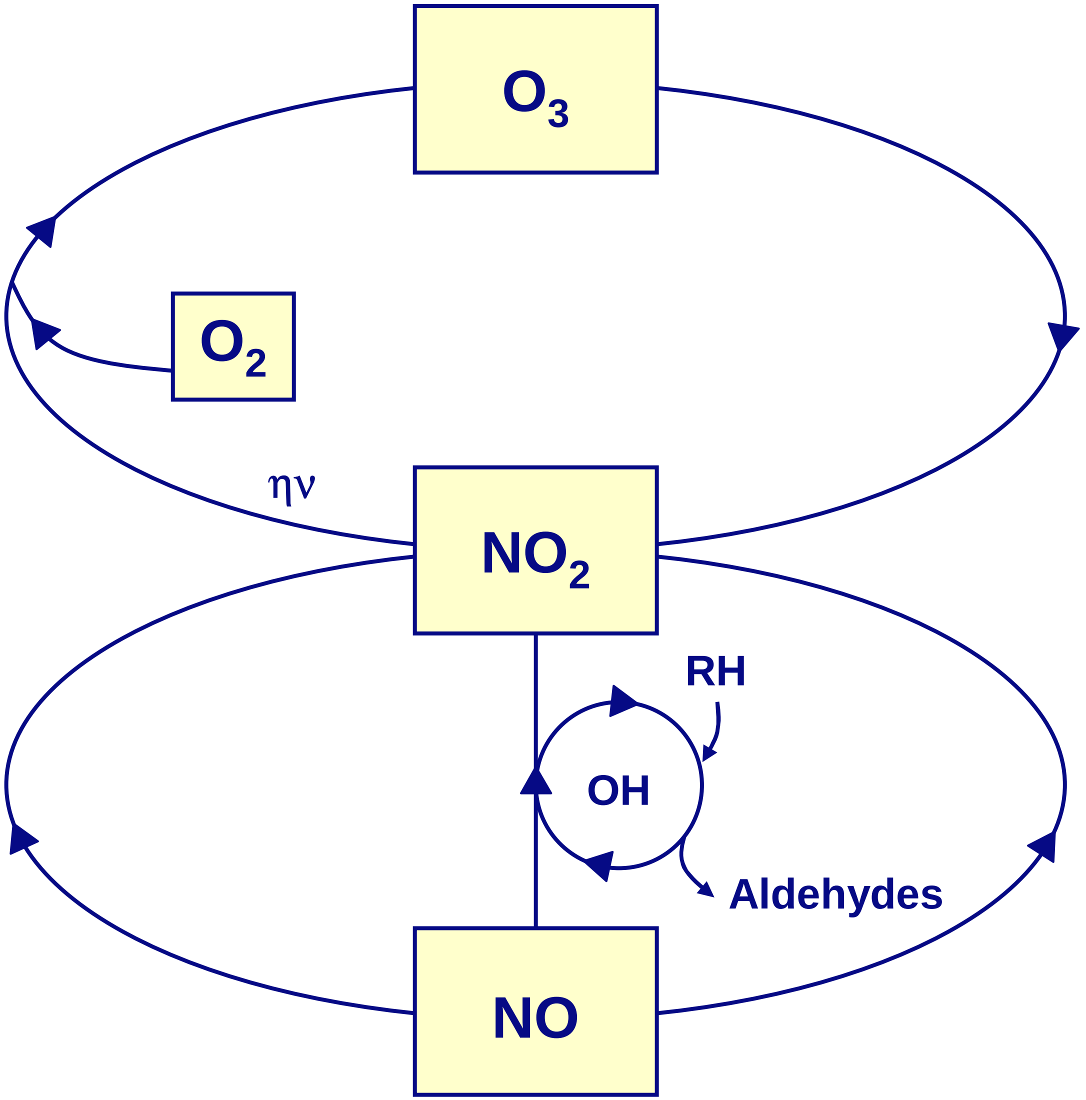
Alkanes : Saturated Compounds

Examples : Ethane C_2H_6 atmospheric life-time : 80 days
Propane C_3H_8 15 days

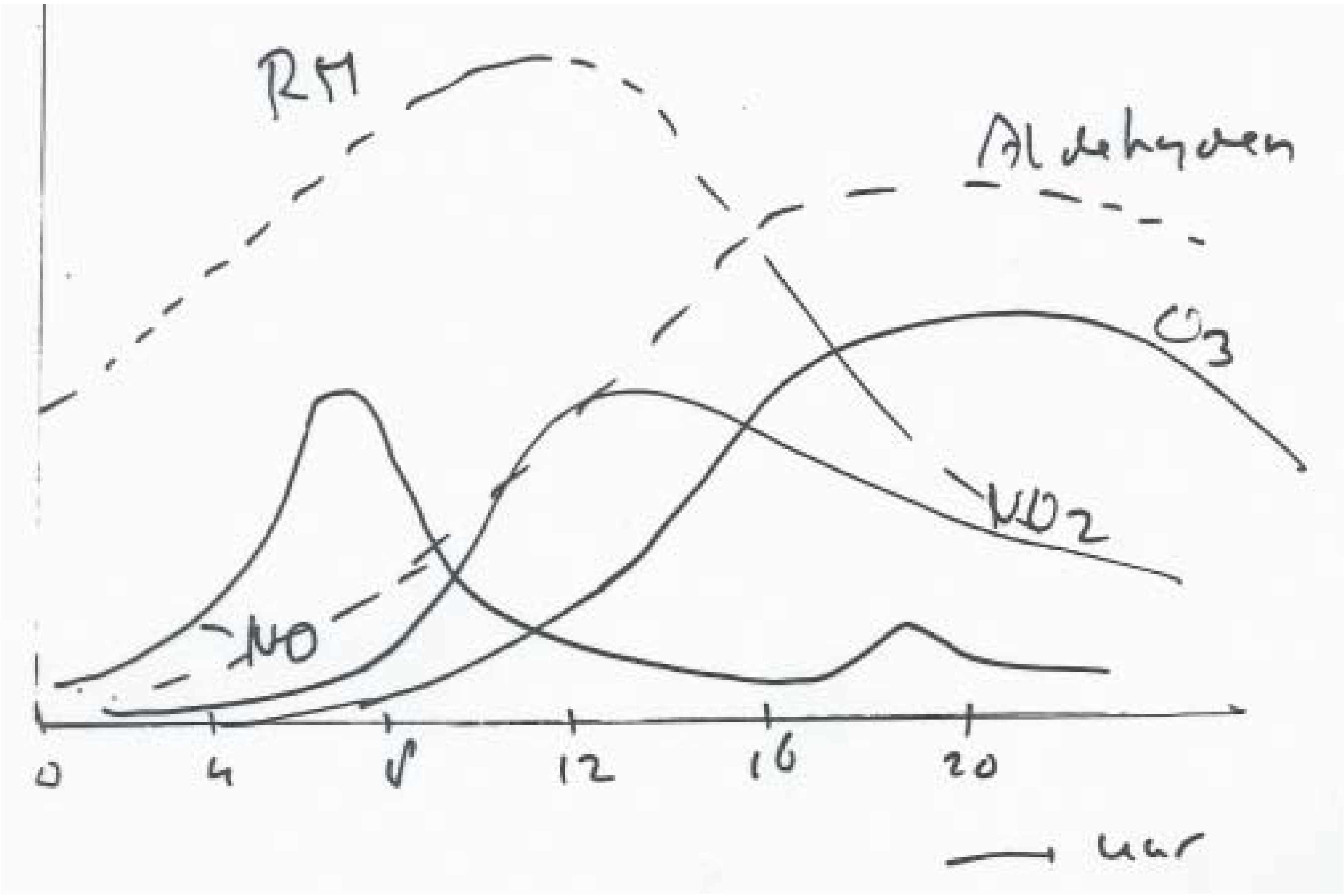
Alkenes : Unsaturated Compounds

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
ην
NO_2
RH
OH
Aldehydes
NO

Messungen in L.A.



$NO \rightarrow NO_2 \rightarrow O_3$
$RH \rightarrow$ Aldehyden

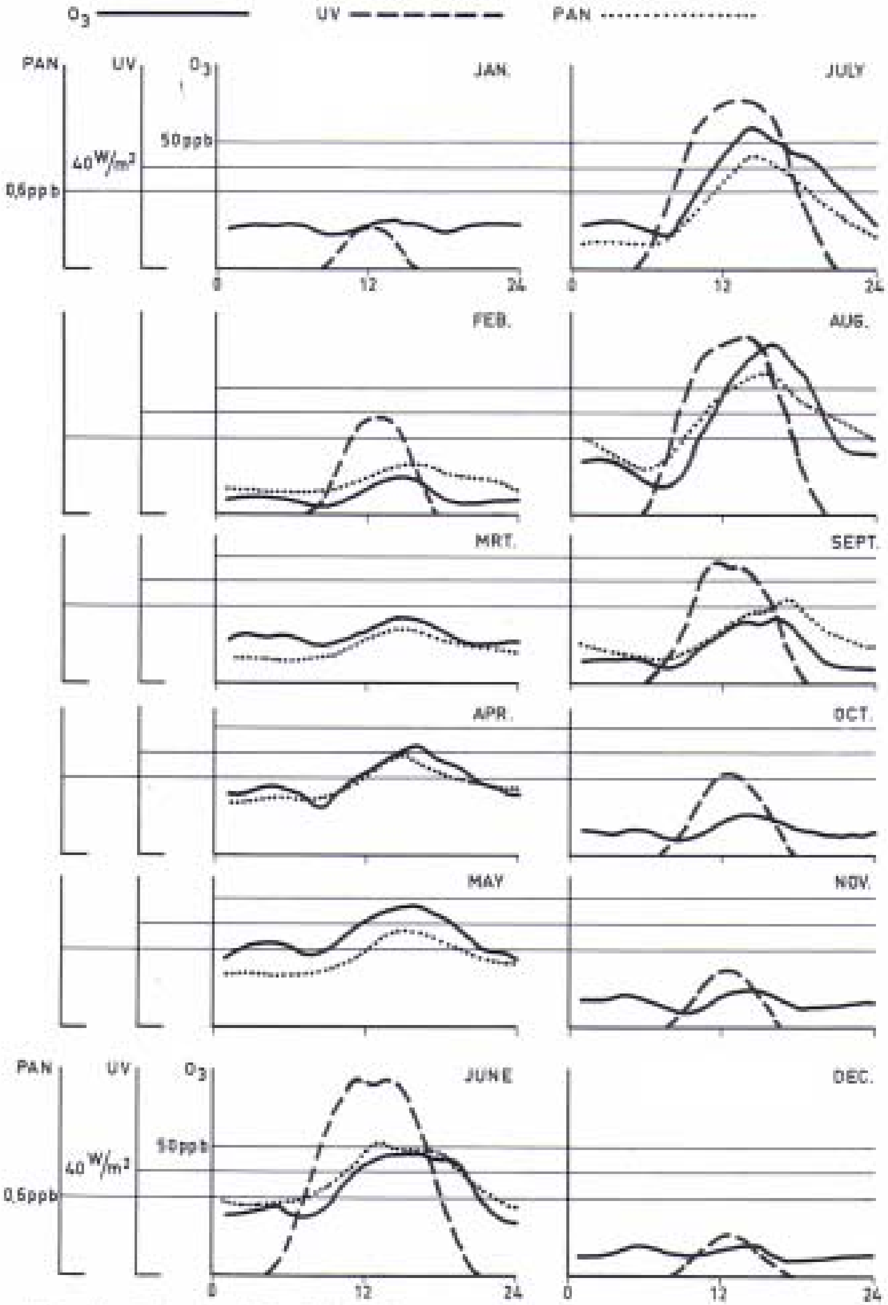


Fig. 18 Daily trend of the O_3 and PAN concentrations and the UV (290-400 nm) light intensity measured at Delft, 1975

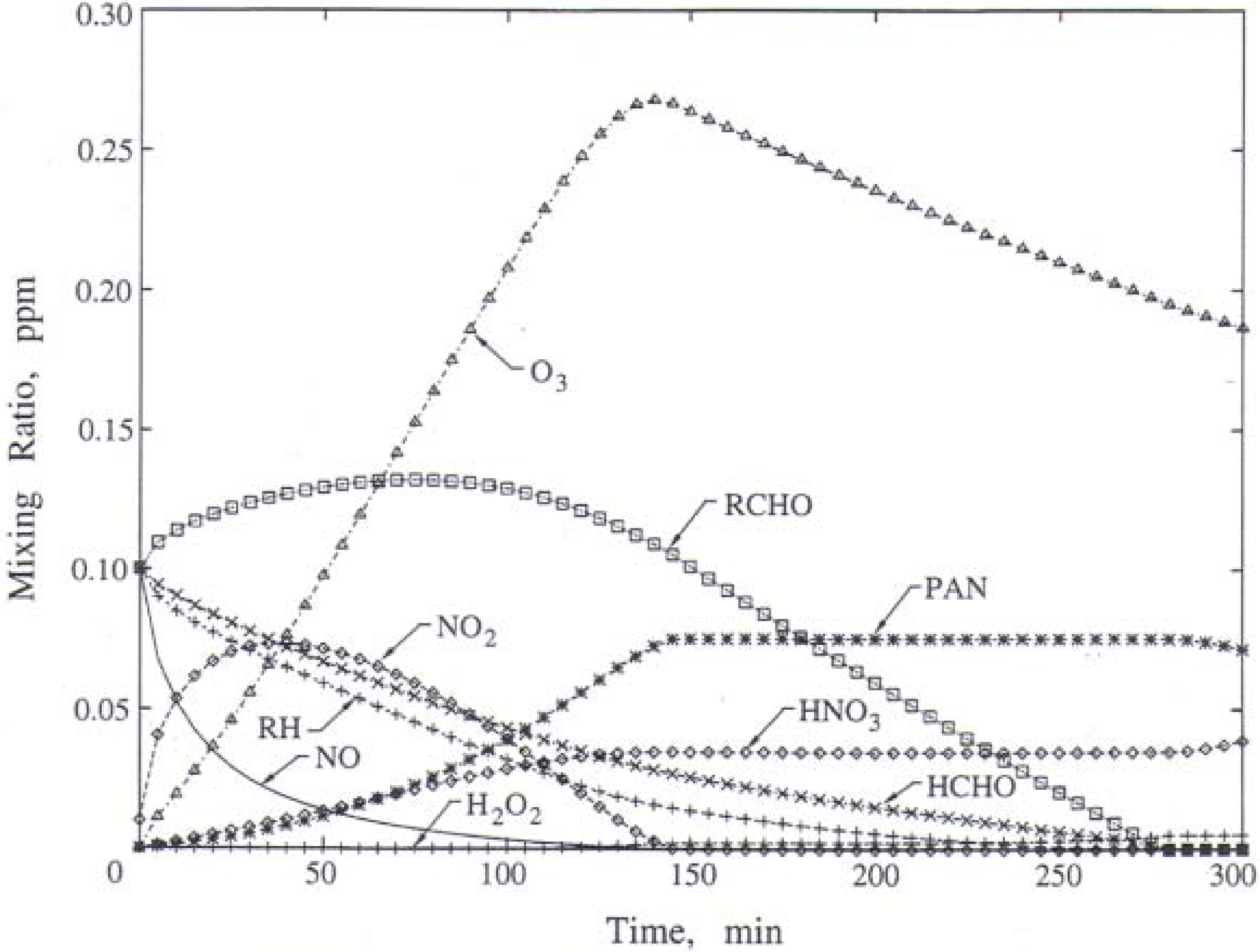


FIGURE 5.14 Behavior of the generalized mechanism in Table 5.3.

Policy for tropospheric O_3

RH versus NO_x abatement,

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

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

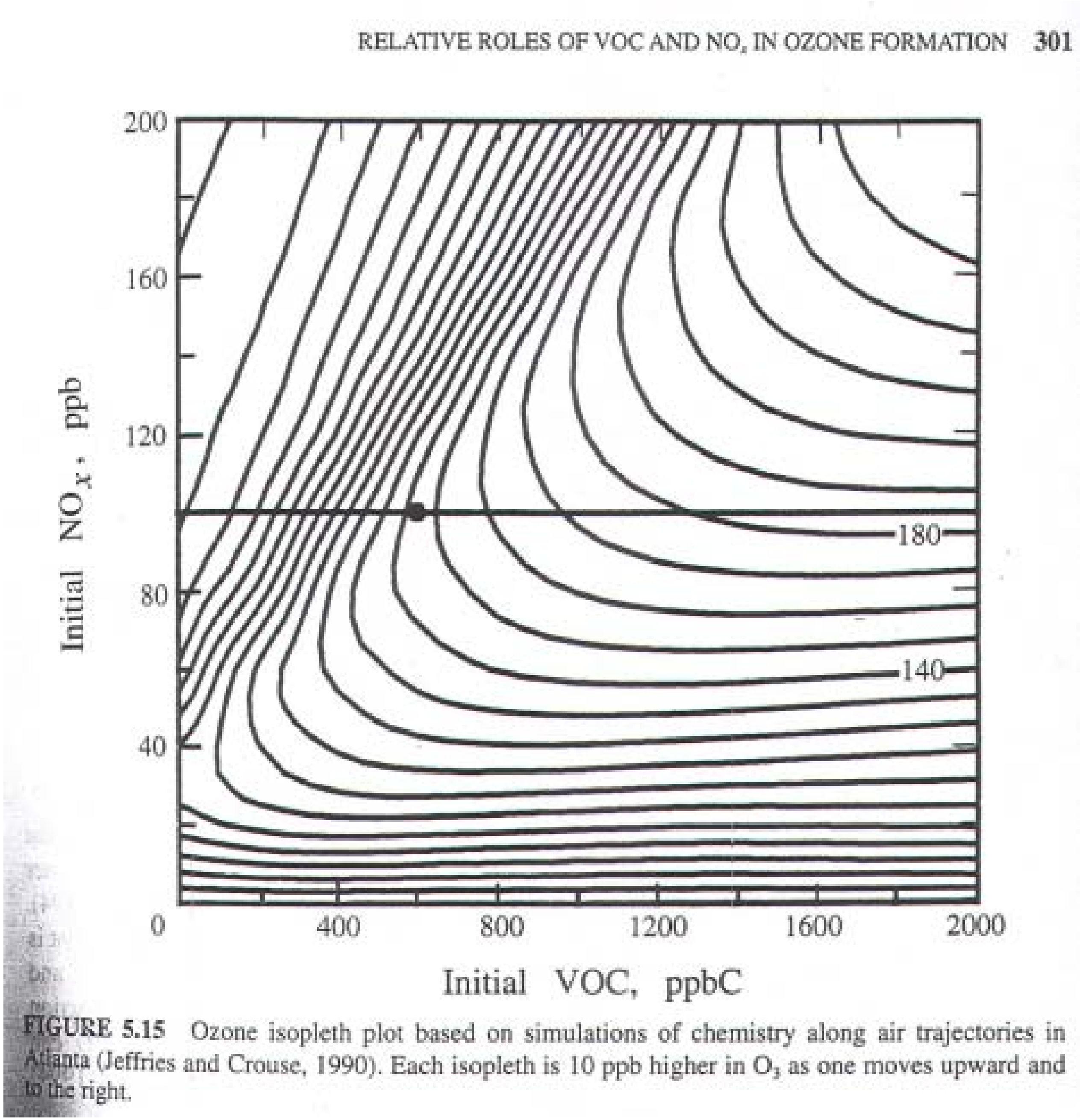
Biogenic RH/VOC Emissions

From Decidious and Coniferous Forest:
Isoprene and Terpene

Strong dependence on Temperature and Radiations
(PAR+ Photosynthetic Active Radiation)

Biogenic NO Emissions

From surface, bacteria



RELATIVE ROLES OF VOC AND NO_x IN OZONE FORMATION 301

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

Atmospheric Chemistry and the OH Radical

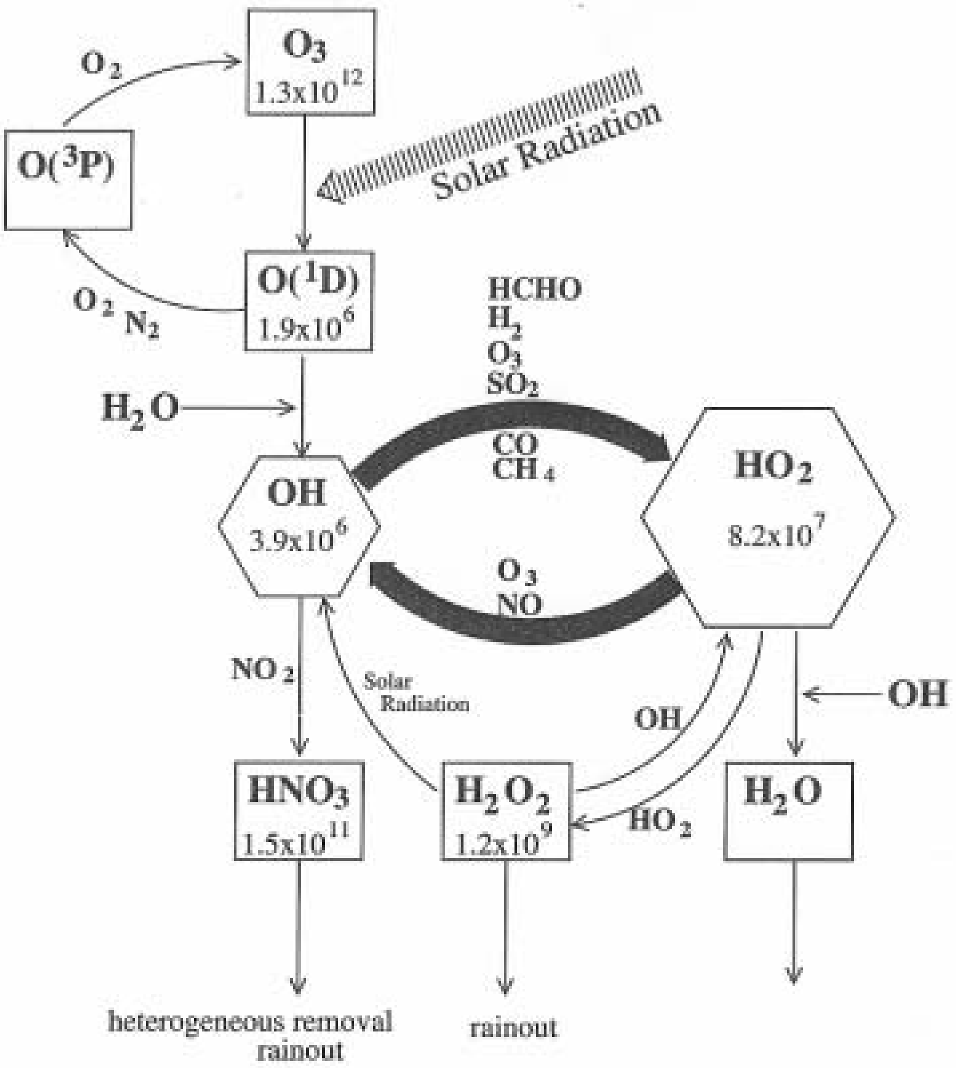


Figure 1.1: Production, recycling and destruction processes of OH in the troposphere. The numbers in the boxes and hexagons are number densities (molecules · cm^{-3}). After *Seinfeld and Pandis* [1998]

OH Daytime summer : 5-10 x 10^6 molecules/cm^3

Daytime winter : 1-5 x 10^6 molecules/cm^3

Night time : $< 2 \times 10^5$ molecules/cm^3

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.

Studies to analyse the Budget of a Species

- Emissions
- Chemical formation and destruction
- Dry and Wet Deposition

Can I understand the resulting concentrations?

Are emissions in balance with the loss terms?

Dry Deposition

Flux = Fs [conc. m/s]

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

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

$$= (\,C\;(z)ref \;-\; C\;(o)\,)\,/\;ra\;(z)$$

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

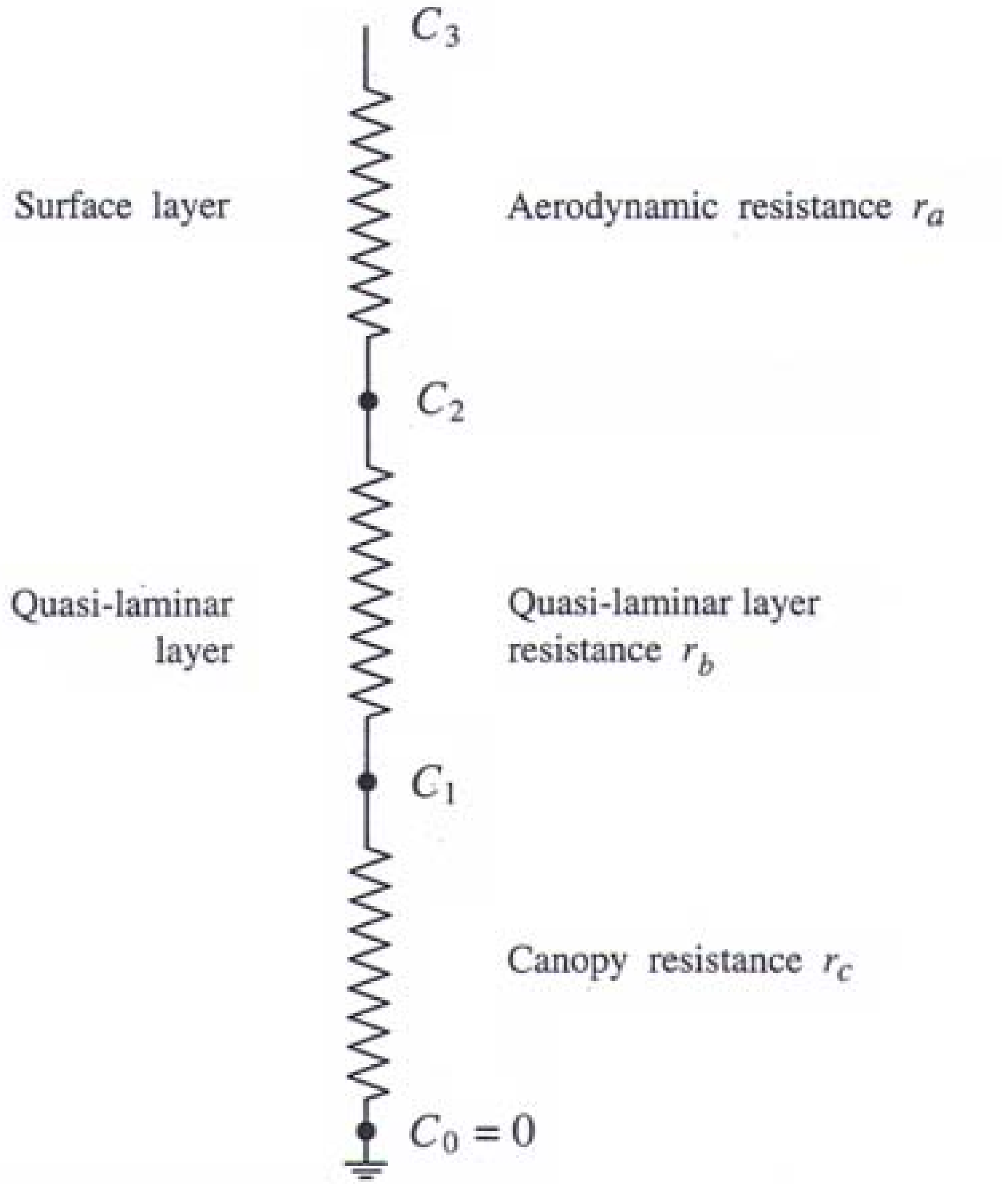


FIGURE 19.1 Resistance model for dry deposition.

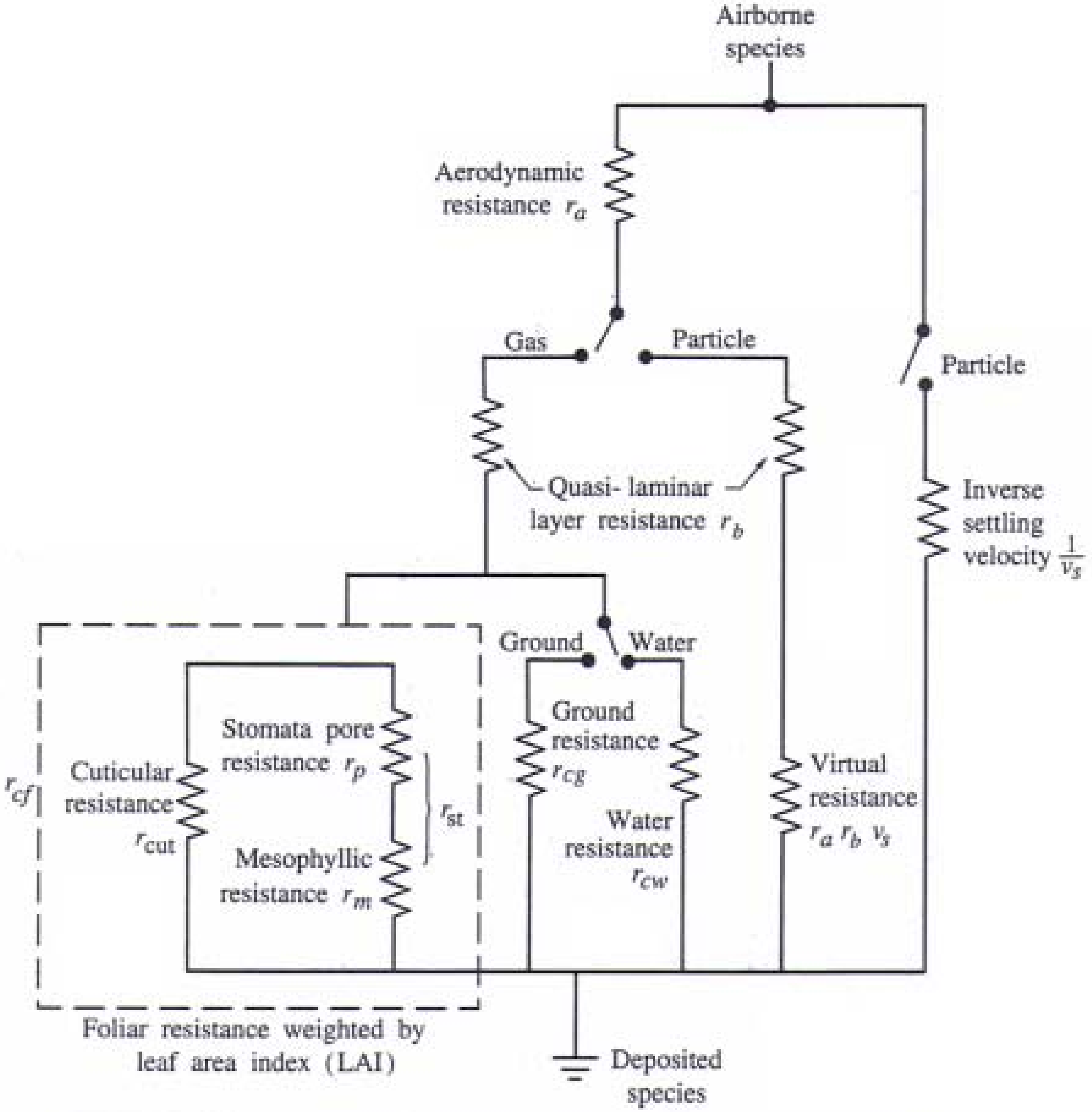
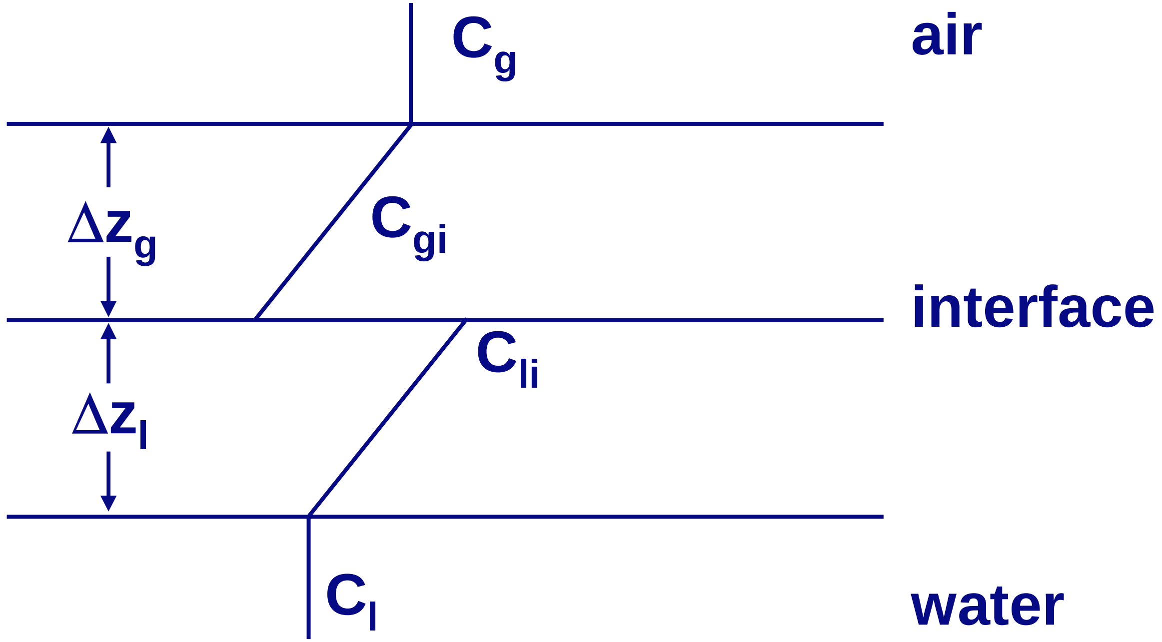


FIGURE 19.2 Extension of resistance model to include vegetative removal paths.

Dry deposition velocity V_d in cm/ s

	Grassland	**Water**
SO_2	0.8	0.4
O_3	0.8	0.05
HNO_3	2.5	1.0
NO_2	0.5	0.02

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)

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

kg, kl : fct (windspeed)

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

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

Below cloud scavenging of species C is given by

$$\frac{dC}{dt} = \frac{\Lambda_{bc} * P}{\Delta z}$$

Λ_{bc} = Below-cloud scavenging coefficient
P = precipitation rate [m/s]
z = scavenging scale depth [=1000 m]

The scavenging coefficients

Component	**Λ_{bc} (*10^6)**
SO_2	0.15
HNO_3	0.5
NH_3	0.5
H_2O_2	0.5
HCHO	0.05

Overview of below cloud scavenging coefficients for gases

For particles the wet deposition is calculated by:

$$\frac{dC}{dt} = \frac{A * P}{V_{rd}} * \overline{E}$$

$A = 5.2\ m^3\ kg^{-1}\ s^{-1}$

P = precipitation rate [m/s]

V_{rd} = Fall speed of rain droplet [m/s]

E = Collection efficiency

SO_4	0.1
NO_3	0.1
NH_4	0.1
PPM fine	0.1
PPM coarse	0.4

Collection efficiency for aerosol particles

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

Terra 10^{12}
Giga 10^{8}
Mega 10^{6}

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

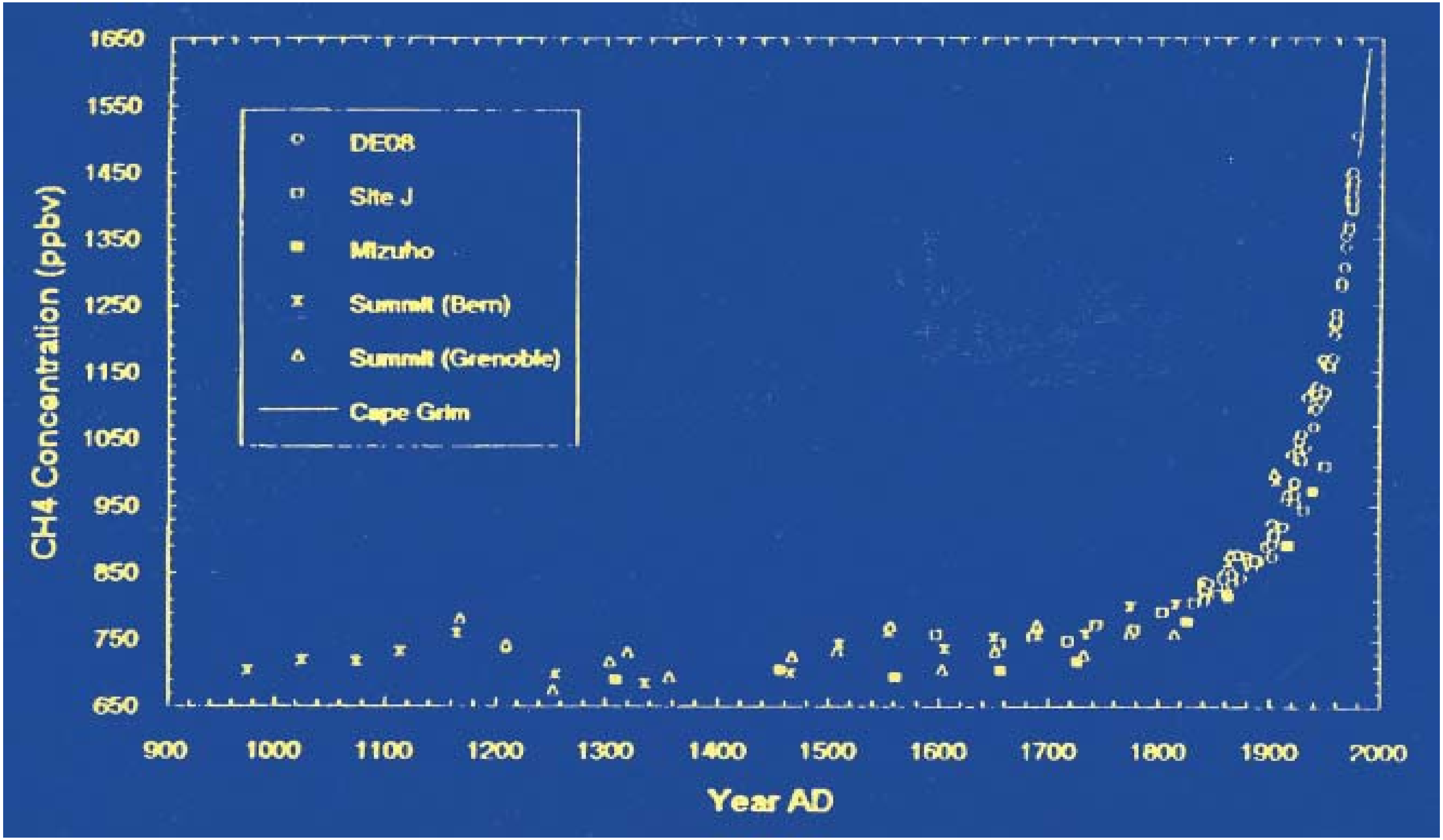
Aerob : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

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


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

Trend increase CH_4-concentration

1970-1985 : 1.5 % / year

1985-1989 : 0.8 % / year

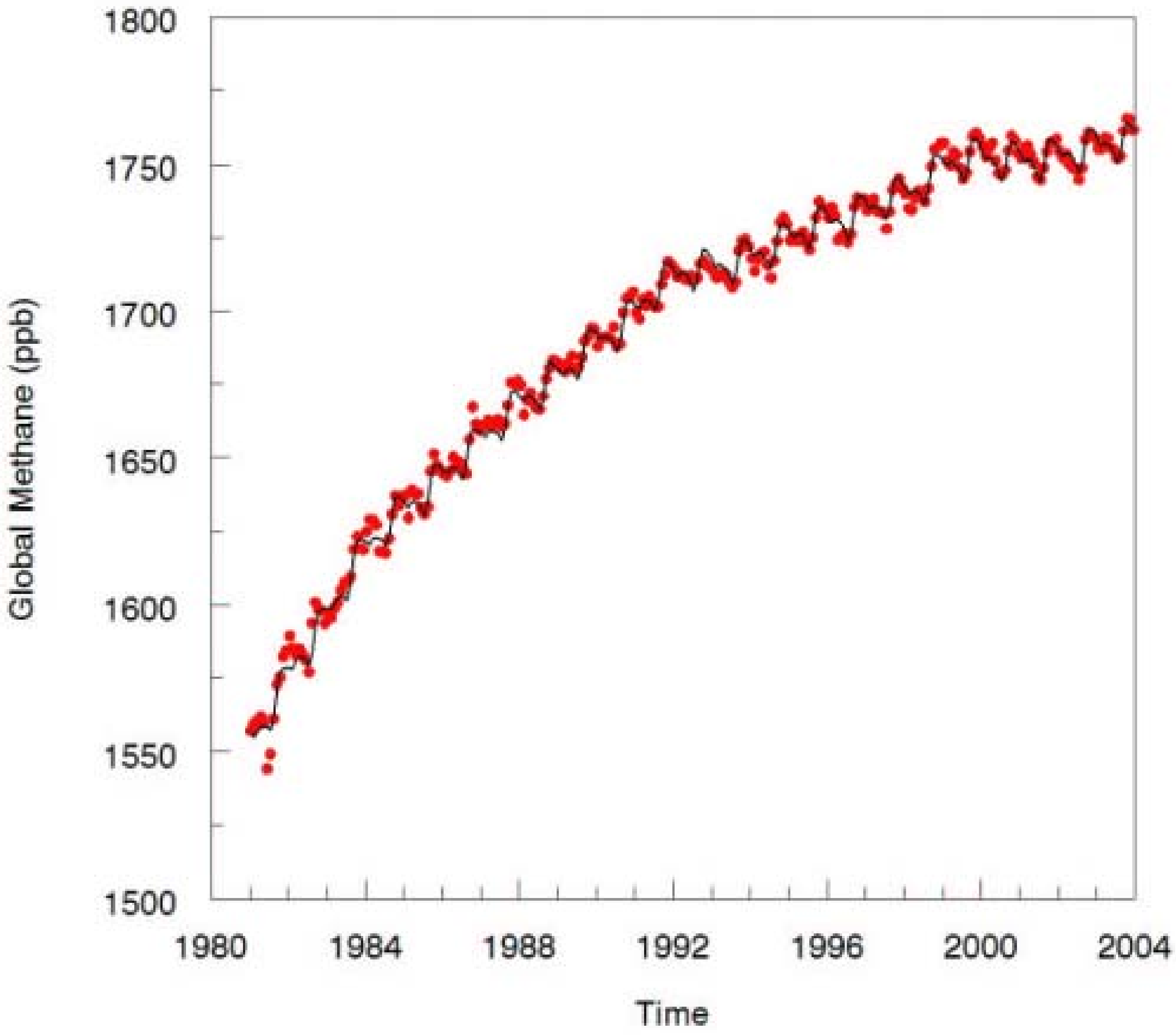
around 1993 : 0 %

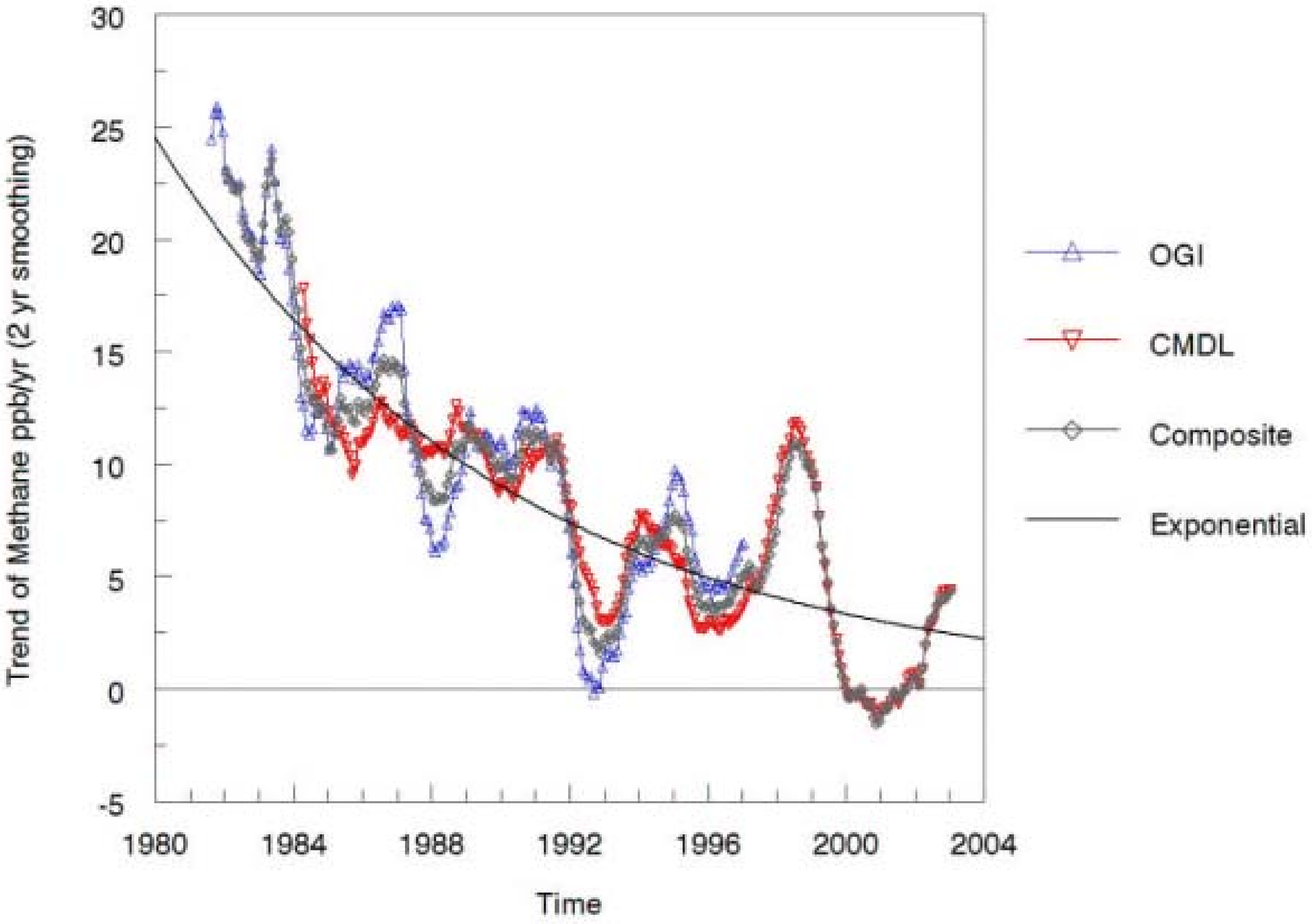
1995-2003 : 0.3 % / year

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

M. Khalil et al

“Atmospheric Methane: Trends and Cycles of Sources and Sinks”, Draft Paper 01/2007


1800
1750
1700
1650
1600
1550
1500
Global Methane (ppb)
1980
1984
1988
1992
1996
2000
2004
Time



Trend of Methane ppb/yr (2 yr smoothing)
30
25
20
15
10
5
0
-5
1980
1984
1988
1992
1996
2000
2004
Time
OGI
CMDL
Composite
Exponential

Conclusions

Global CH_4-emissions and life time (OH) constant over the last 20 years

Result: No further increase in CH_4-concentrations

Fluctuations due to temporary increases in CH_4-emissions on the northern hemisphere

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 $h\nu$

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

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	%

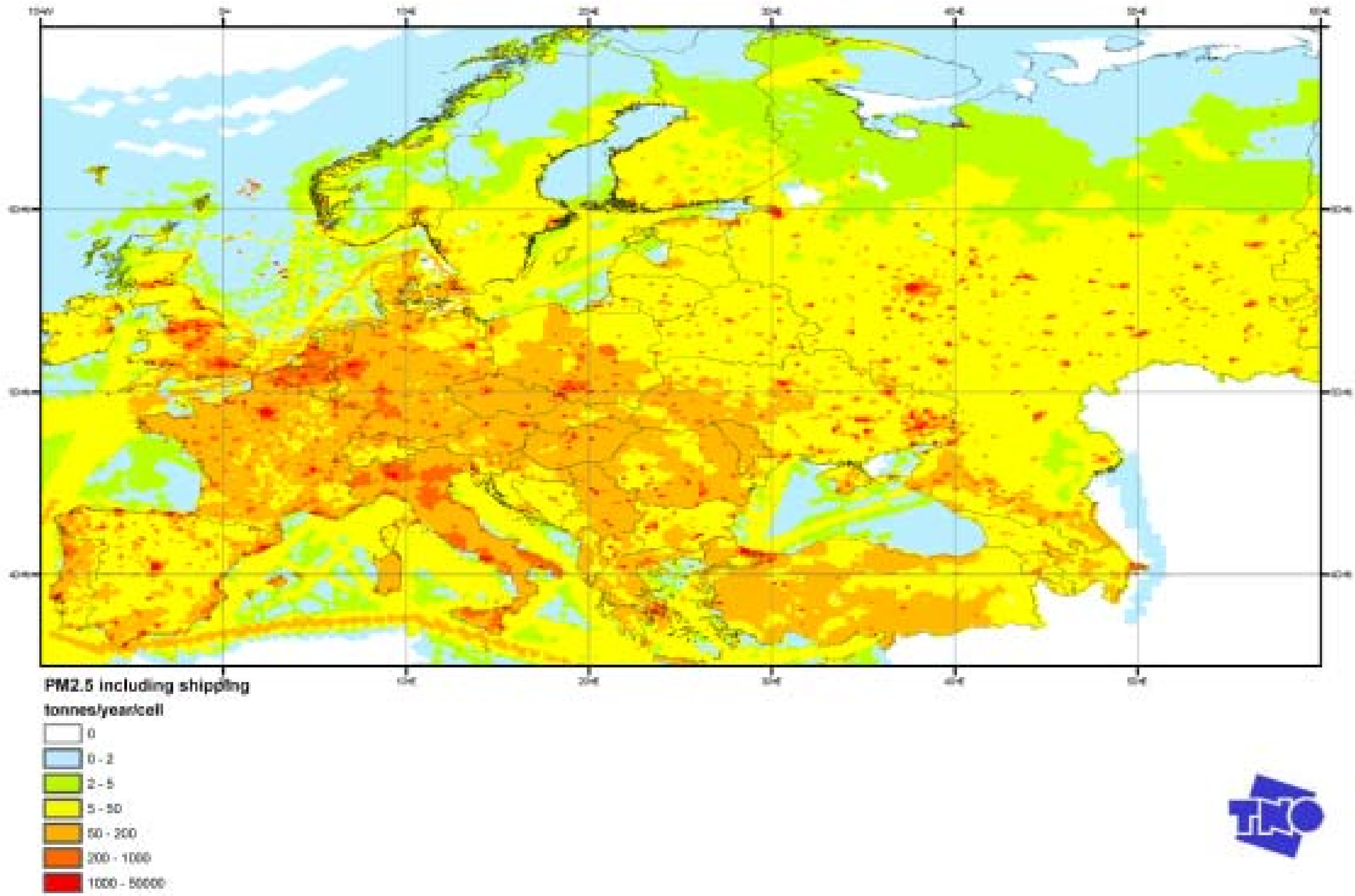
Biogenic Emissions

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

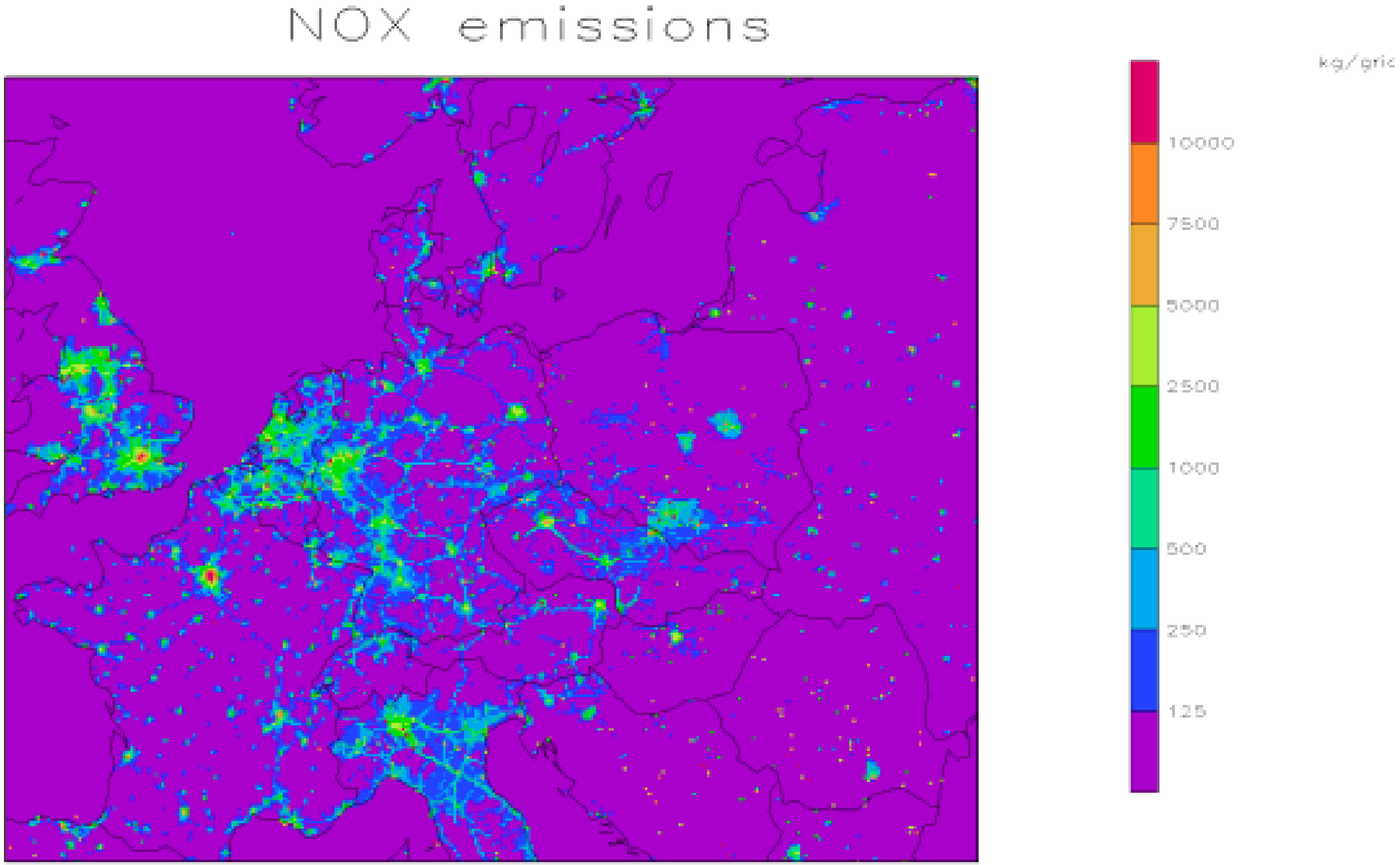
Natural emissions

- 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)

Anthropogenic PM2.5 emissions over Europe in 2000 including shipping



Resolution needed?
Emission Test file TNO Europe NOX total at ~ 6 x 6 km



A more refined Budget Analysis

- By the development and use of Chemical Transport Models-CTM’s
- CTM’s describe the relation between emissions and concentrations/deposition

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

Examples of the use of Chemical Transport Models

- Global Models
  - Troposphere + Lower Stratosphere
  - Horizontal grids of ca. 2.5 x 2.5 latlong

- Regional Models, for example covering Europe

- Urban Models

- Local Models, Street scale

CTM's are 3-D Eulerian Grid Models

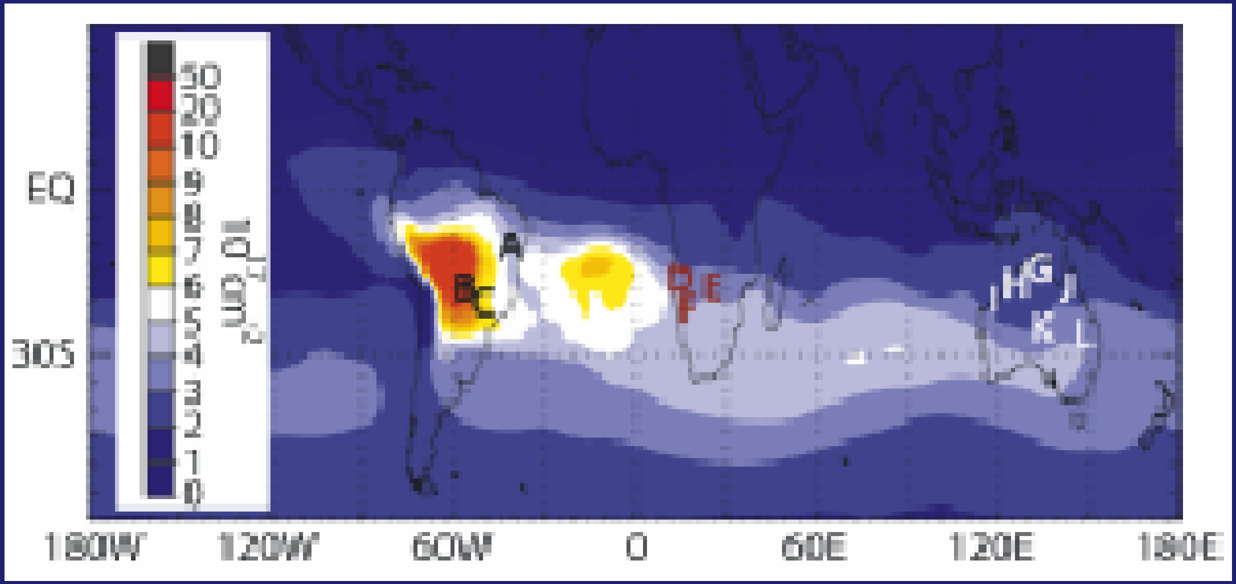
Horizontal grids globally 2.5 x 2.5 latlong, down to 1 x 1
Europe 25 x 25 km^2 down to 10 x 10 km^2

Vertical layers 10-30 upto 5 - 10 km

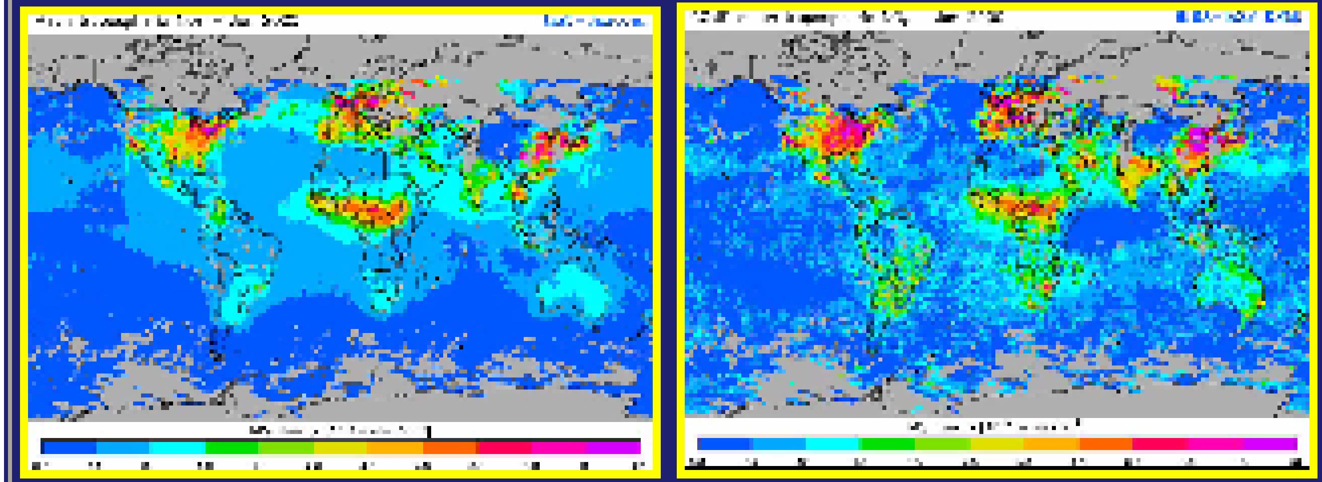
Concentrations calculated in boxes

Local models: Plume models and line source/street canyon models
Often empirical models

Some examples of global modelling with the TM-5 Model



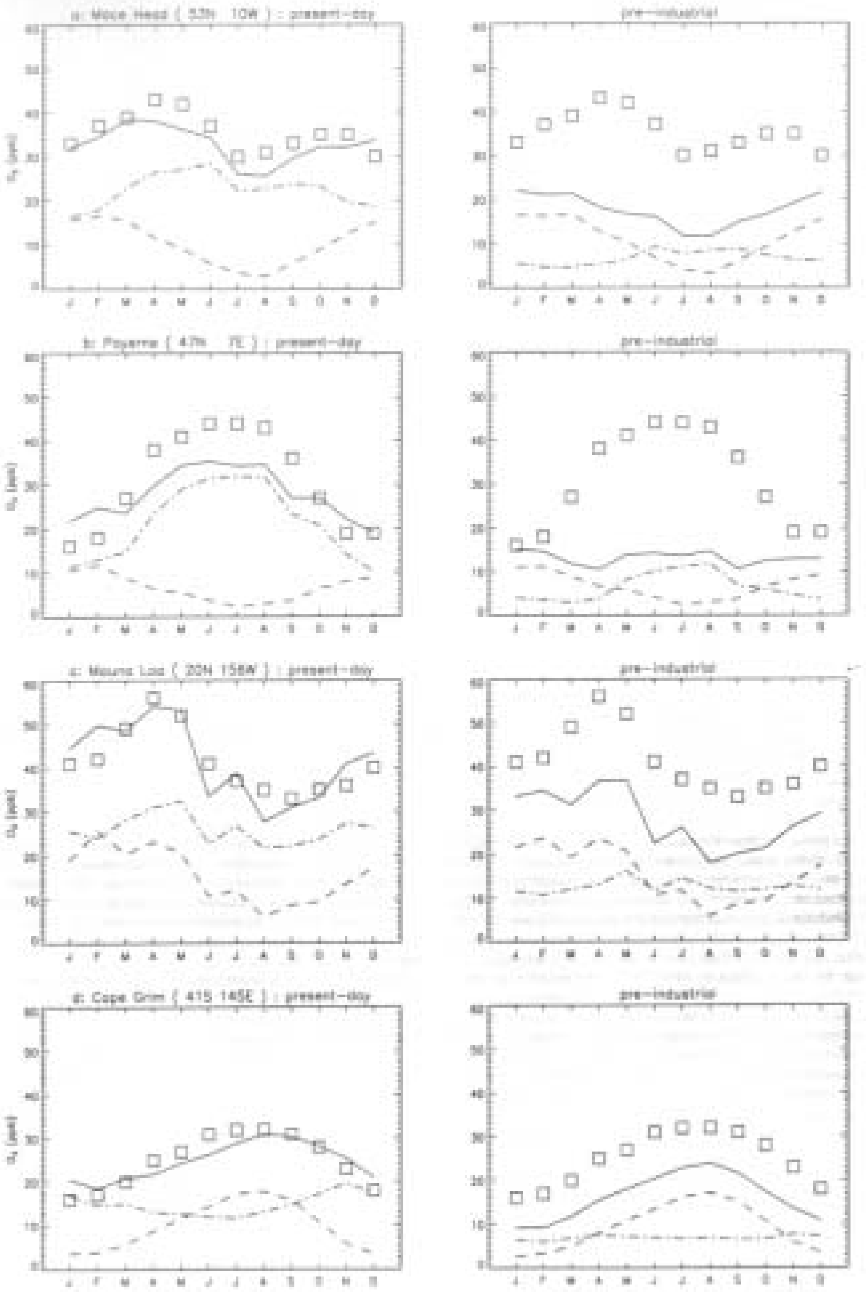
CO total columns from biomass burning emissions in South America. From Gloudemans et al. (2006).



Movie of tropospheric NO_2 columns for the year 2000 (**left**) compared with GOME satellite observations (**right**). See Van Noije et al. (2006).

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


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

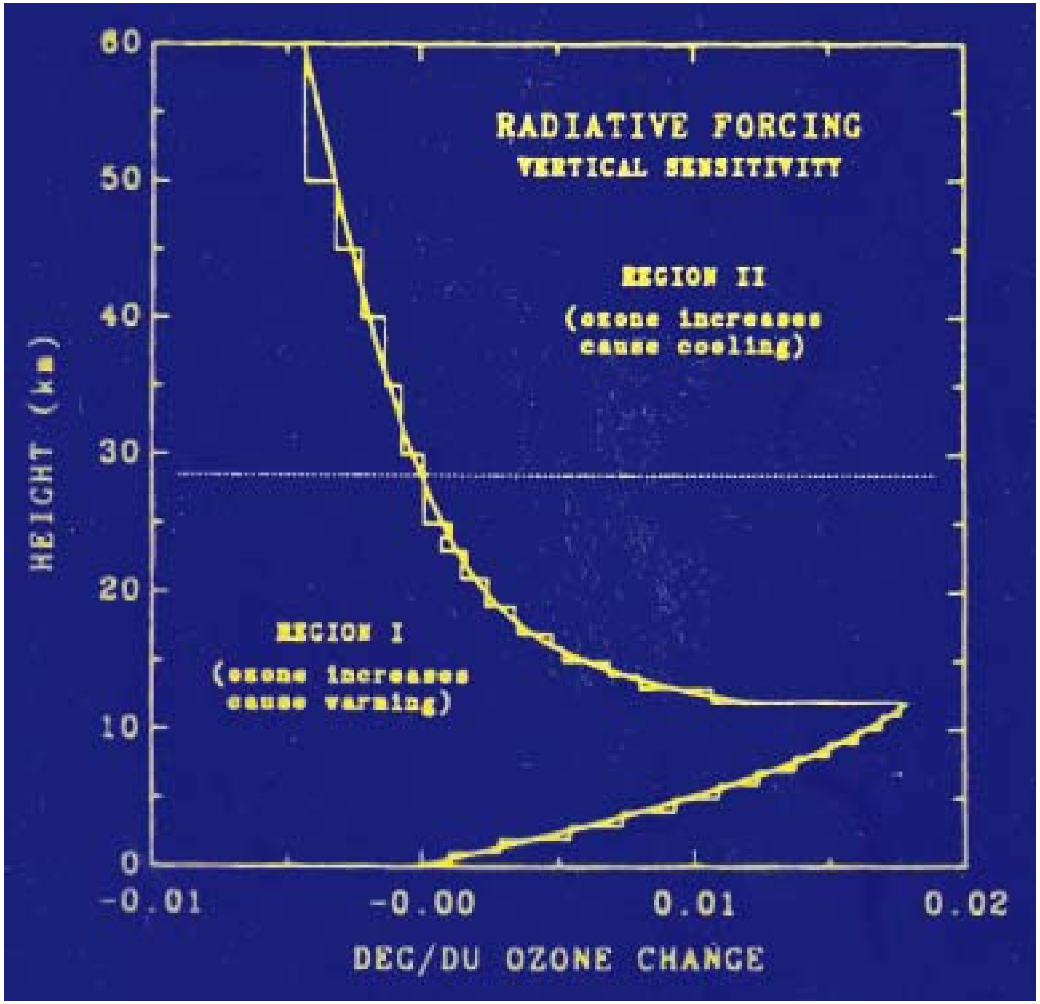
O_3 Tropospheric Budget

By anthropogenic emissions : 30 %

By biogenic emissions : 30 %

From stratosphere : 40 %

Radiative forcing by O_3 : 0.5 W/m^2 NH
0.3 W/m^2 SH



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

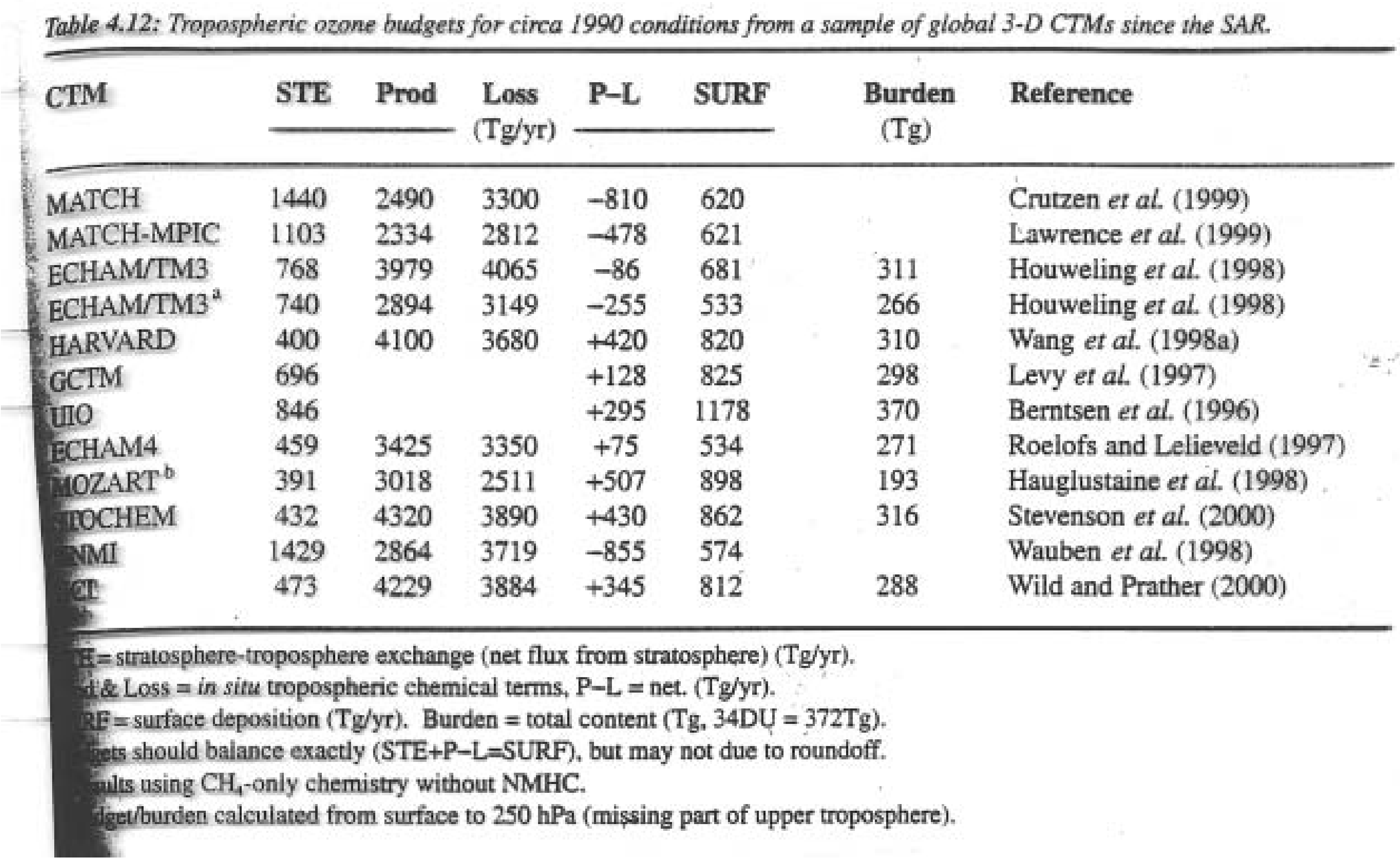
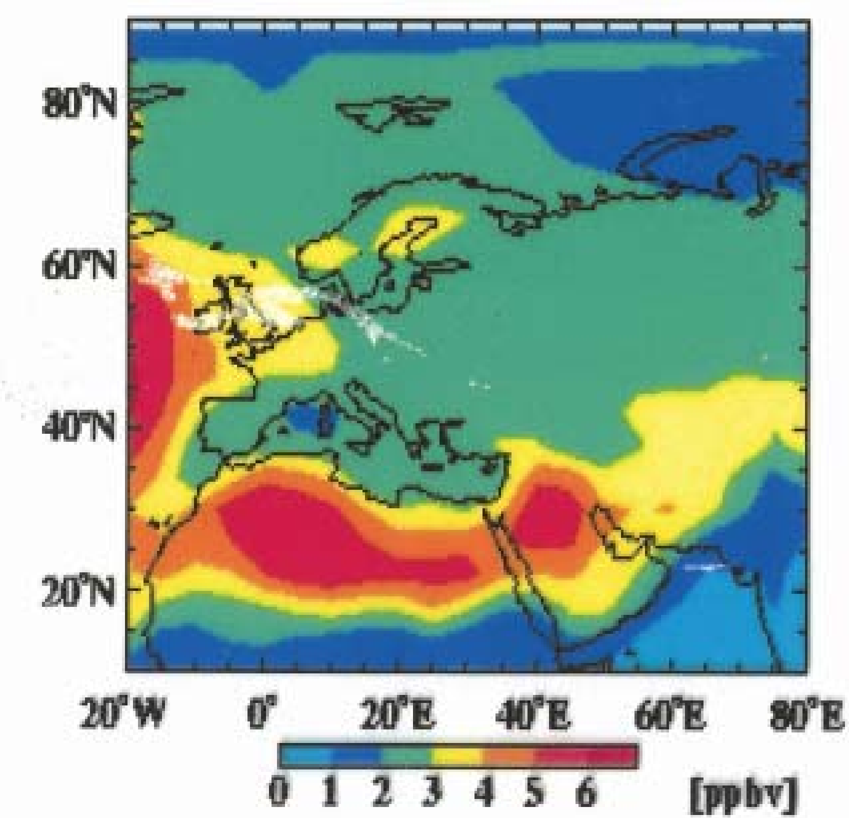


Table 4.12: Tropospheric ozone budgets for circa 1990 conditions from a sample of global 3-D CTMs since the SAR.

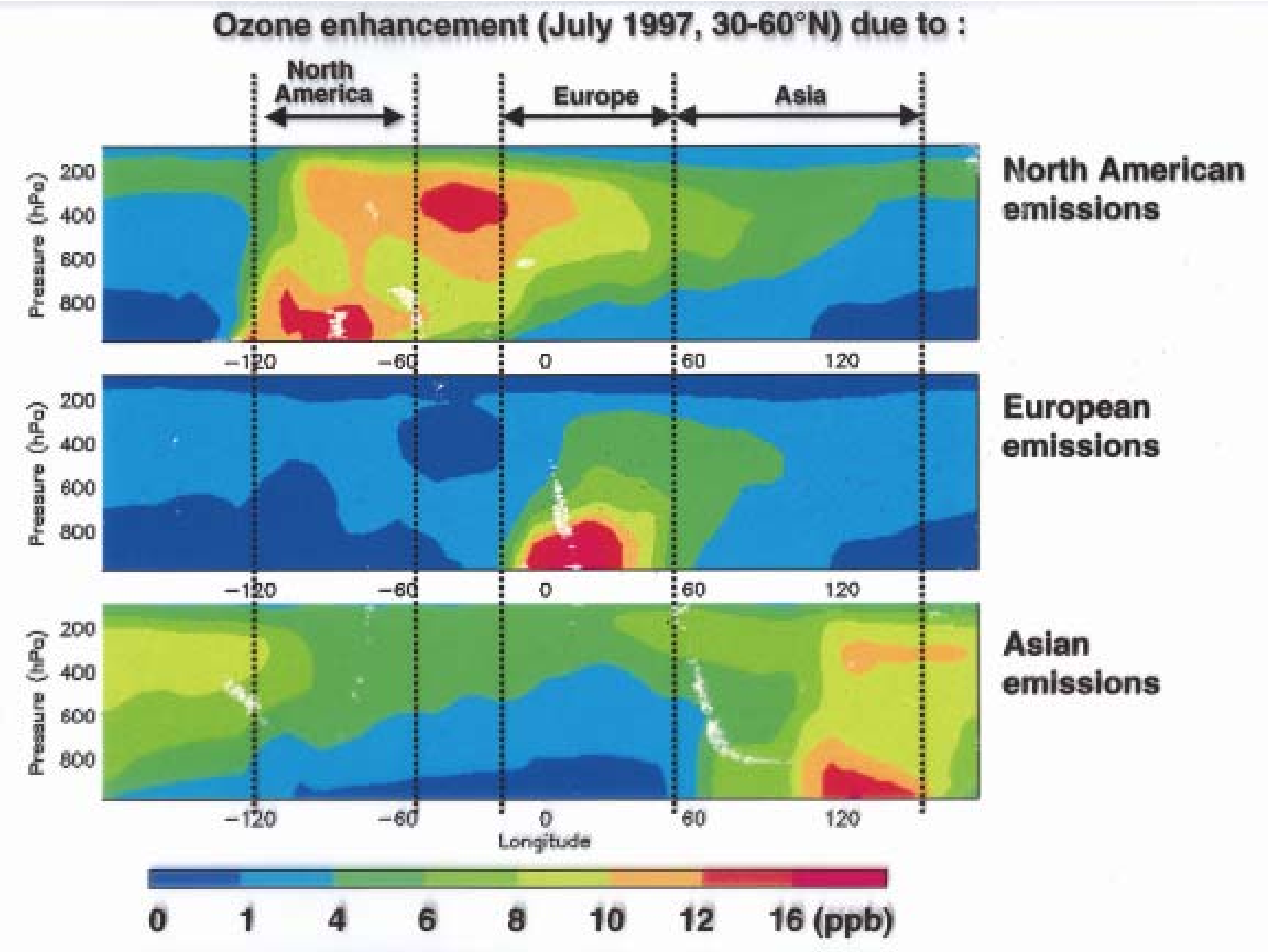
CTM	STE (Tg/yr)	Prod (Tg/yr)	Loss (Tg/yr)	P–L (Tg/yr)	SURF (Tg/yr)	Burden (Tg)	Reference
MATCH	1440	2490	3300	−810	620		Crutzen *et al.* (1999)
MATCH-MPIC	1103	2334	2812	−478	621		Lawrence *et al.* (1999)
ECHAM/TM3	768	3979	4065	−86	681	311	Houweling *et al.* (1998)
ECHAM/TM3[a]	740	2894	3149	−255	533	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)
TOCHEM	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).

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 :
North America
Europe
Asia
North American emissions
European emissions
Asian emissions
Pressure (hPa)
200
400
600
800
−120
−60
0
60
120
Longitude
0
1
4
6
8
10
12
16 (ppb)

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

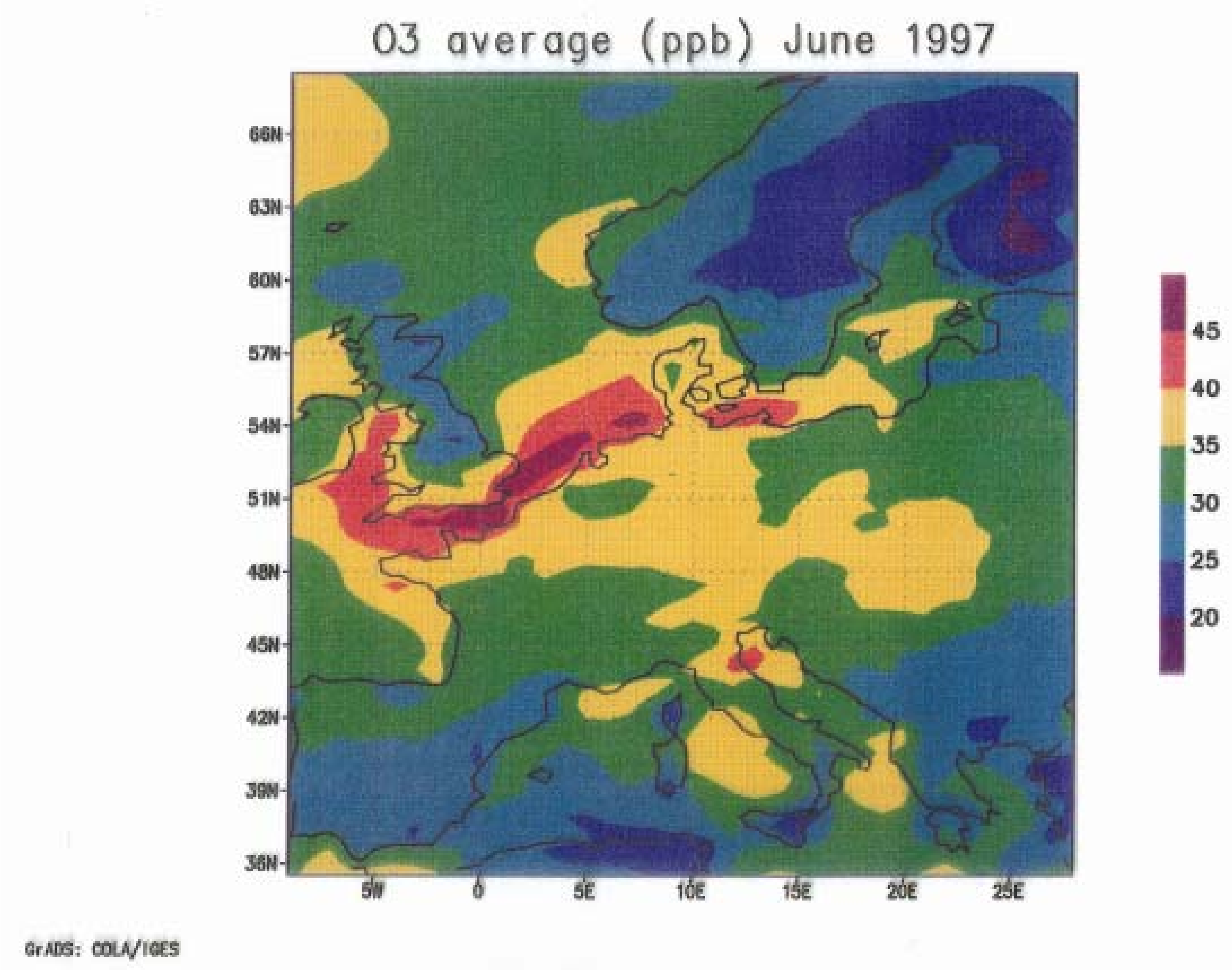
Gasphase chemistry (O_3) and aerosol physics and chemistry

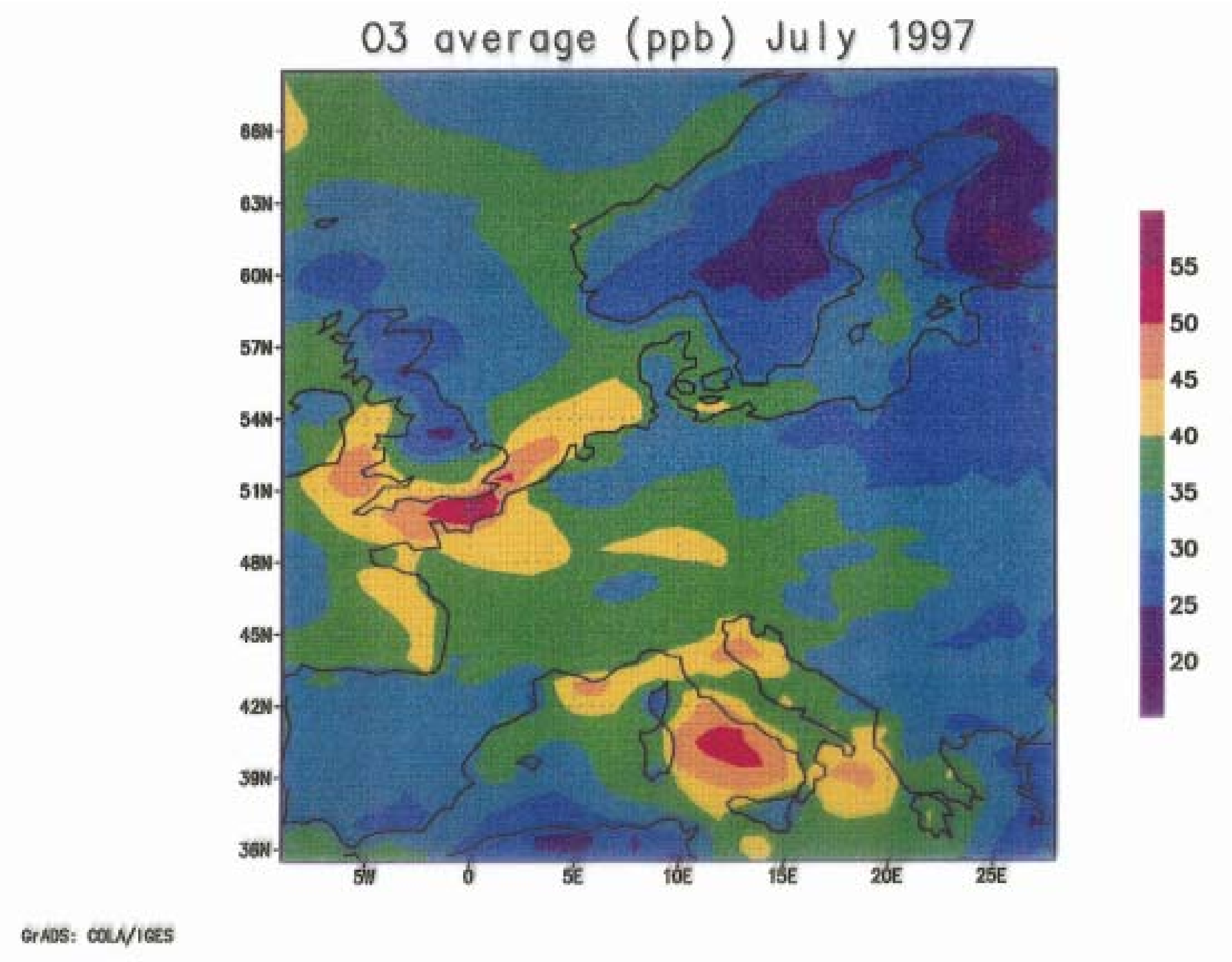
Required input data

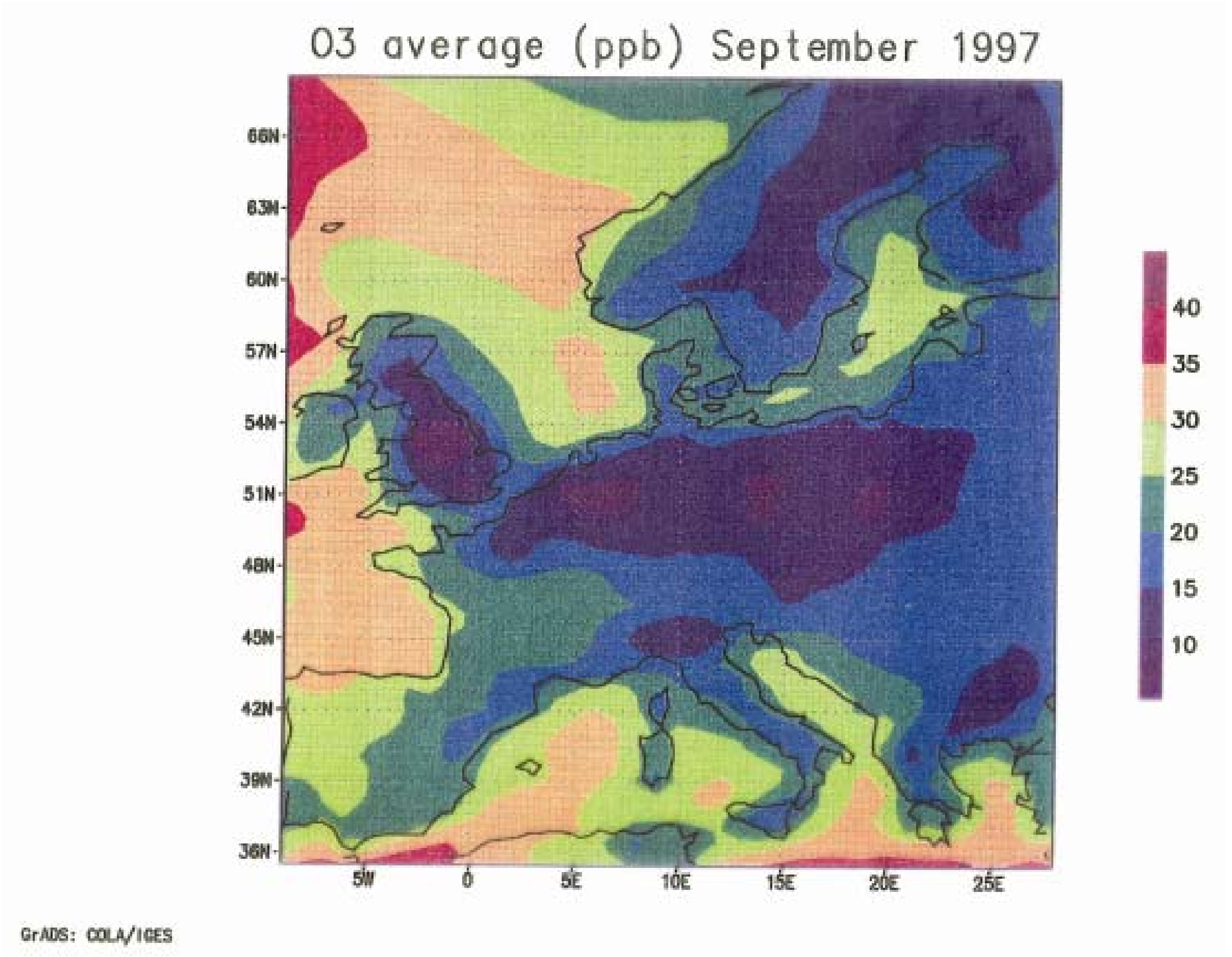
- Boundary conditions from observations, or global modelling (TM-5)
- Anthropogenic and biogenic and natural emissions
- Land use data base
- Diagnostic meteorological fields (by Eberhard Reimer)
- Prognostic meteorological fields:
  - DWD-LM
  - NWP
  - MM5-reanalysis
  - ECMWF-ERA 40

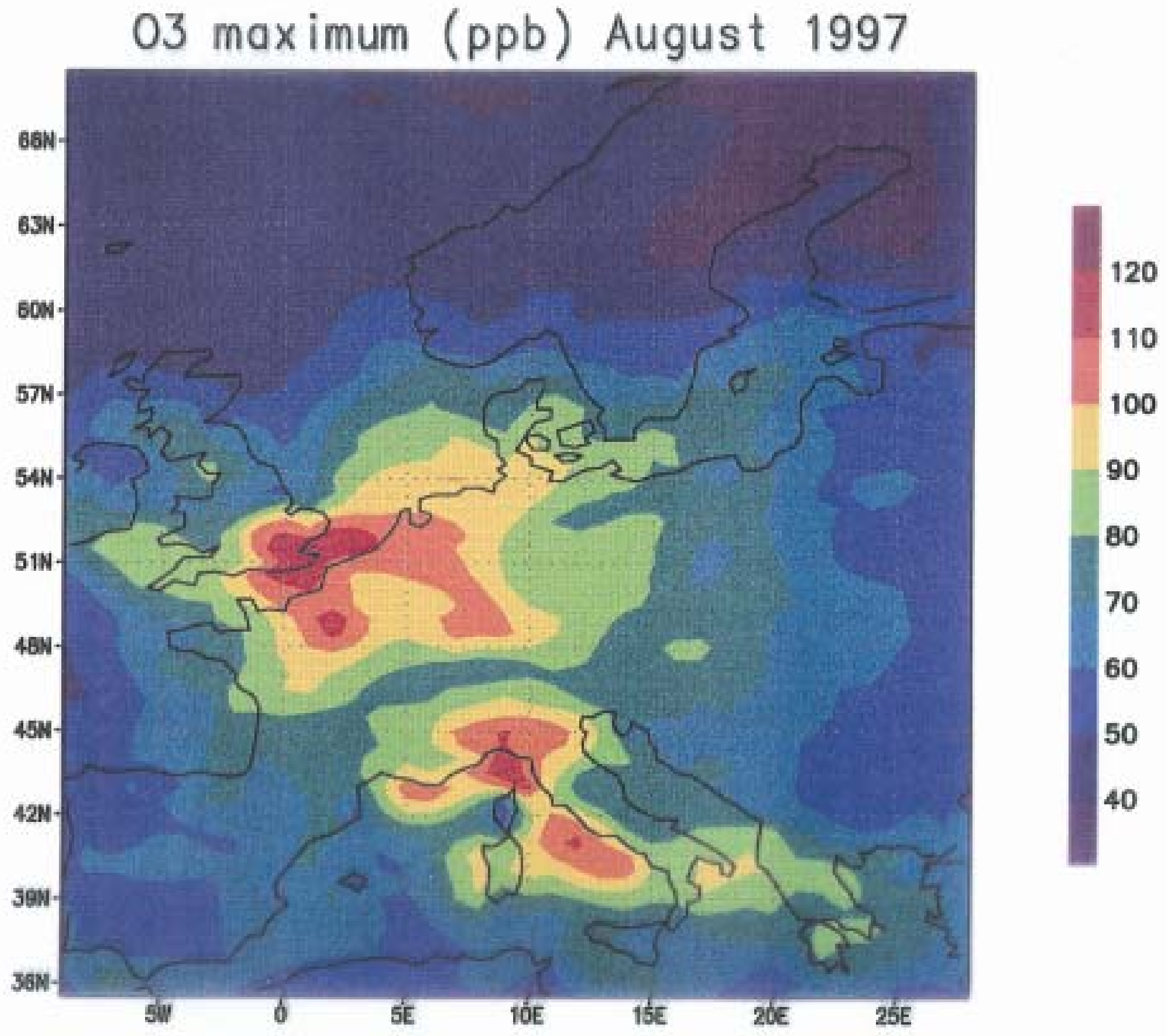
Model calculations hour-by-hour for one year, or more

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


O3 average (ppb) July 1997
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
5W
0
5E
10E
15E
20E
25E
55
50
45
40
35
30
25
20
GrADS: COLA/IGES


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



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

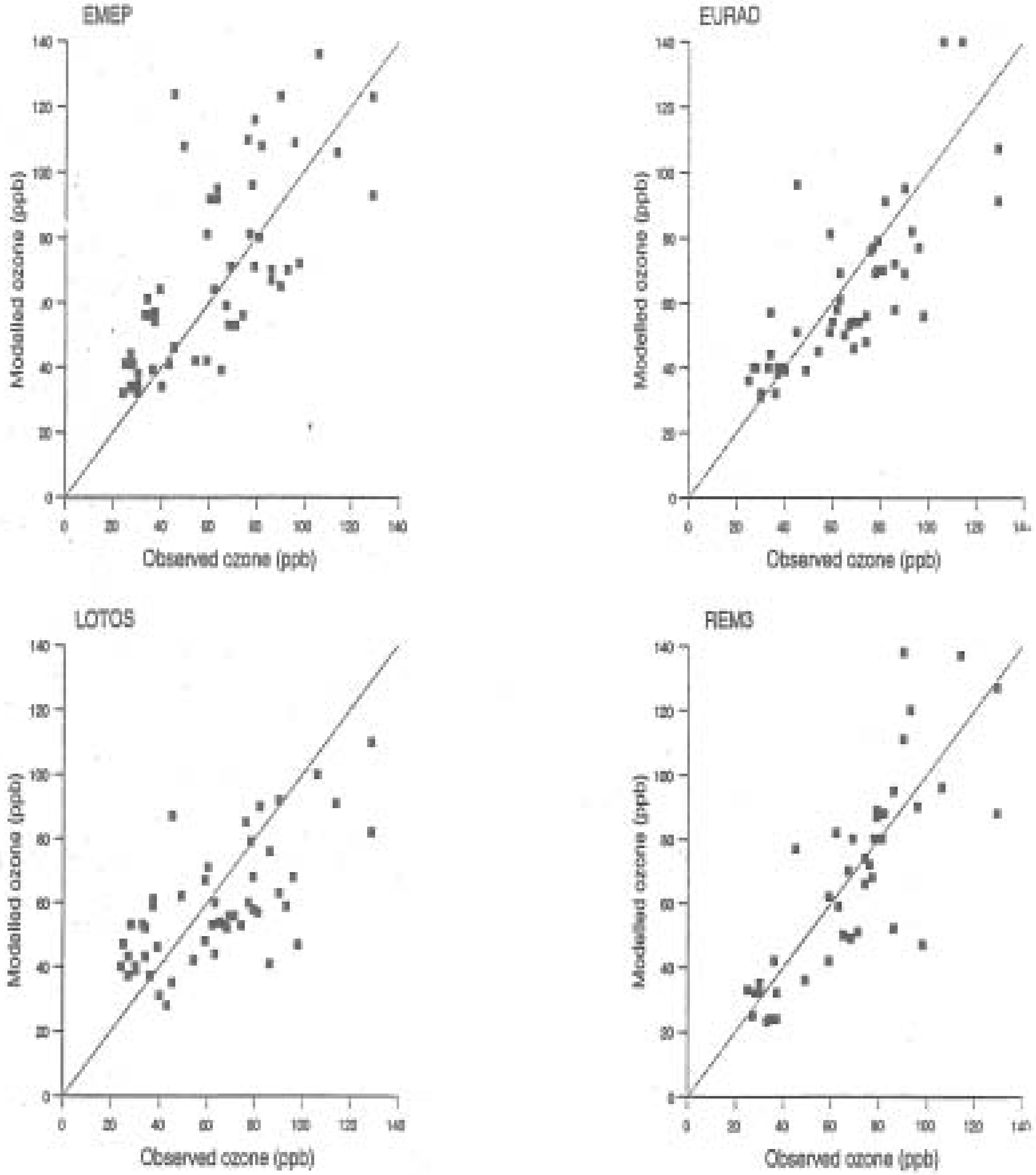
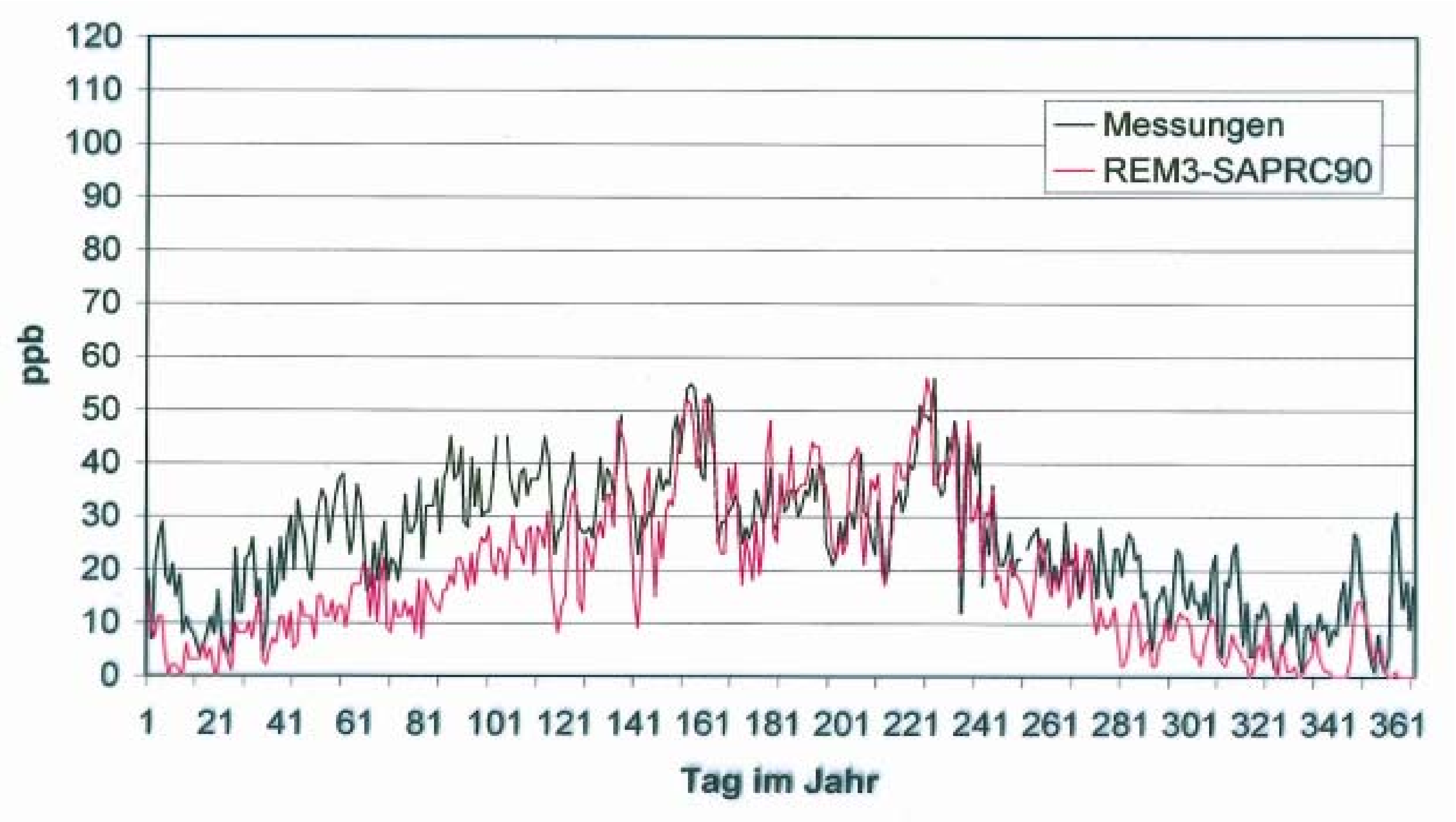
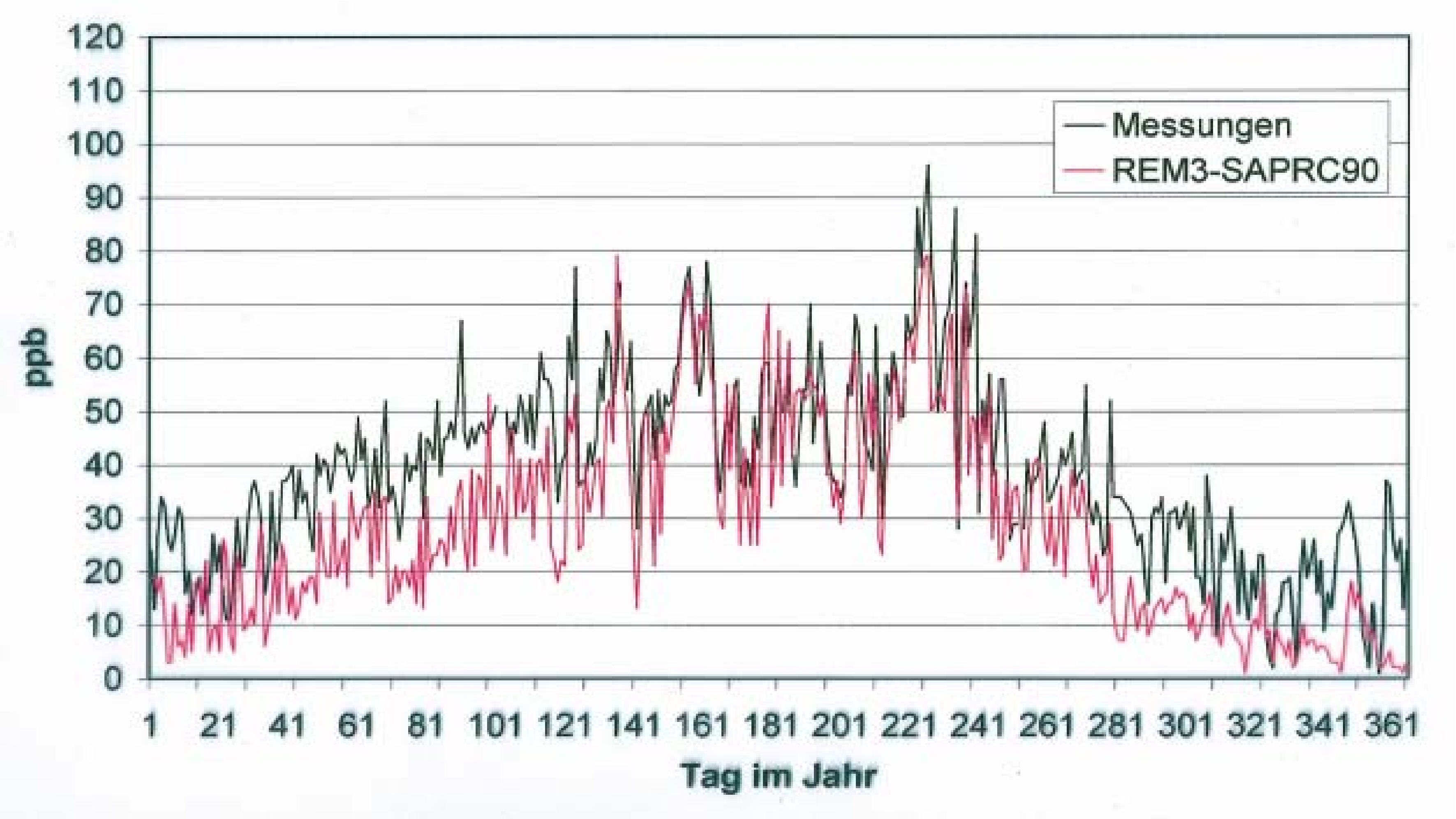


Figure 6.4: Scatter diagrams of modelled versus observed ozone at 12 UTC, 4th August, 1990.

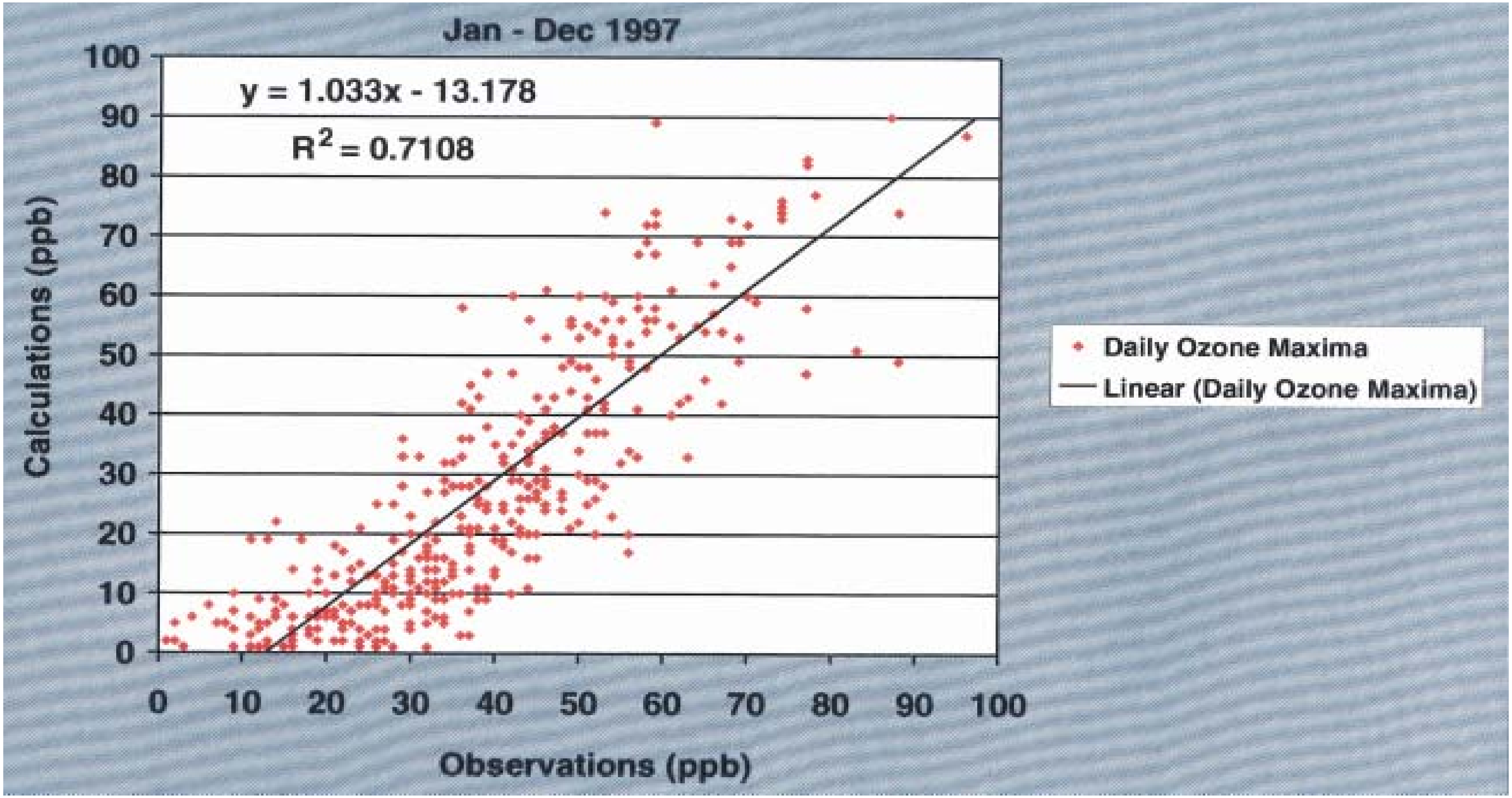
Waldhof: Tagesmittelwerte Ozon 1997



Waldhof: Tagesmaxima Ozon 1997



REM3-CBM4: Station Waldhof



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

- Policy based on
  - Average Accumulated Exceedance: AAE
  - Accumulation over Threshold of 40 ppb O3 of forest: AOT40f
- AAE and AOT40f are weighted with sensitive areas, resp. forest

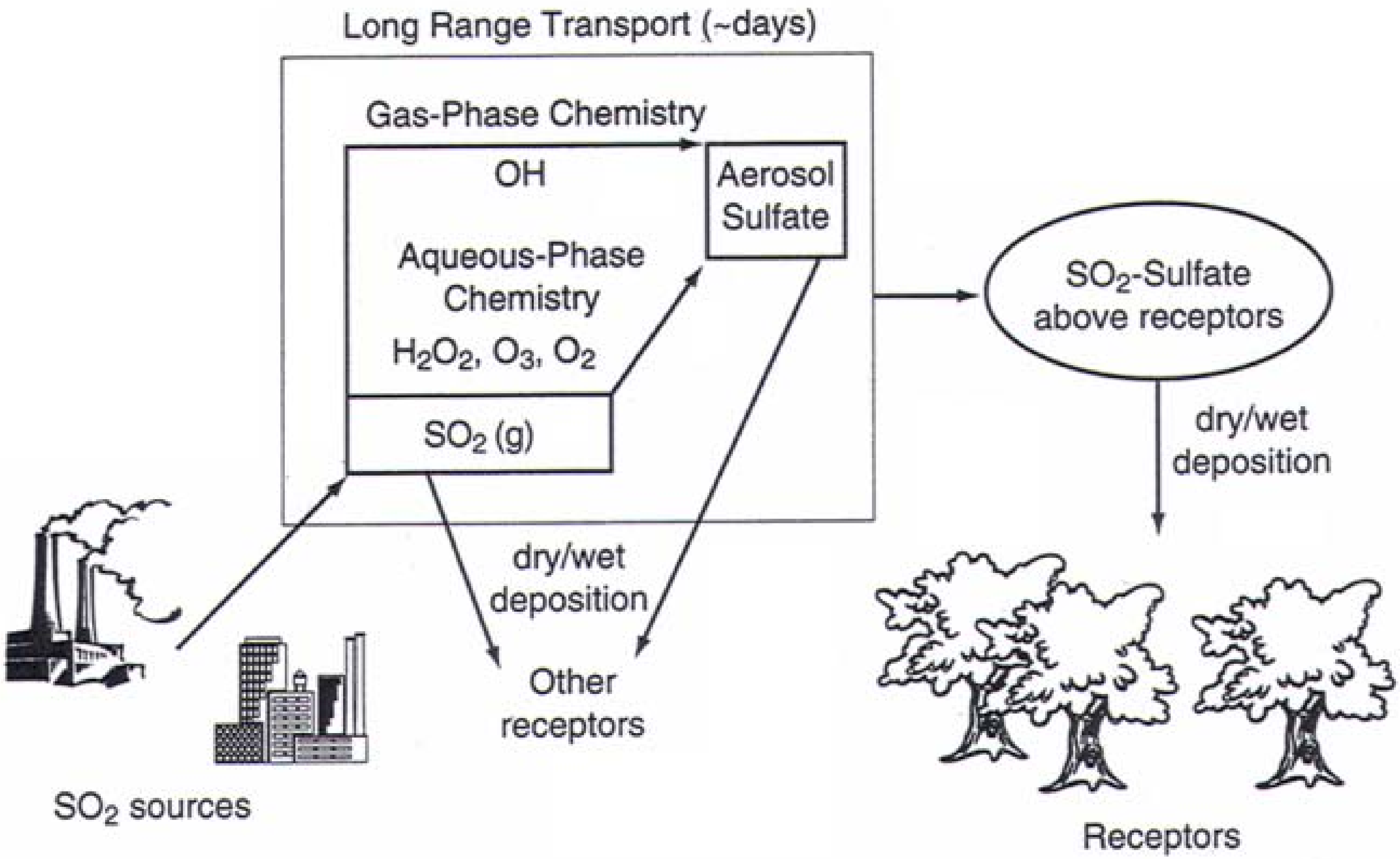
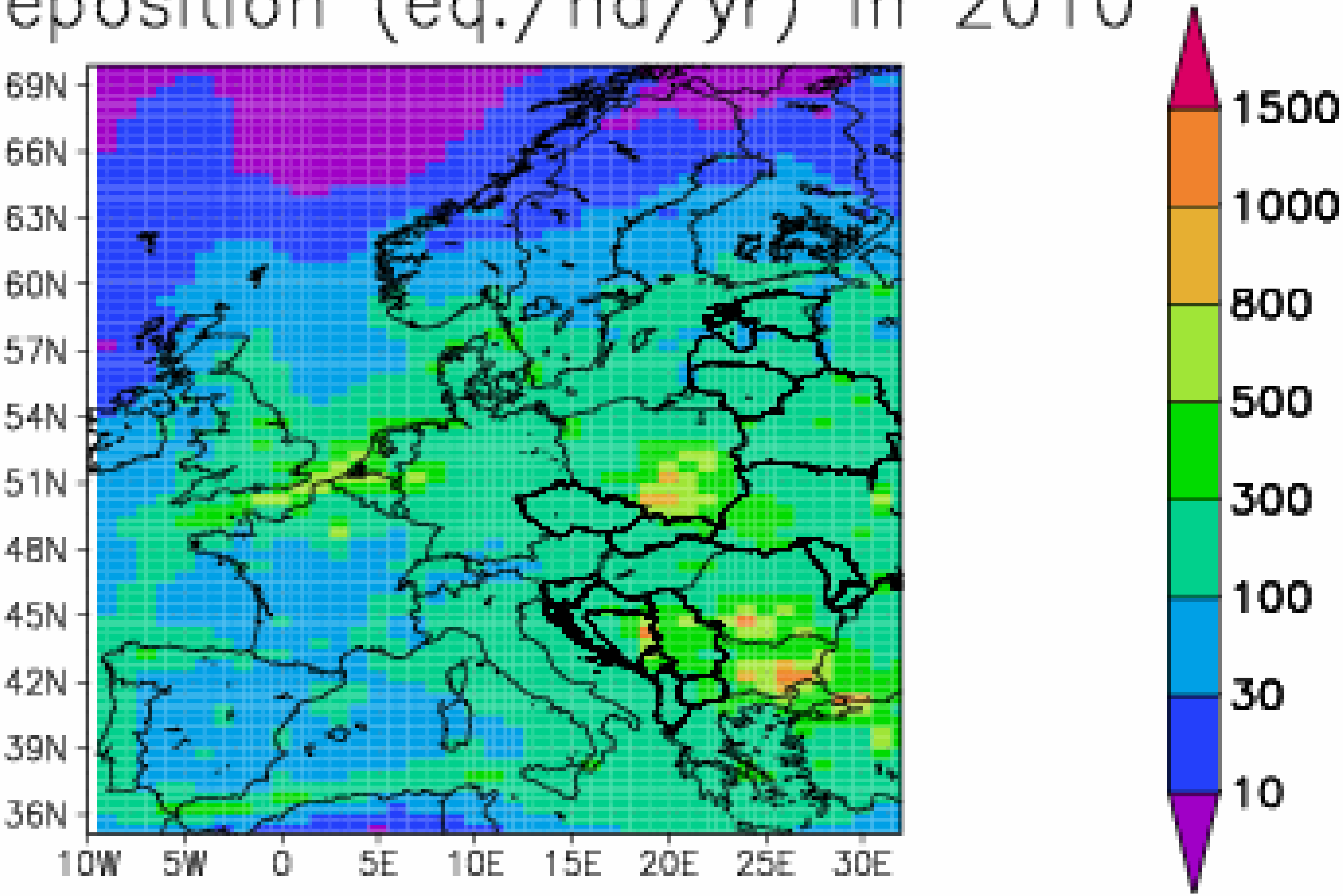
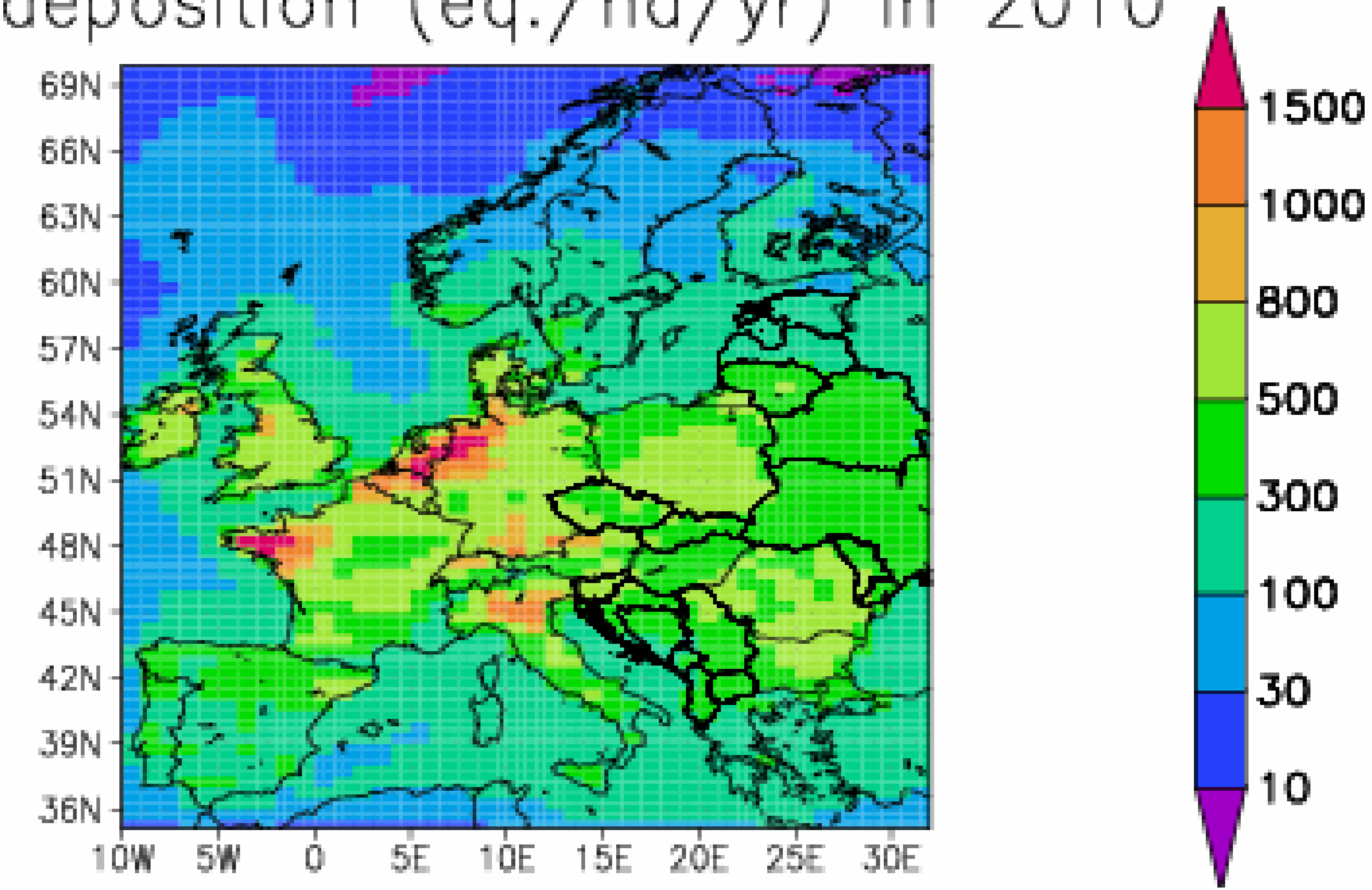


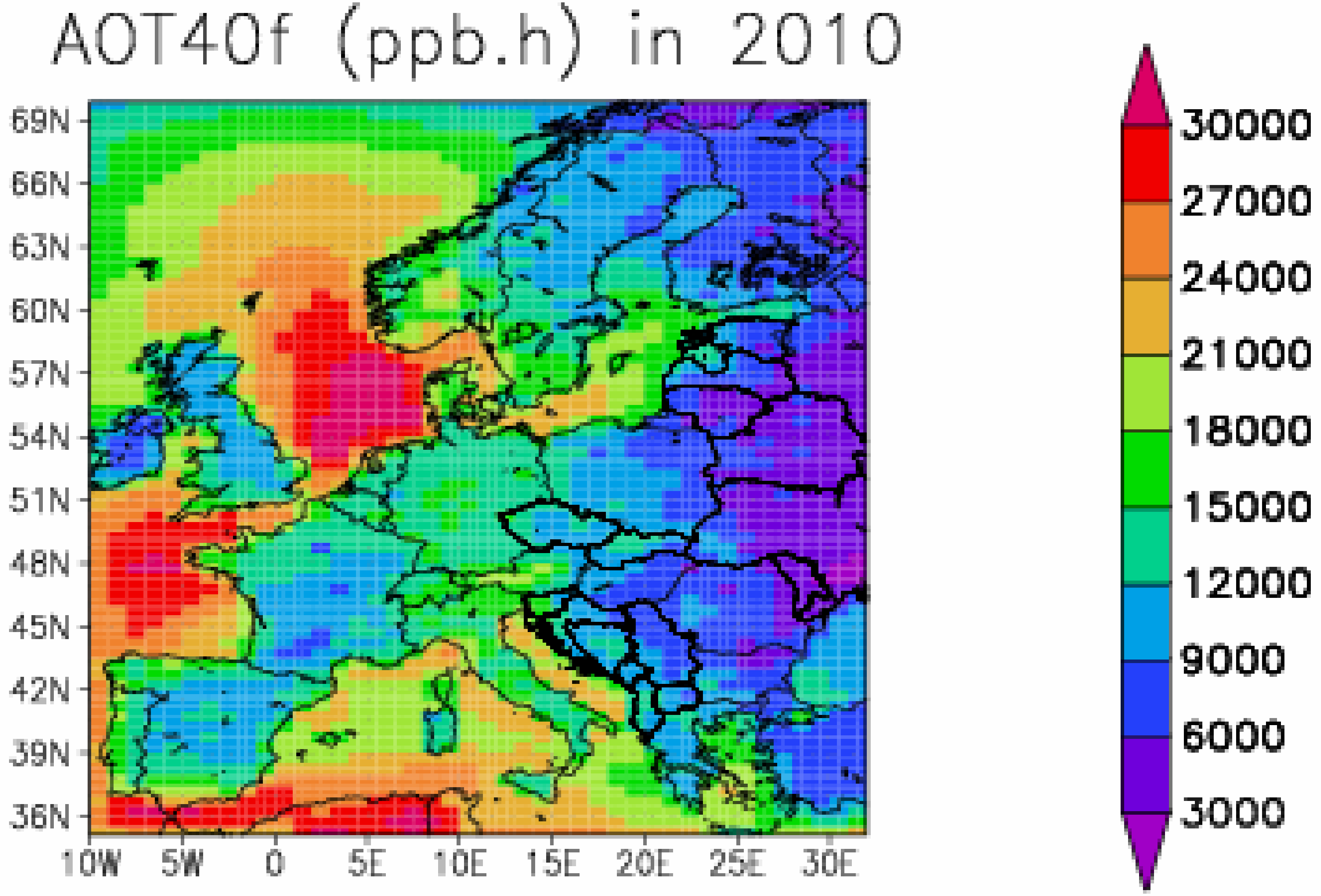
FIGURE 20.32 Conceptual depiction of atmospheric sulfur source–receptor relationship.

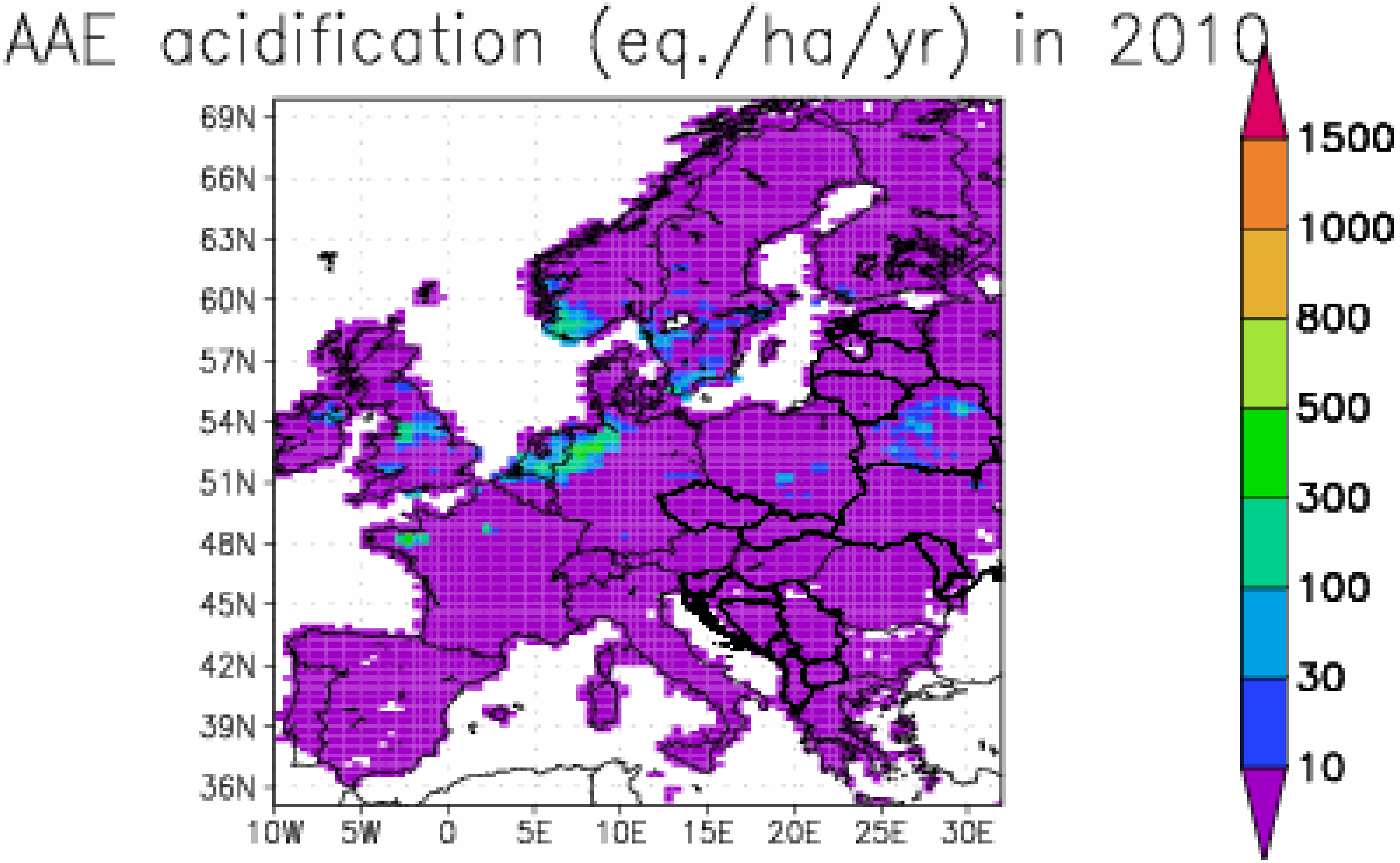
S-deposition (eq./ha/yr) in 2010



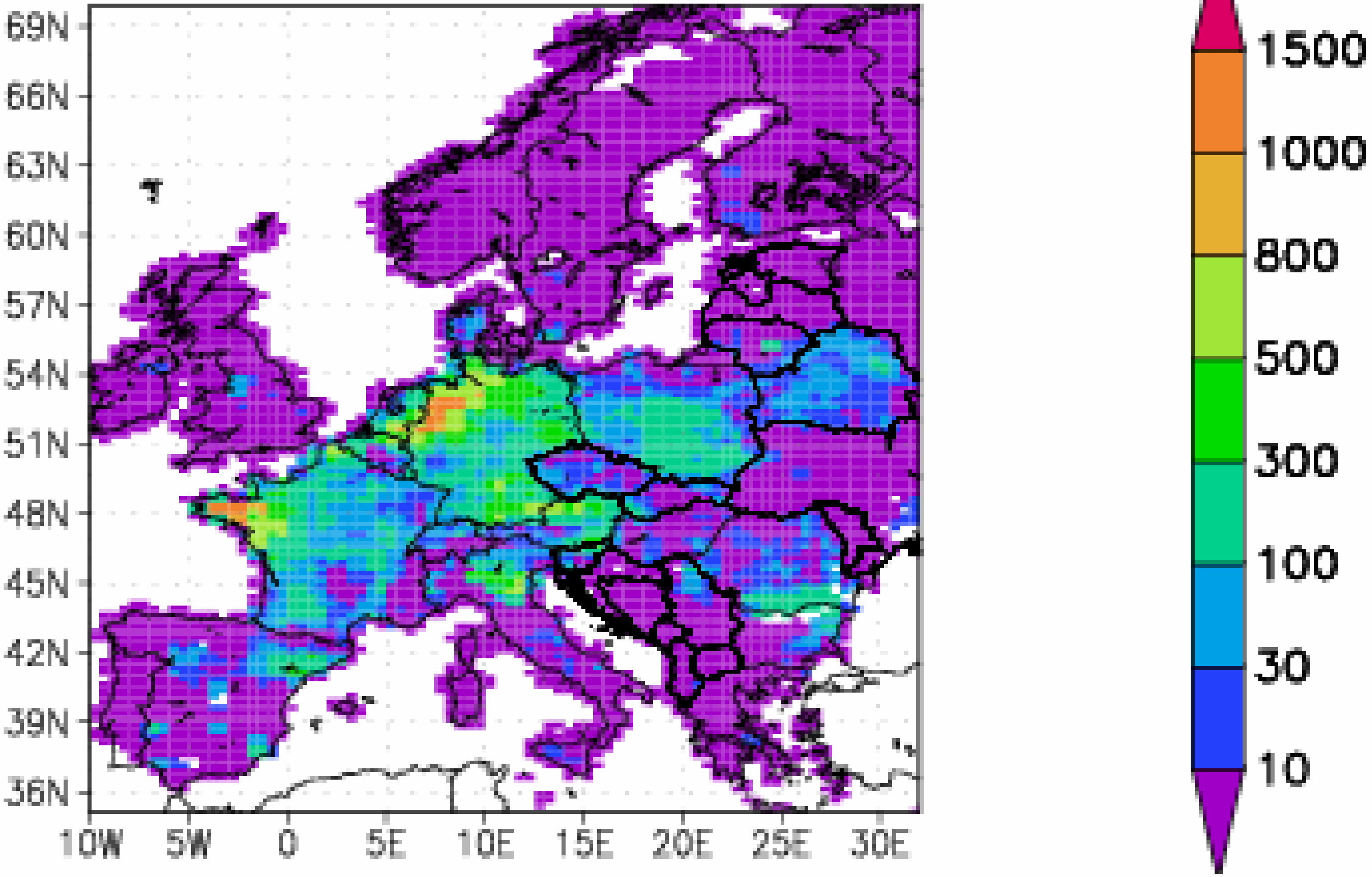
N-deposition (eq./ha/yr) in 2010



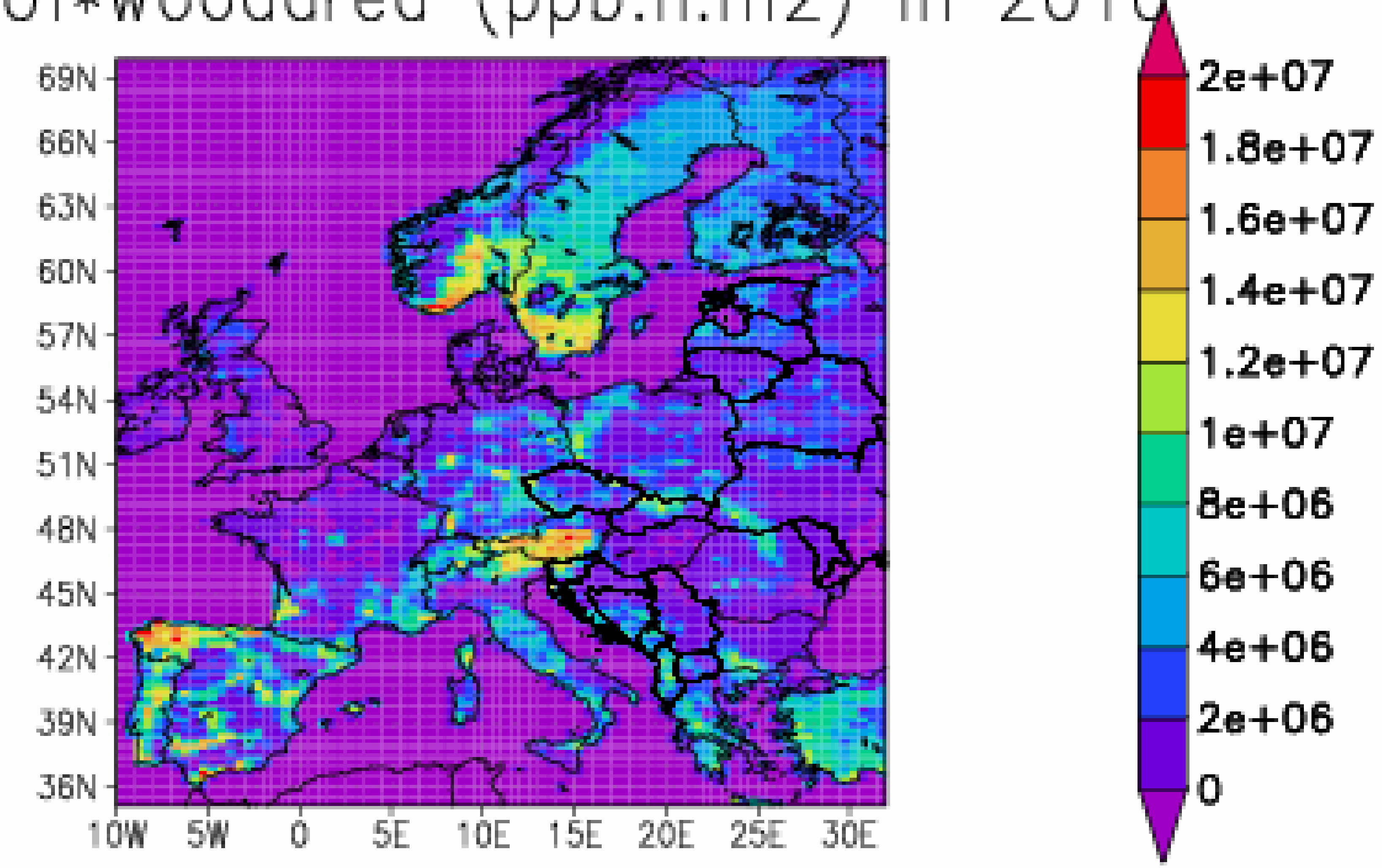

AOT40f (ppb.h) in 2010
69N
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
10W
5W
0
5E
10E
15E
20E
25E
30E
30000
27000
24000
21000
18000
15000
12000
9000
6000
3000


AAE acidification (eq./ha/yr) in 2010
69N
66N
63N
60N
57N
54N
51N
48N
45N
42N
39N
36N
10W
5W
0
5E
10E
15E
20E
25E
30E
1500
1000
800
500
300
100
30
10

AAE eutrophication (eq./ha/yr) in 2010



AOT40f*woodarea (ppb.h.m2) in 2010



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 : $r \sim$ wavelenght of light

Particle size < wavelenght of light: Rayleigh scattering

~ wavelenght of light: Mie scattering

II) Konzentrationen und Grenzwerten.

Bemerkung:

- Die Grenzwerten gibt es für PM_{10} und $PM_{2.5}$
- Basiert auf Epidemiologische Studien/Cohort usw.
- Nicht basiert auf Toxicologische Studien, deswegen kein Grenzwert für Russ/Black Carbon

Grenzwerten

- PM 10:
  - Jahresmittelwert 40 µgr/m^3
  - Tagesmittelwert 50 µgr/m^3, nicht mehr als 35 Tagen pro Jahr
- Grenzwert gillt „überall“ /hot-spots, und von 1-1-2005
- Mann darf das Anteil natürliches Feinstaub (wie Seesalz) separat melden

PM 2.5

- Umgebungs Jahresmittelwert 20 µgr/^{3} (exclusief hot-spots), in 2015
- Allgemeine Jahresmittelwert 25 µgr/m^3 (inclusief hot-spots) in 2015
  20 µgr/m^3 (inclusief hot-spots) in 2020
- Exposure Reduction Target: In 2020 eine Reduktion relatief zu 2008-2010

Indikator f. durchschnittliche Exposition (AEI-Average Exposure Indicator) ist der $PM_{2.5}$-Jahresmittelwert des Referenzjahres = Ausgangskonzentration AK

Ableitung von 5 Immissionsklassen aus dem $PM_{2.5}$-Jahresmittelwerten: Reduzierungsziel bis 2020 in %

Klasse 1: AK <8.5 µg/m^3 0

Klasse 2: 8.5 µg/m^3 >= AK < 13 µg/m^3 10

Klasse 3: 13 µg/m^3 >= AK < 18 µg/m^3 15

Klasse 4: 18 µg/m^3 >= AK < 22 µg/m^3 20

Klasse 5: AK >= 22 µg/m^3 Alle angemessenen Maßnahmen um 18 µg/m^3 zu erreichen

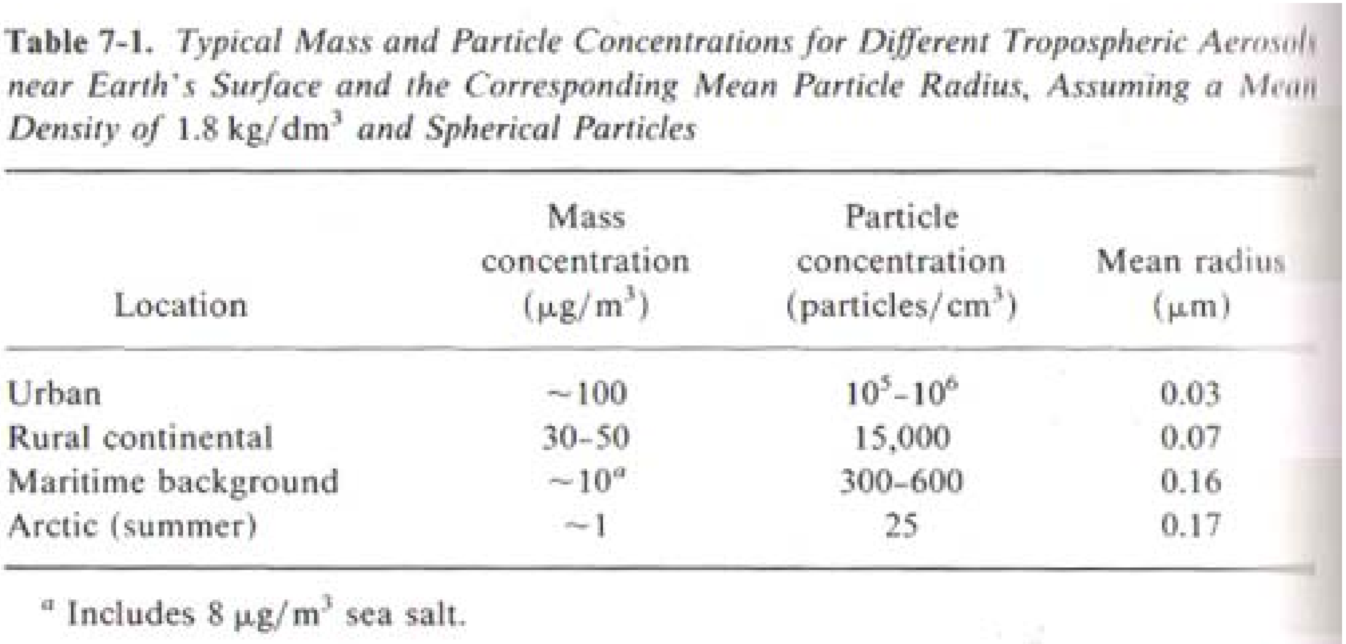


Table 7-1. *Typical Mass and Particle Concentrations for Different Tropospheric Aerosols near Earth's Surface and the Corresponding Mean Particle Radius, Assuming a Mean Density of* 1.8 kg/dm³ *and Spherical Particles*

Location	Mass concentration ($\mu g/m^3$)	Particle concentration (particles/cm³)	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 $\mu g/m^3$ sea salt.

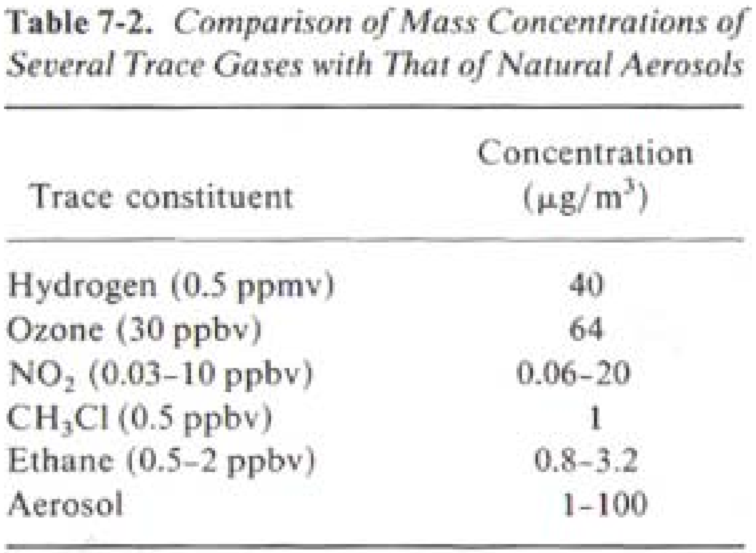


Table 7-2. *Comparison of Mass Concentrations of Several Trace Gases with That of Natural Aerosols*

Trace constituent	Concentration ($\mu g/m^3$)
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

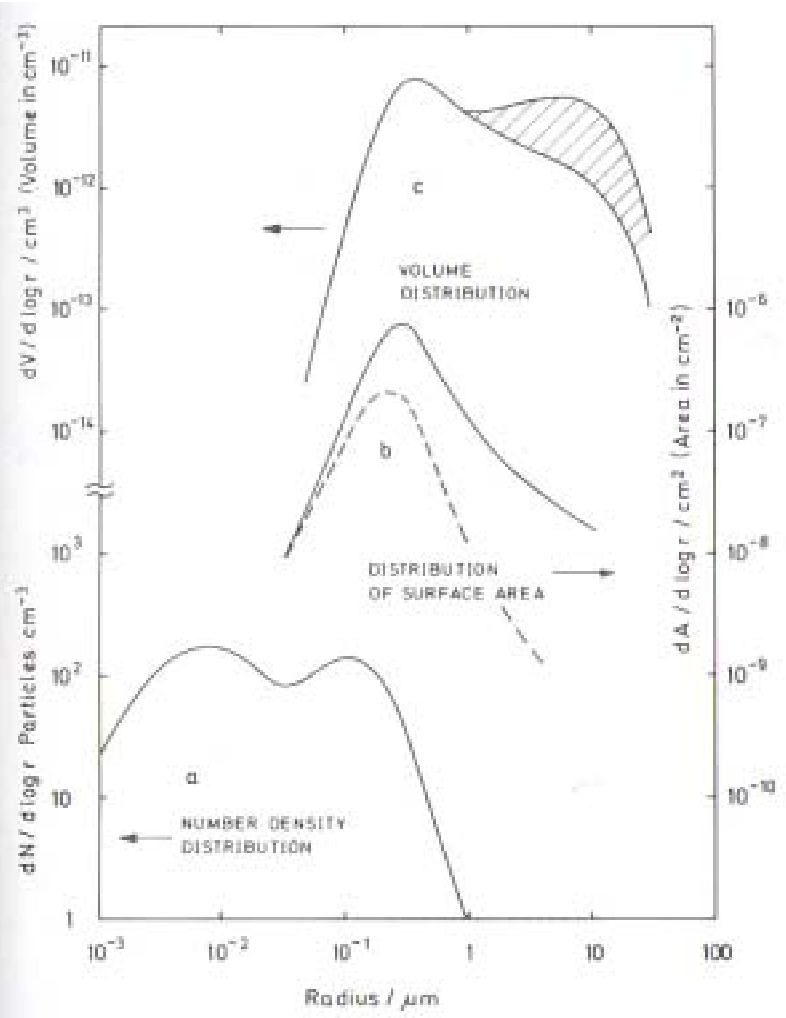
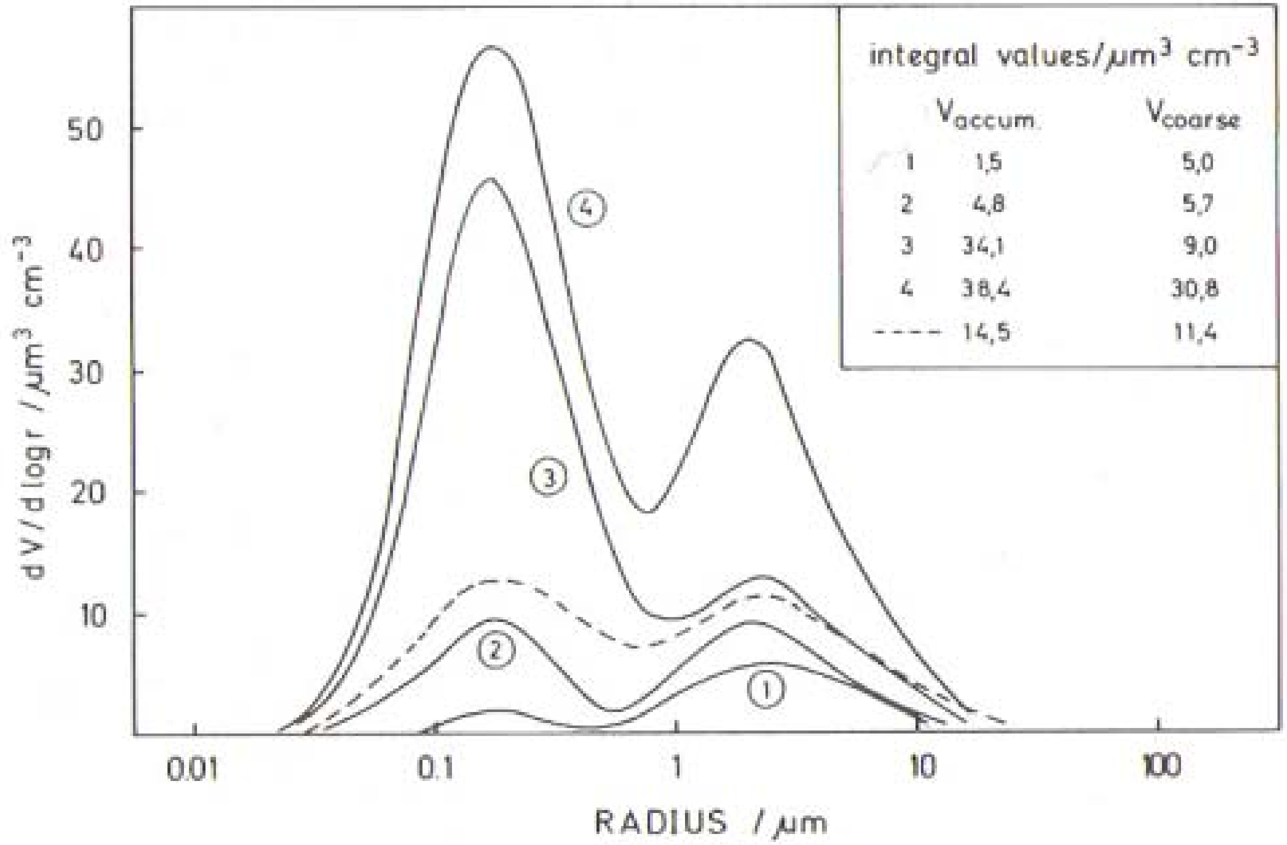


Fig. 7-2. Model size distributions of the marine background aerosol: (a) particle number density, (b) surface area, (c) volume. The contribution of sea salt to the volume distribution is indicated by the shaded area, and arrows indicate the appropriate scale. By integration one obtains a total number density $N = 290$ particles/cm^3, a total surface area $A = 1.8 \times 10^{-7}$ cm^2/cm^3, and a total volume $V = 1.1 \times 10^{-11}$ cm^3/cm^3. For an average density of 10^3 kg/m^3, the mass concentration is 11 μg/m^3 (5 μg/m^3 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.



integral values/$\mu m^3\ cm^{-3}$

	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.

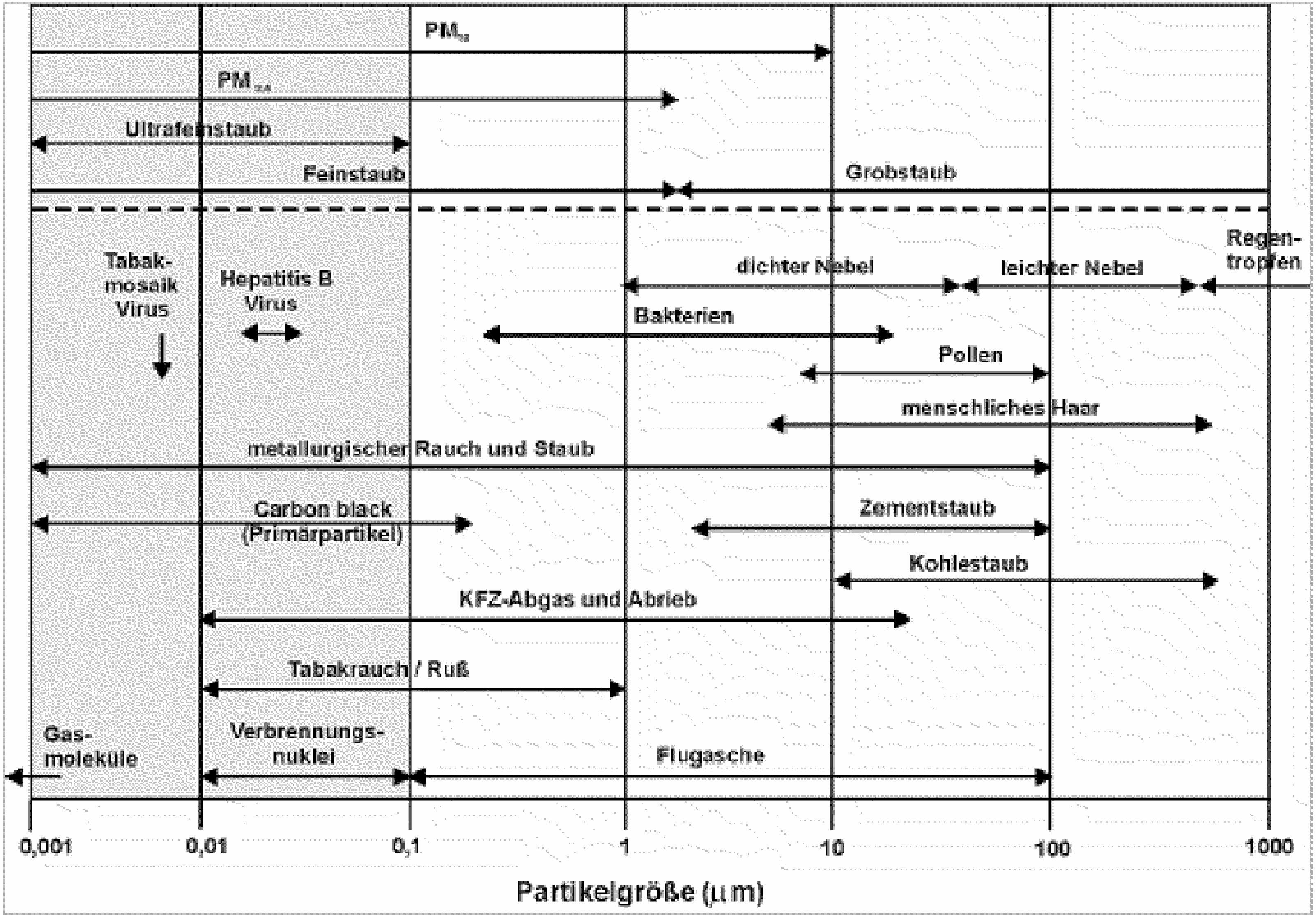


Abb.1: Partikeldefinitionen und Größenbereiche umweltrelevanter Partikel [Krug 2003

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:

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

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

$SO_3^{2-} + \frac{1}{2} O_2 \rightarrow SO_4^{2-}$

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

Cloud-drops can grow and precipitate

Wash out by raindrops

$$\text{Wash out}: \text{R}: \text{Radius of drop}:$$

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

$$\text{Total mass}:$$

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

$$\text{N(r)}: \text{number concentration}$$

$$\text{r} \quad : \text{radius of aerosol}$$

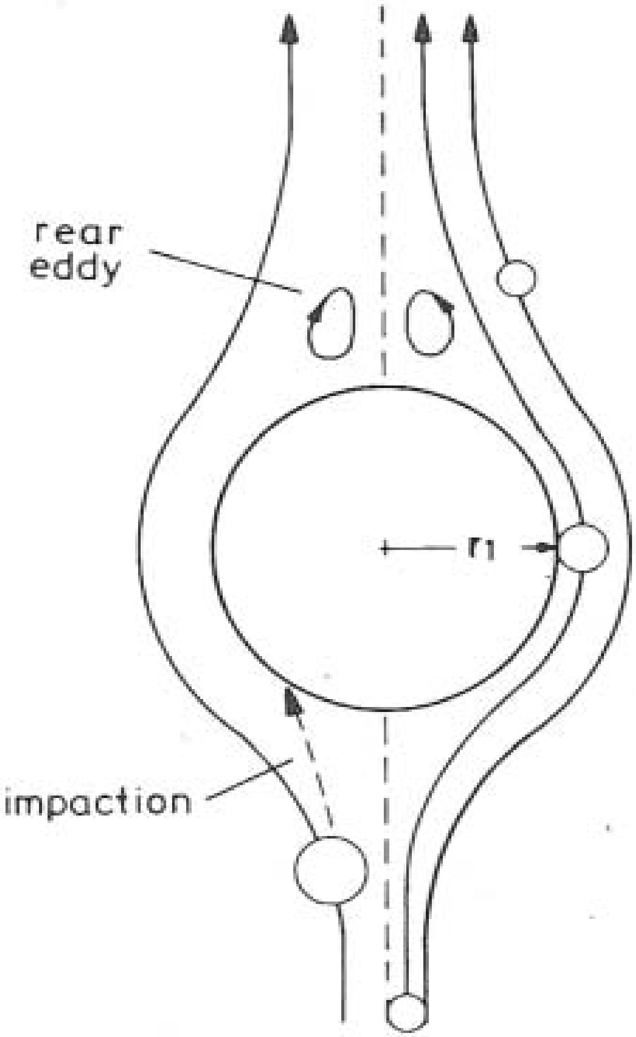


Fig. 8-4. Schematic representation of the air flow around a falling sphere.

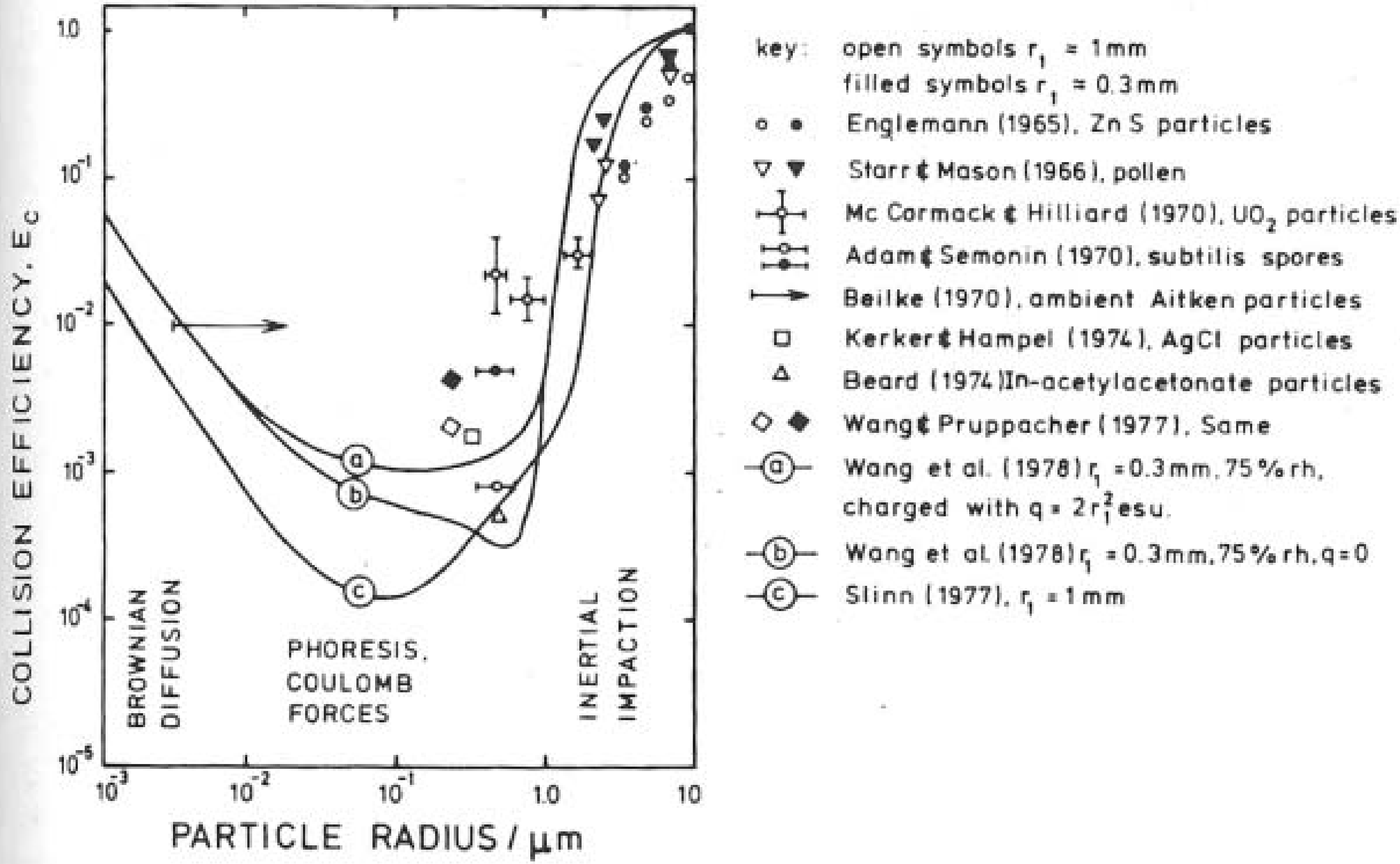


Fig. 8-6. Collision efficiency for the capture of particles by rain drops as a function of particle radius. Solid curves indicate calculations, and points represent laboratory results. Three size regimes may be distinguished depending on the dominant type of capture process.

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

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

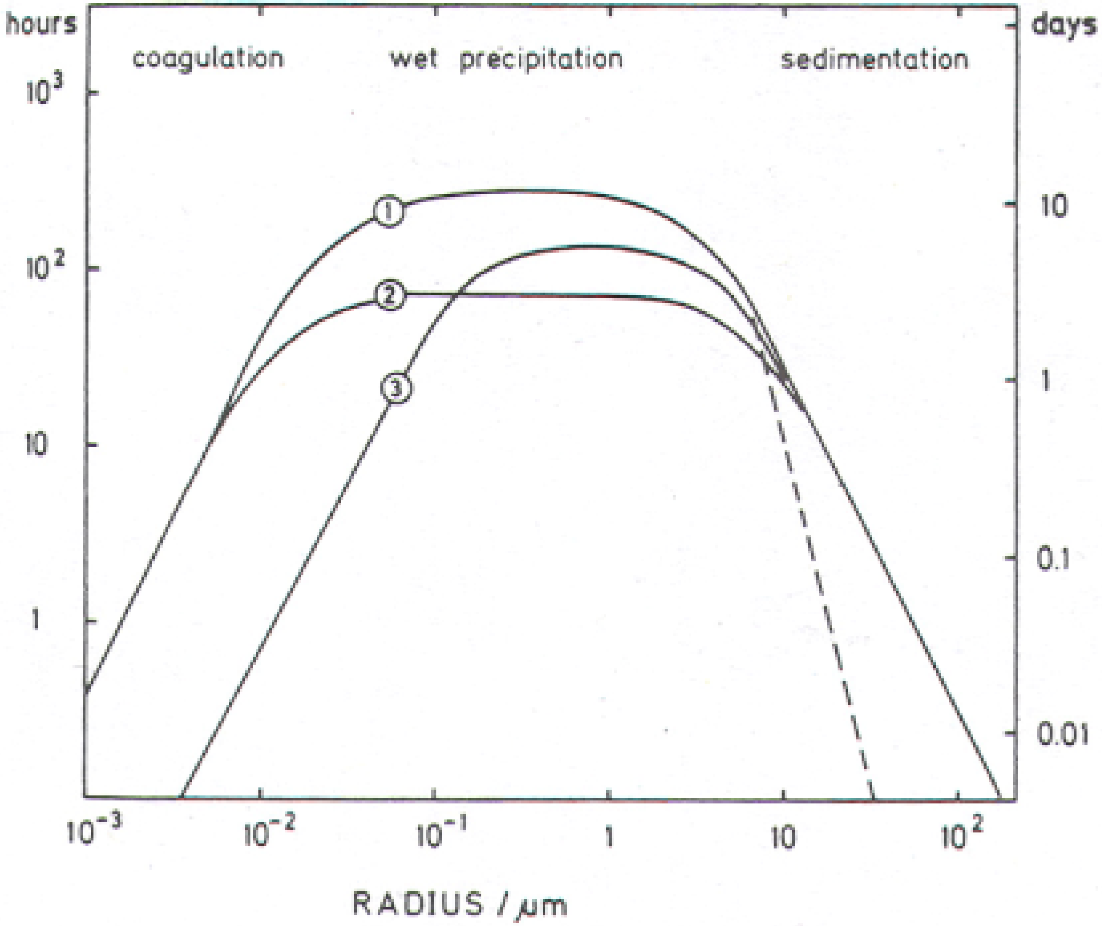


Fig. 7-28. Combined residence lifetimes of aerosol particles as a function of size. [Adapted from Jaenicke (1978c, 1980).] Important removal processes, active in various size ranges, are indicated. Coagulation and sedimentation time constants were calculated; the time constant for wet removal is the 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.

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

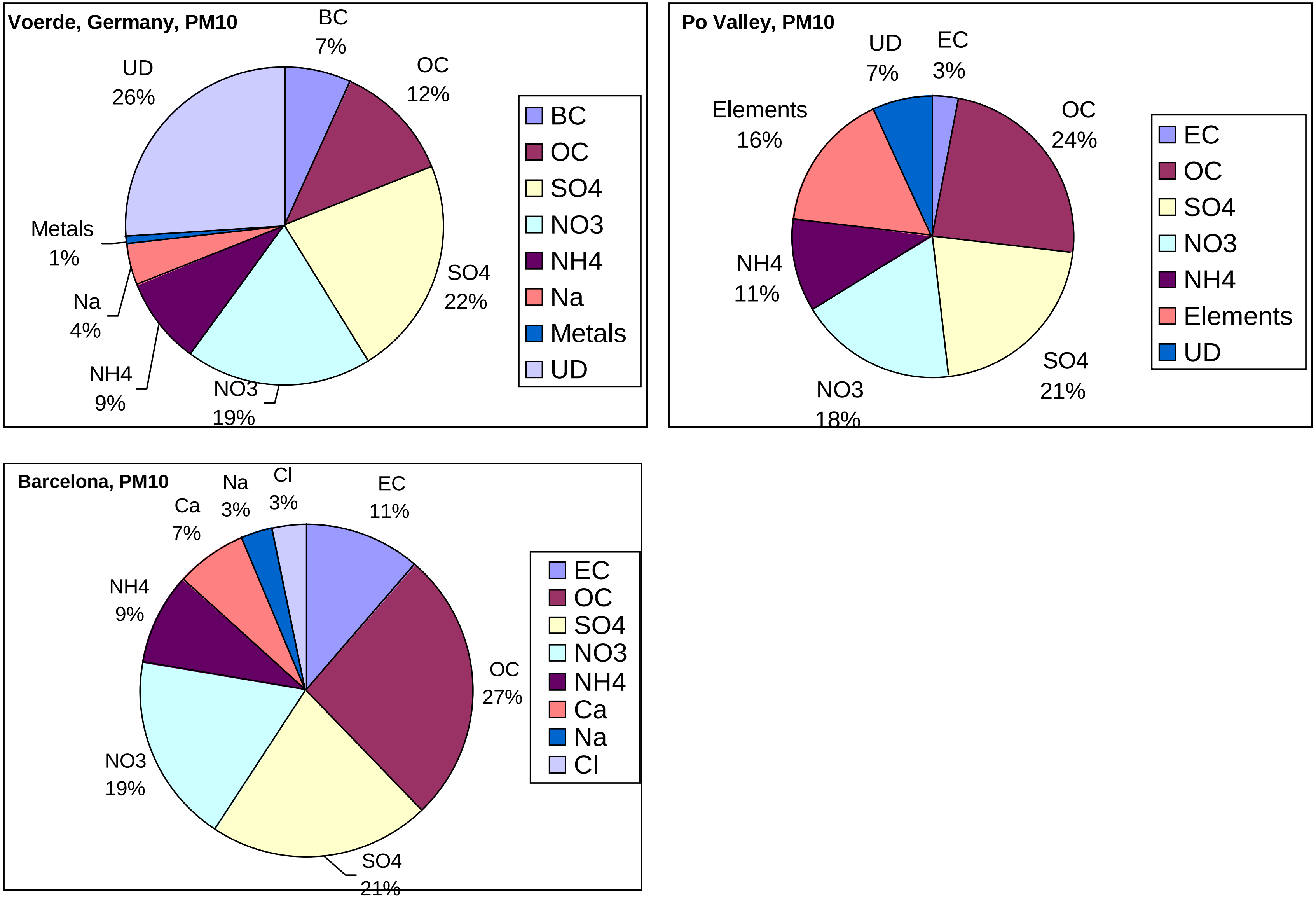


Figure 1 Composition of PM10 expressed in relative units at three sites in Europe.

Satelliet-messungen von

- Aerosol Optical Depth-AOD
- Grosse Verteilung, Ångström Coefficient

Versuch um mit LOTOS-EUROS und Data assimilation PM2.5 zu bestimmen

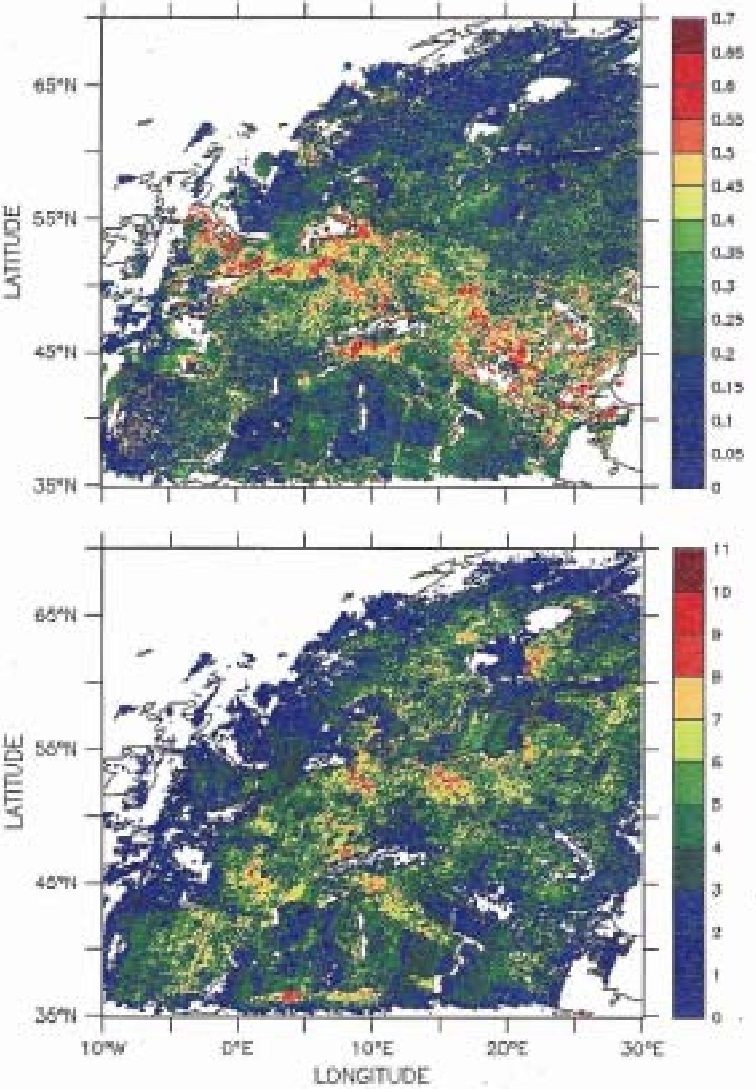
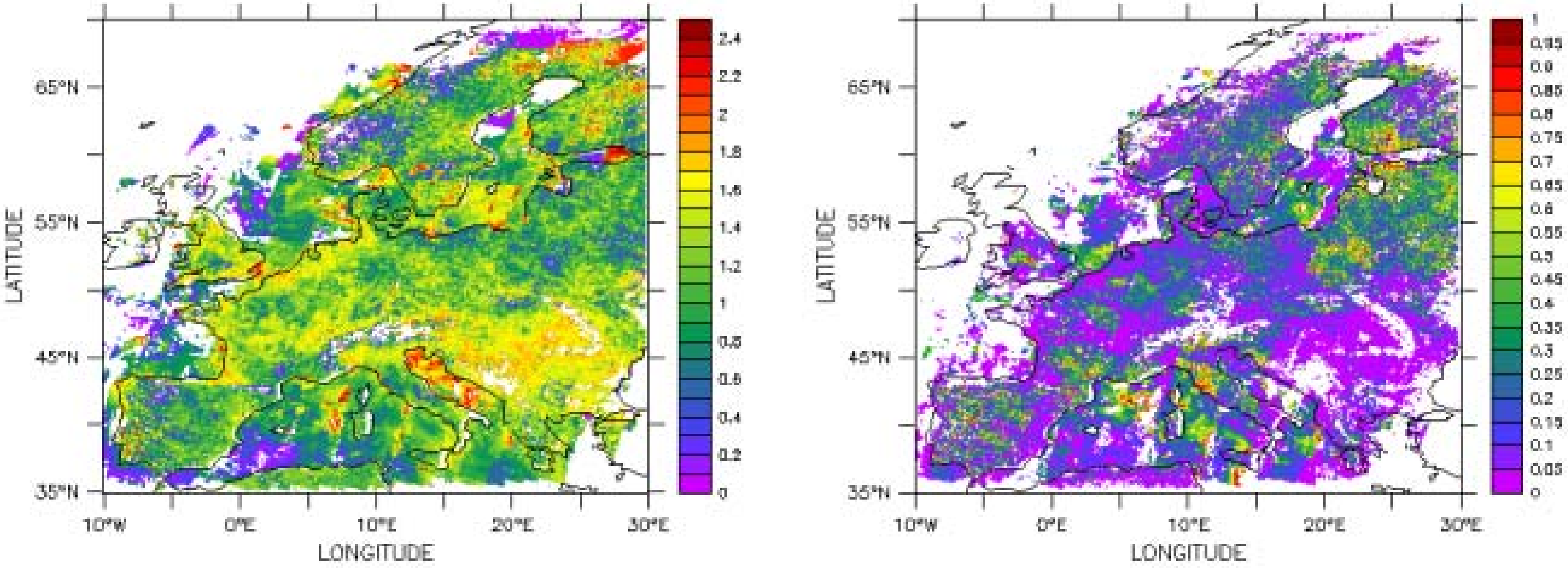
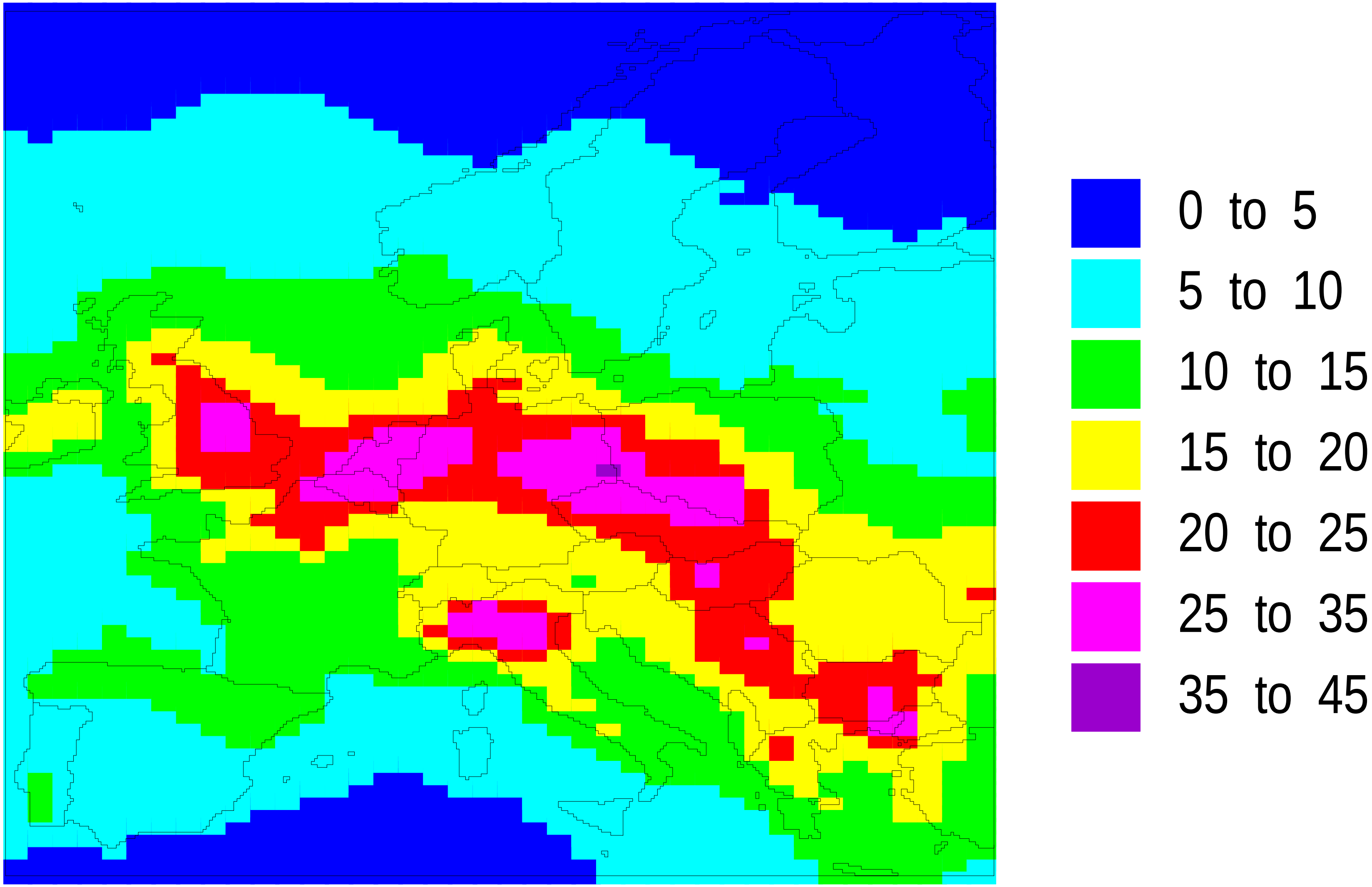


Figure 4.1. Composite map of the (a) mean aerosol optical depth at 0.555 µm over Europe for August 1997 and (b) the number of observations used to derive the mean value. AOD has been retrieved by application of the dual view algorithm to the ATSR-2 satellite data over land and the single view algorithm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



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



Preliminary estimate of the average PM$_{2.5}$ (µg/m^3)concentration for August 1997, based on ATSR-2 data.

QuickTime™ en een
TIFF (ongecomprimeerd)-decompressor
zijn vereist om deze afbeelding weer te geven.

Europe and air quality

Global Monitoring for Environment and Sequrity (GMES)

http://www.gmes.info/

Atmosphere projects: PROMOTE en GEMS

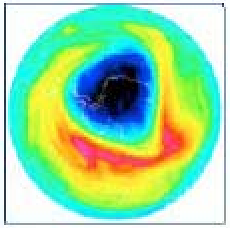
KNMI contributes to both on Air Quality

PROMOTE

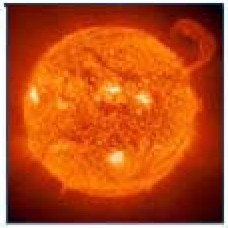
GMES Atmosphere Service: (2009 onward)

Ensemble air quality forecast Europa

with Dutch contribution (TNO-KNMI)



Ozone Service



UV Service

Air Quality Service

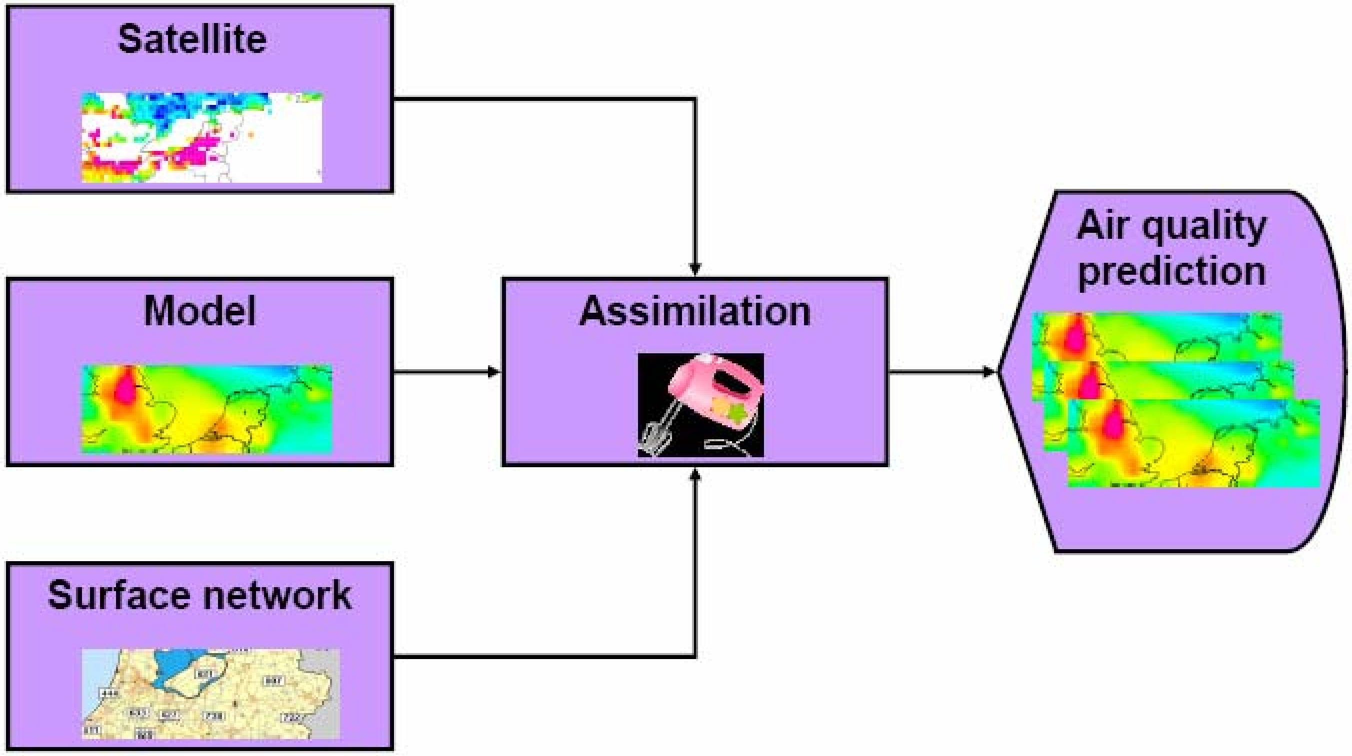
Greenhouse Gas and Aerosol Service

Special Services

••••

Gloream/Accent, Nov 2007

The aim



Satellite

Model

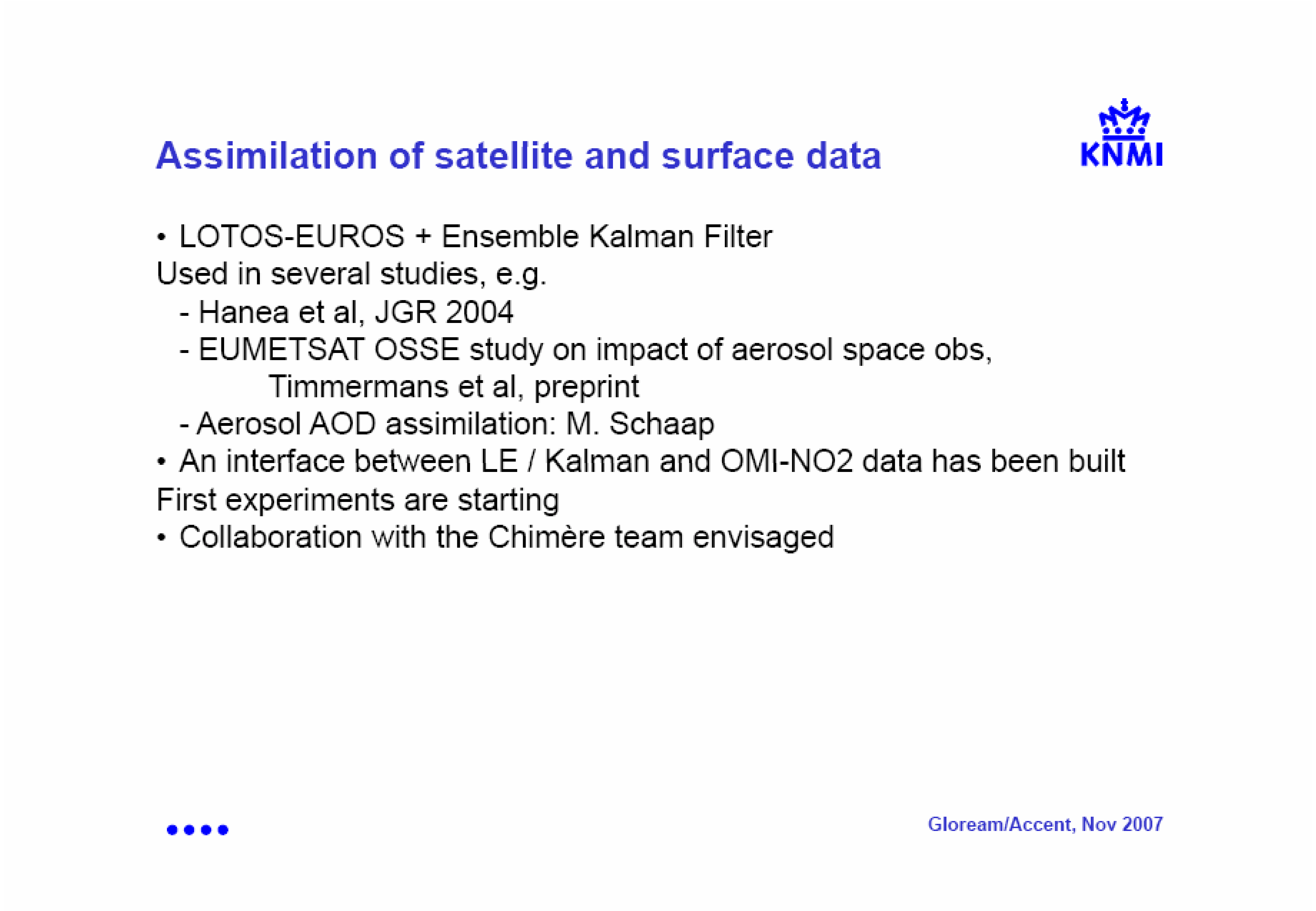
Surface network

Assimilation

Air quality prediction

••••

Gloream/Accent, Nov 2007



Assimilation of satellite and surface data

- LOTOS-EUROS + Ensemble Kalman Filter

Used in several studies, e.g.

  - Hanea et al, JGR 2004
  - EUMETSAT OSSE study on impact of aerosol space obs,
    Timmermans et al, preprint
  - Aerosol AOD assimilation: M. Schaap

- An interface between LE / Kalman and OMI-NO2 data has been built

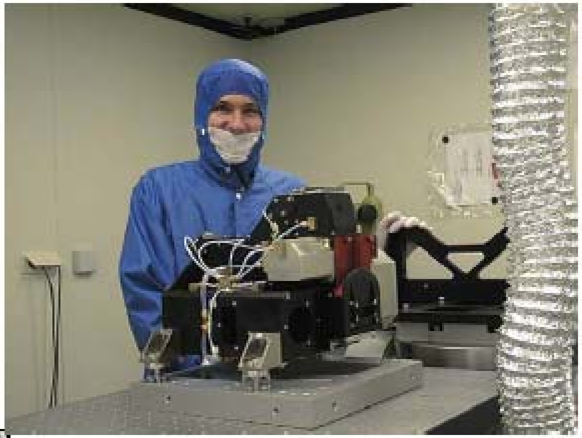
First experiments are starting

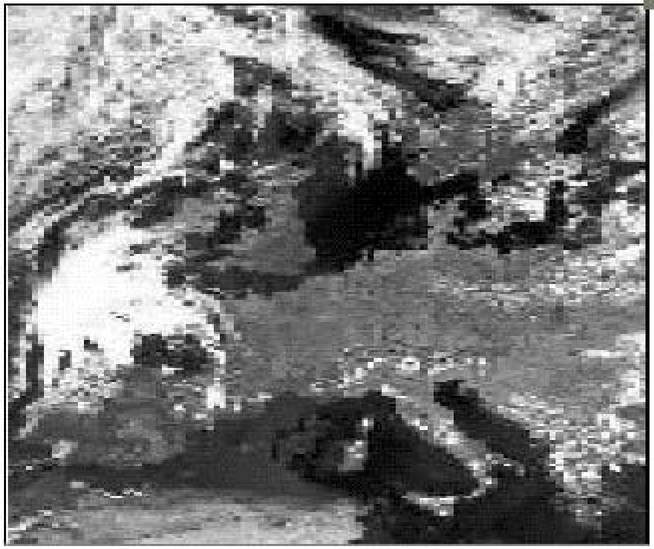
- Collaboration with the Chimère team envisaged

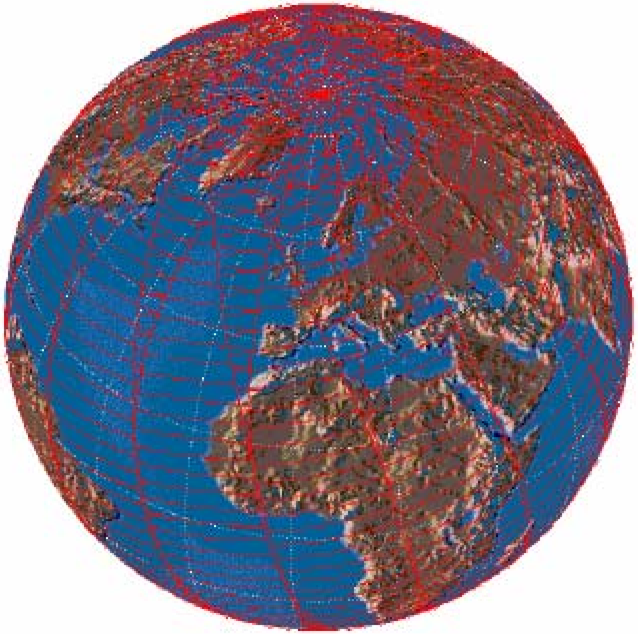
Gloream/Accent, Nov 2007

OMI: unique instrument

EOS-AURA satellite
July 2004 - present

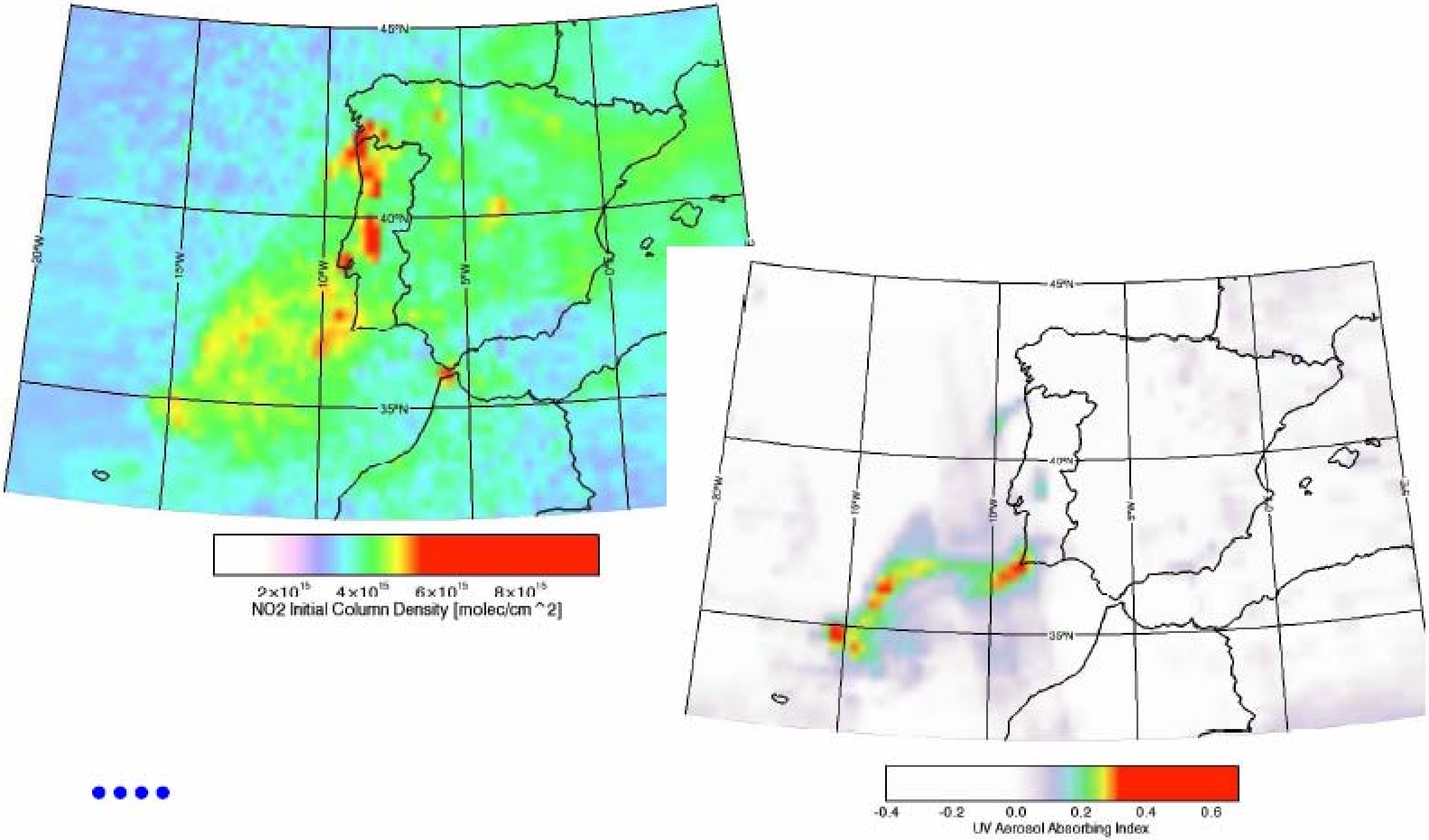






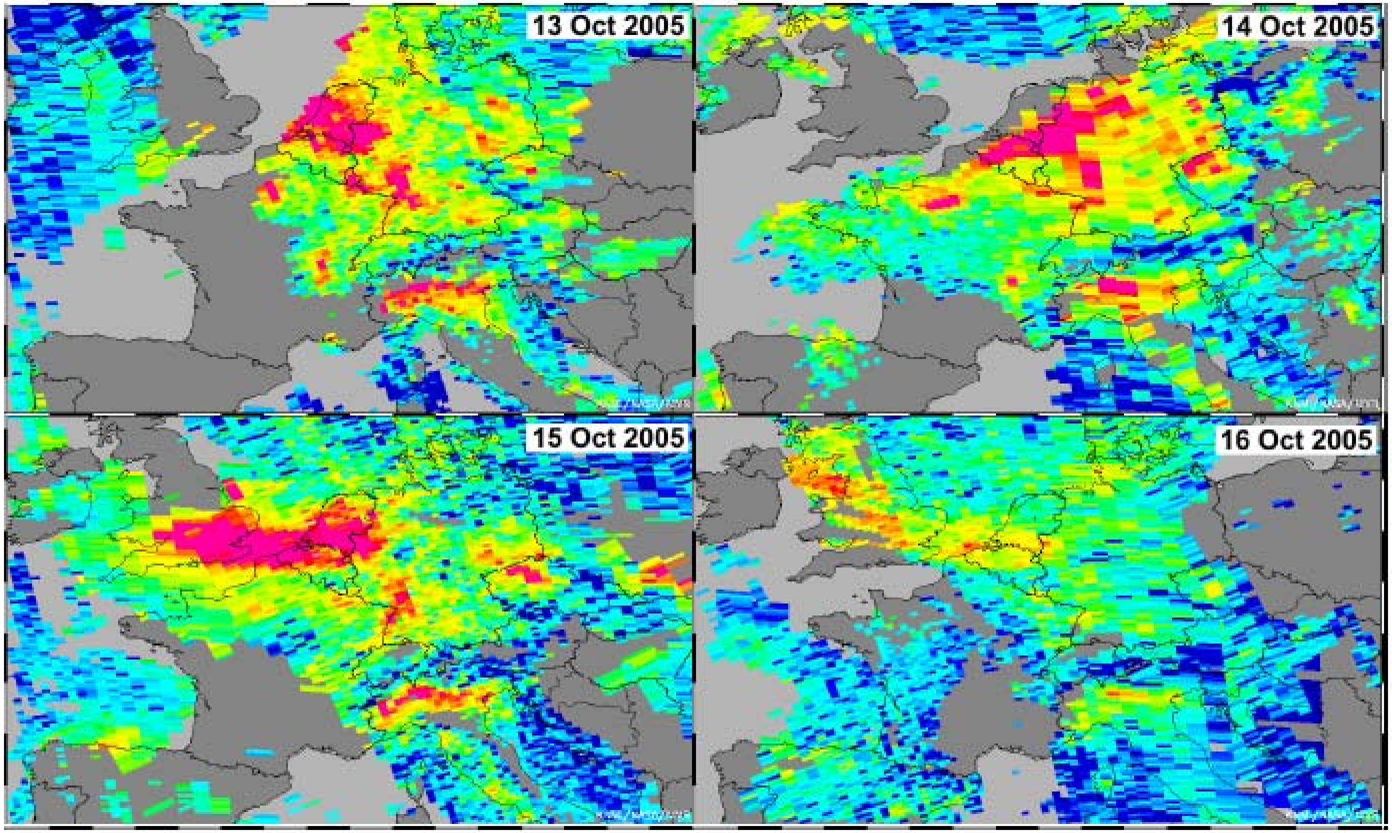
- ....

Fire events seen by OMI



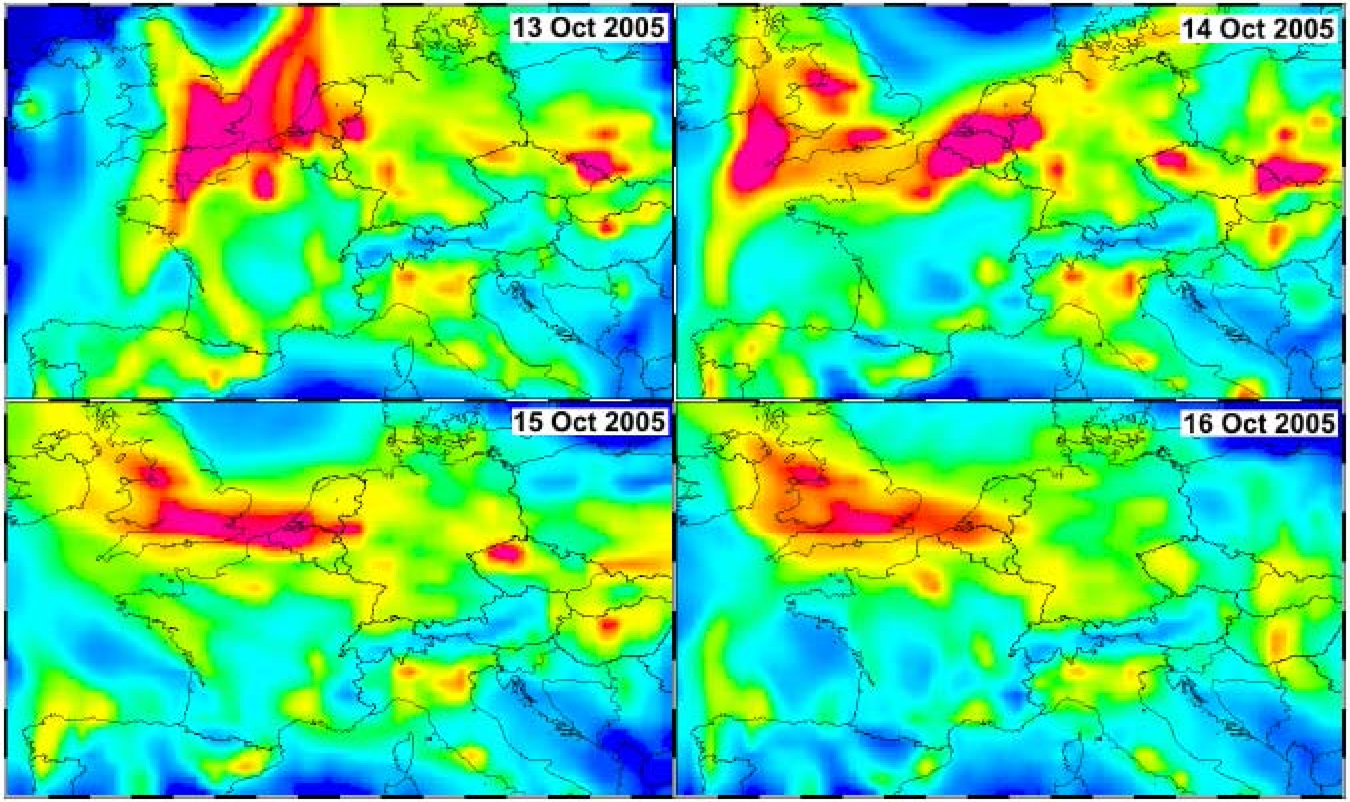
••••

OMI near-real time NO2, 13-16 October 2005

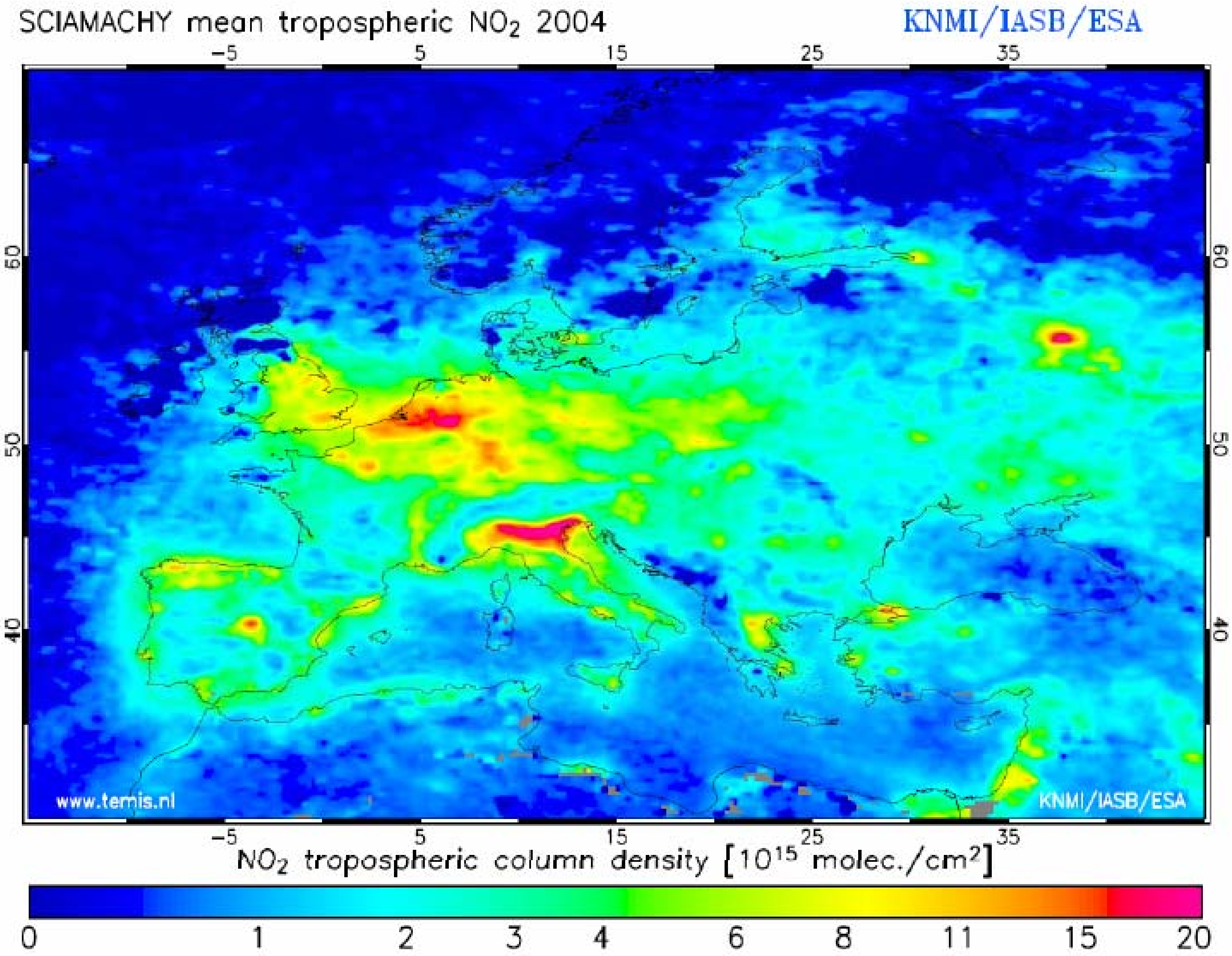


Gloream/Accent, Nov 2007

Chimere @ OMI overpass time, 13-16 Oct 2005

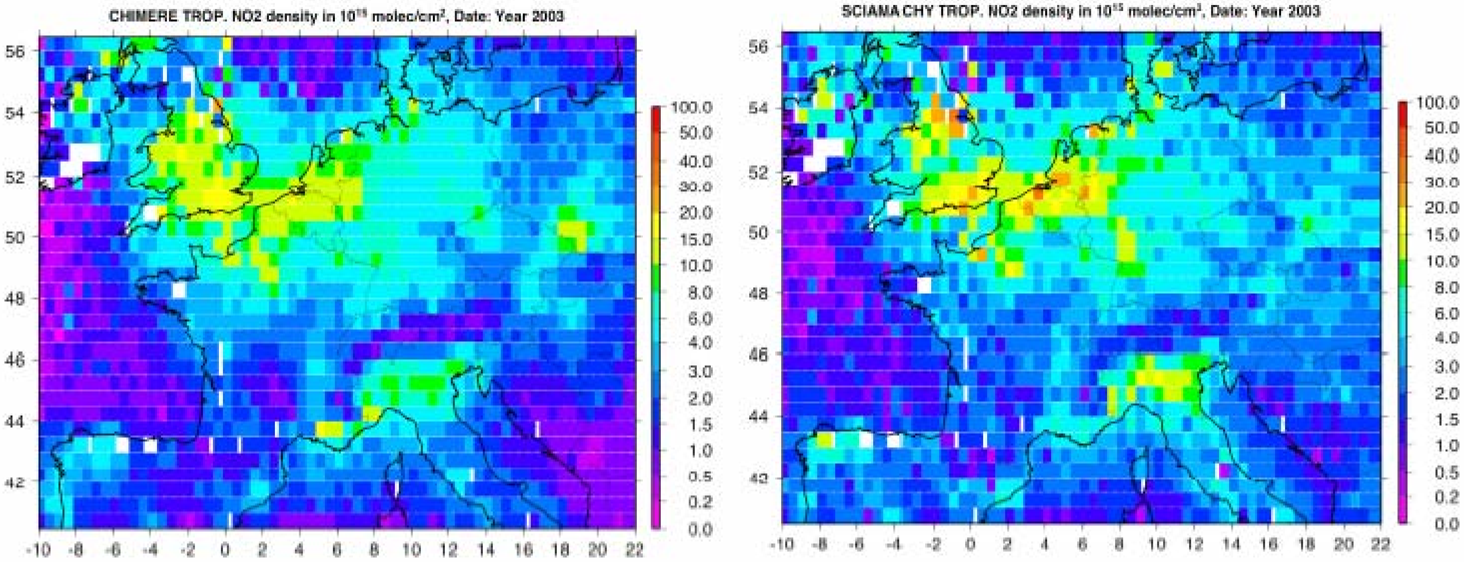


Gloream/Accent, Nov 2007


SCIAMACHY mean tropospheric NO_2 2004
KNMI/IASB/ESA
−5
5
15
25
35
60
50
40
www.temis.nl
KNMI/IASB/ESA
NO_2 tropospheric column density [10^{15} molec./cm^2]
0
1
2
3
4
6
8
11
15
20

SCIAMACHY vs. Chimère: yearly mean

KNMI


CHIMERE TROP. NO2 density in 10^{15} molec/cm², Date: Year 2003

SCIAMACHY TROP. NO2 density in 10^{15} molec/cm², Date: Year 2003

Yearly-mean bias = 0.2 10^{15} molec cm^{-2}, RMS 2.9, correl.coeff. 0.73

Cloud-free pixels

Nadege Blond - JGR 2007

Gloream/Accent, Nov 2007

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

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

Example PM10 consists of

- Secondary Inorganic Aerosol: SIA
- Biogenic Secondary Organic Aerosol: BSOA
- Anthropogenic Secondary Organic Aerosol: ASOA
- Primary Aerosol, BC = Black Carbon and OC + Organic Carbon

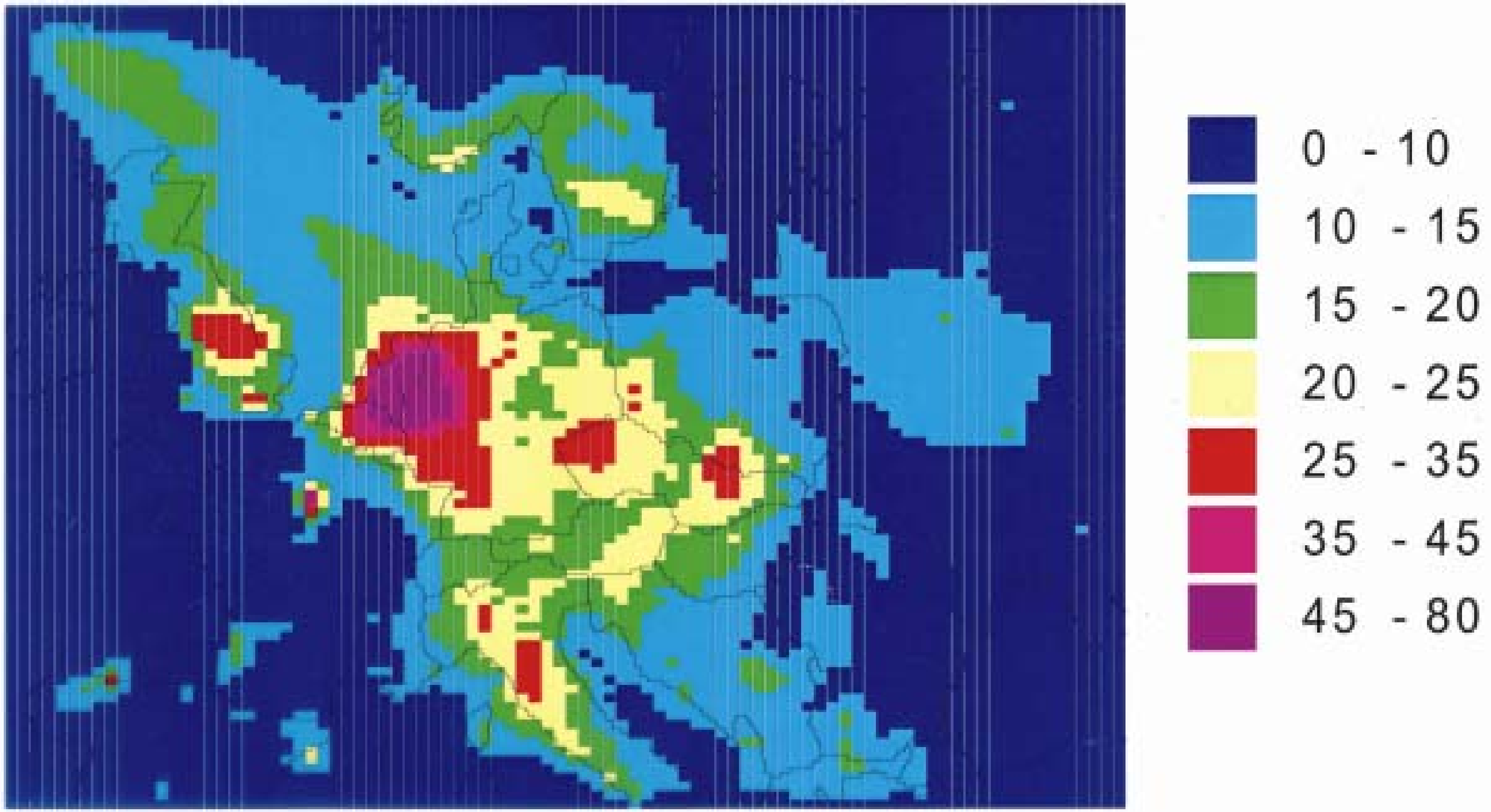
Erste Ergebnisse Modellierung von Aerosolen

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

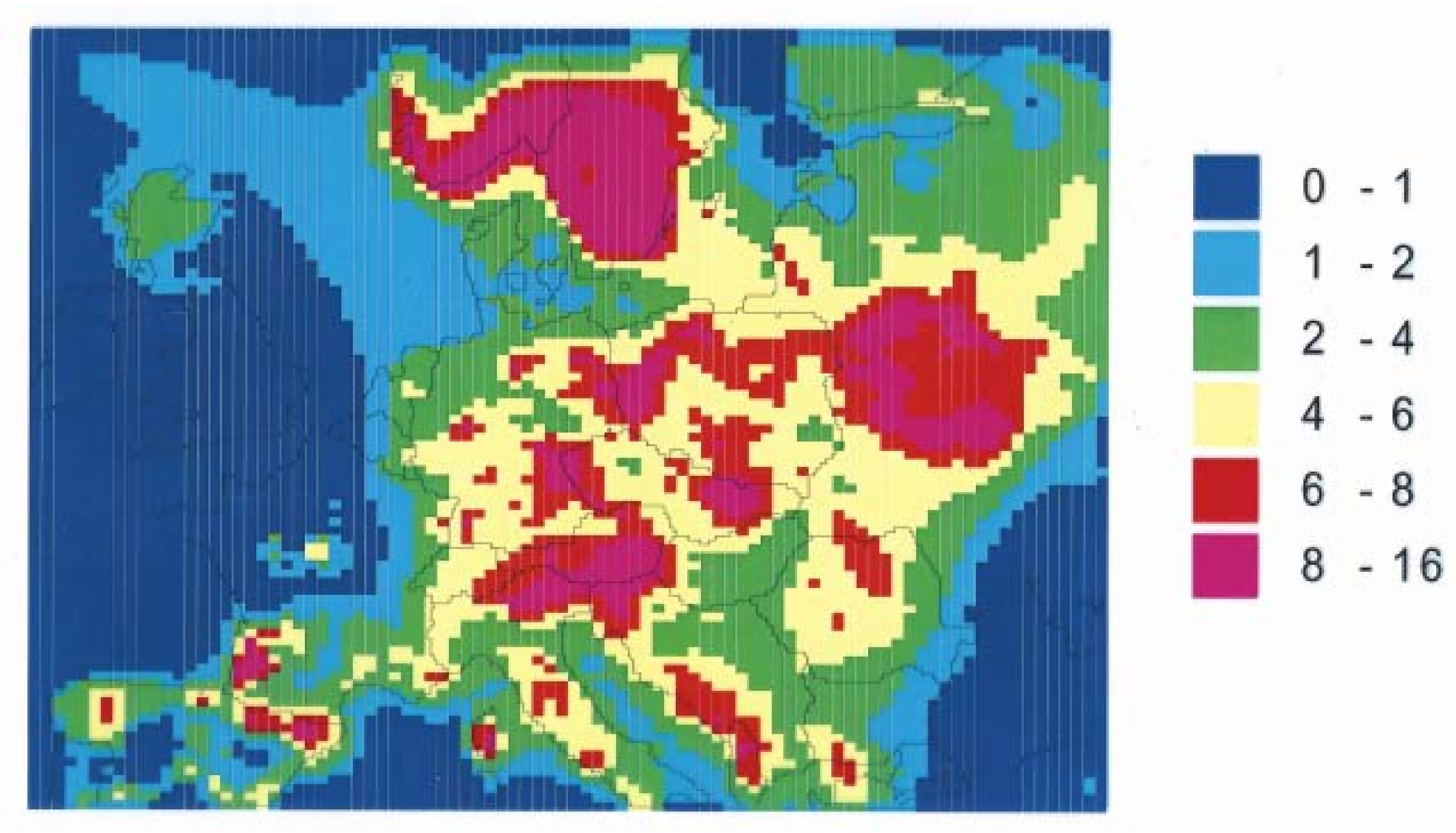
Hauptbeschränkungen Modellierung:

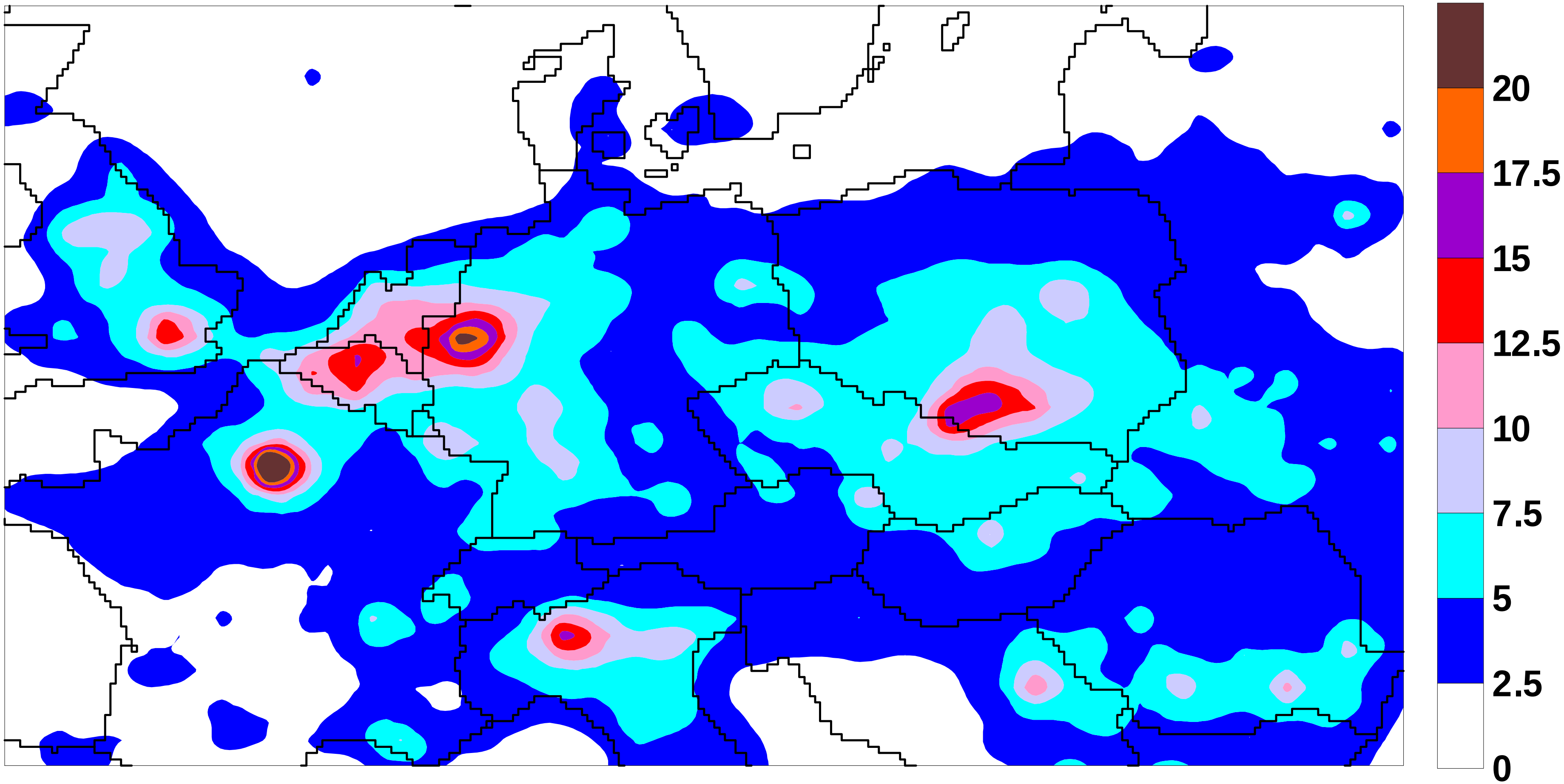
- Zu wenig gute Beobachtungen
- Wolkenbeschreibung / Chemie / CCN

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

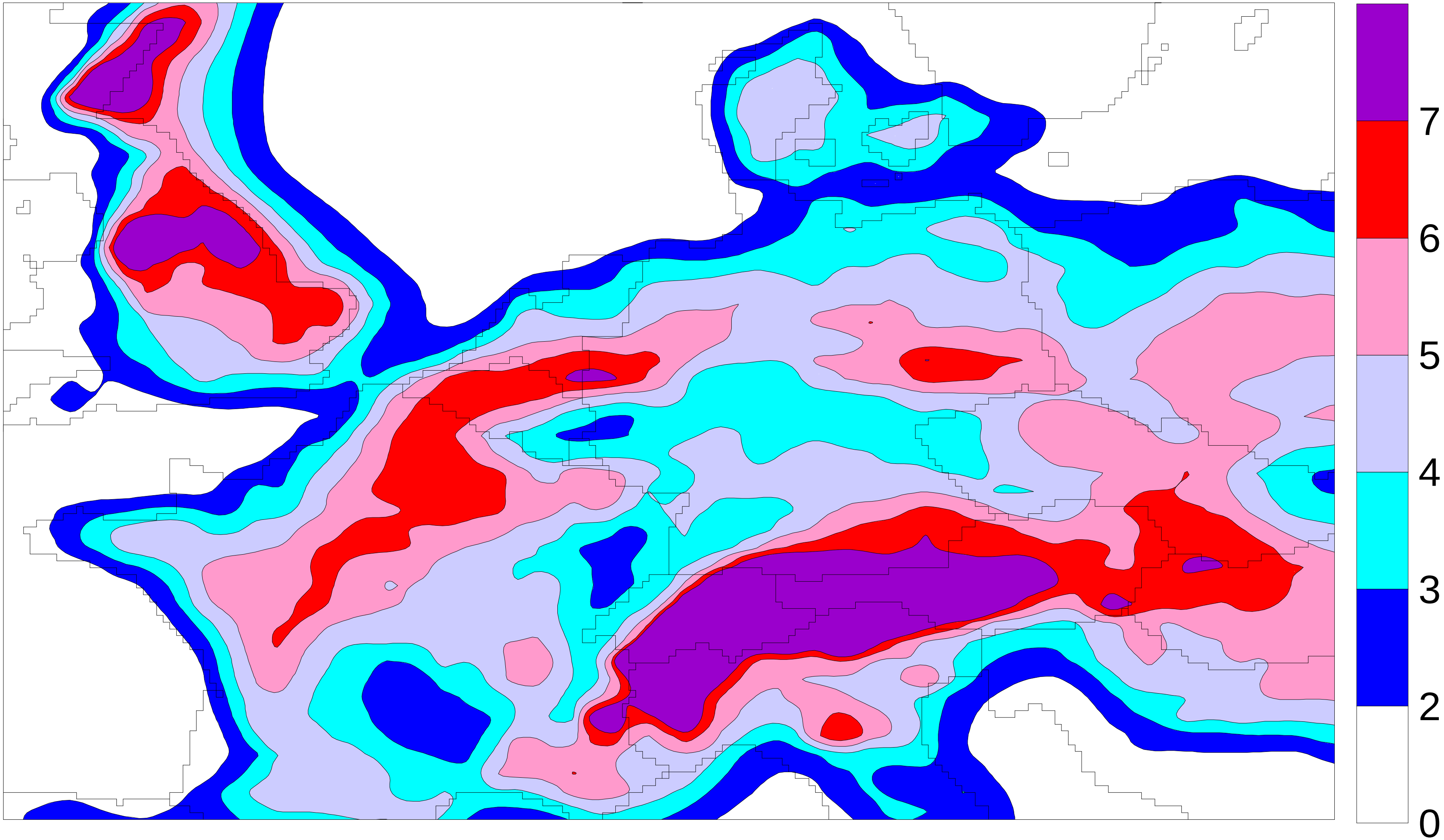


Average BSOA 28 July - 13 August 1997





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



Average computed (LOTOS) wind blown dust concentration (µg/m^3) in 1995

Windgeblasenen Sand

- Funktion von
  - Landnutzung
  - Bodenfeuchte
  - Windgeschwindigkeit + Grenzwert

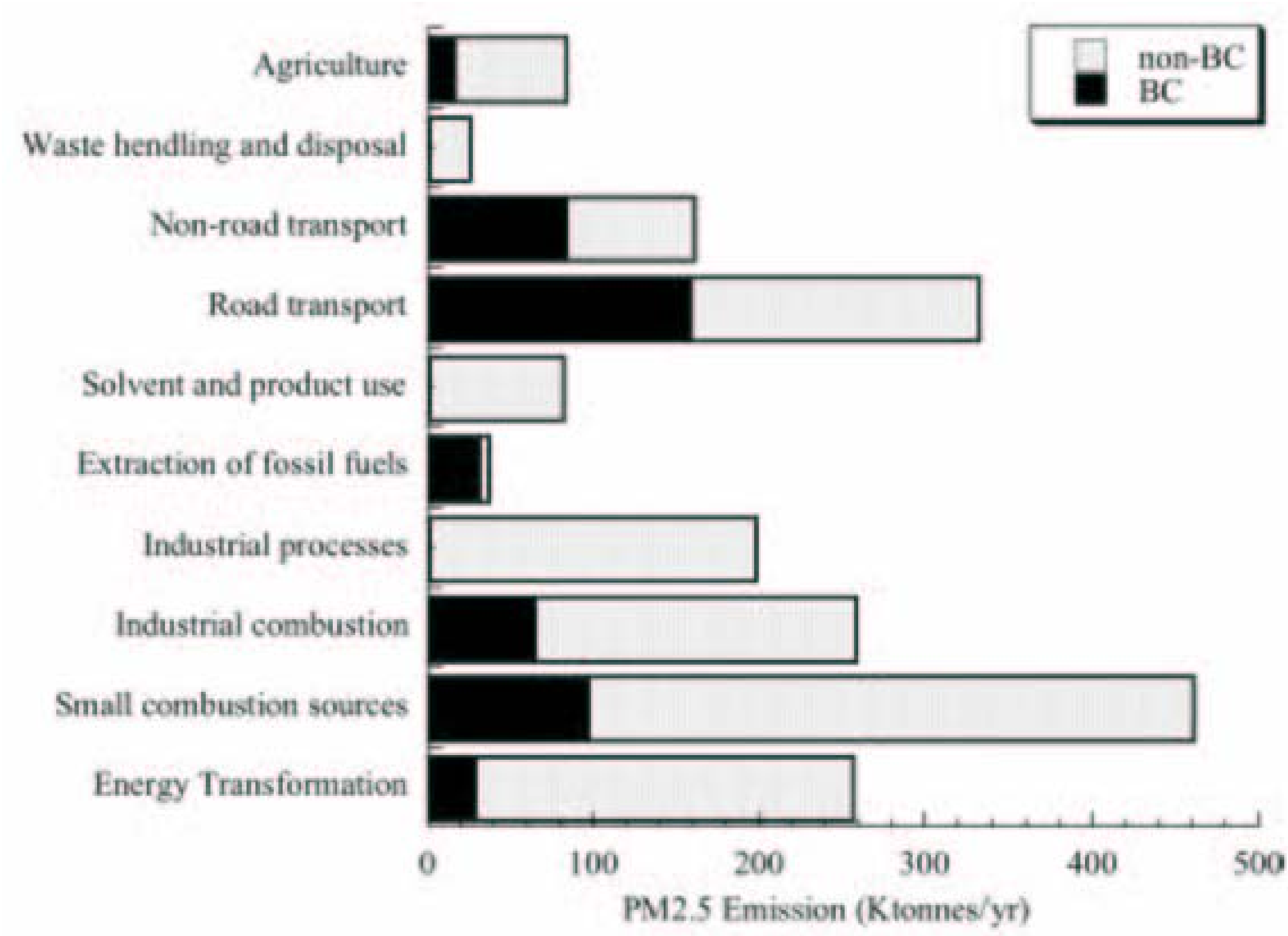
- Agrar bodenbearbeitung

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

MODELLING BLACK CARBON OVER EUROPE



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

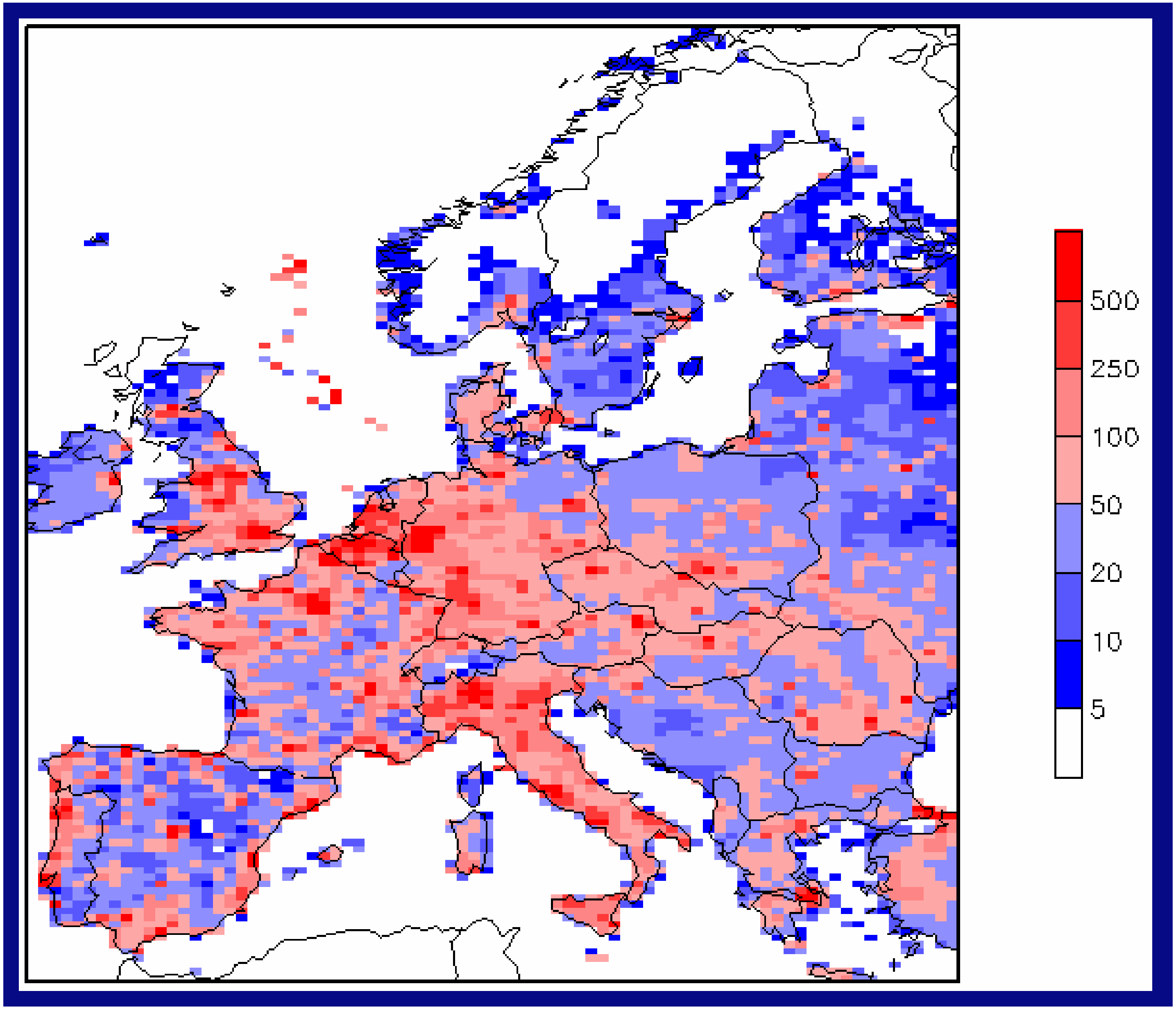
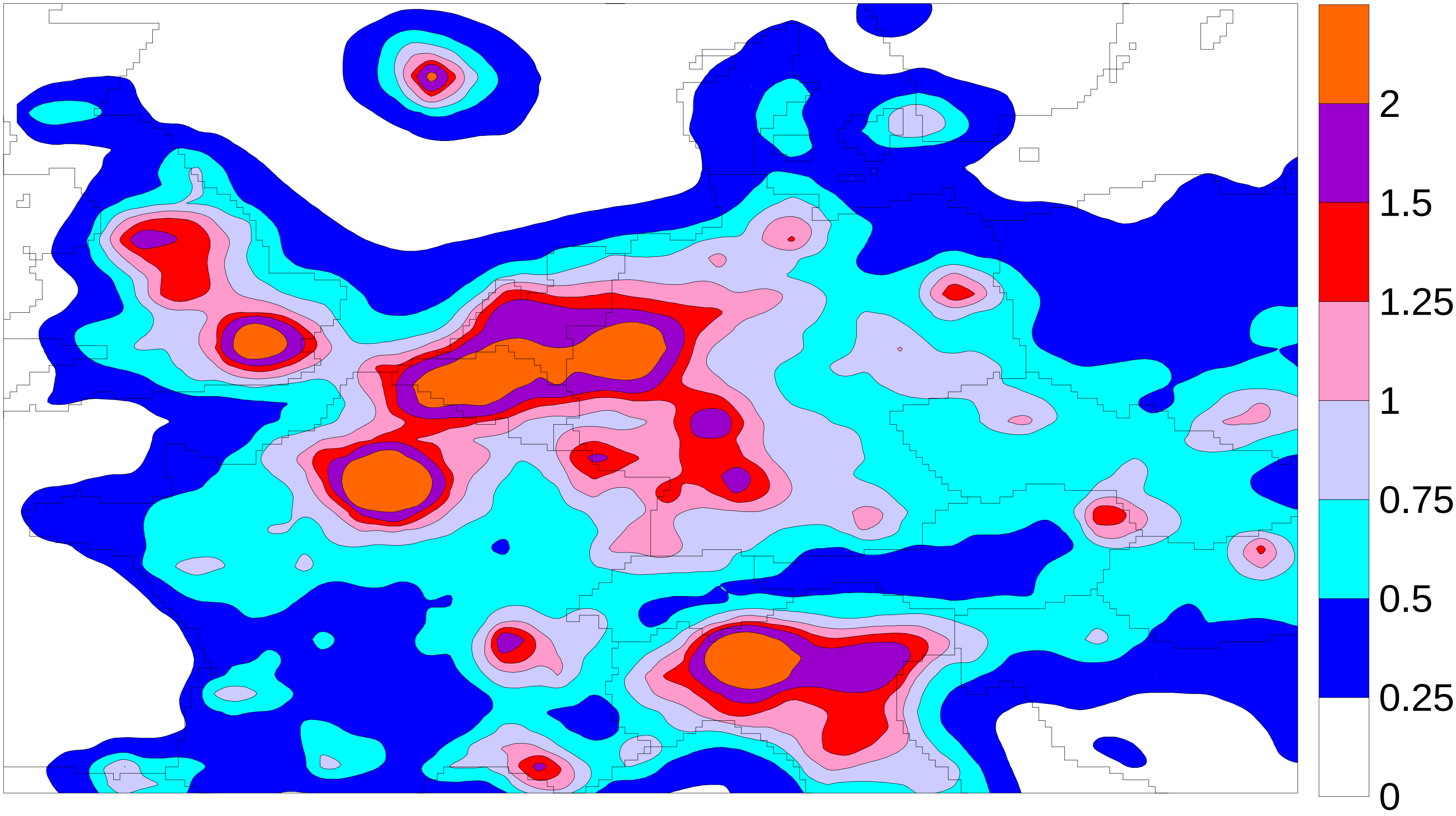


Figure 2 European BC emission (tonnes) derived in this study



Average computed (LOTOS) Black Carbon concentration (µg/m^3) in 1995

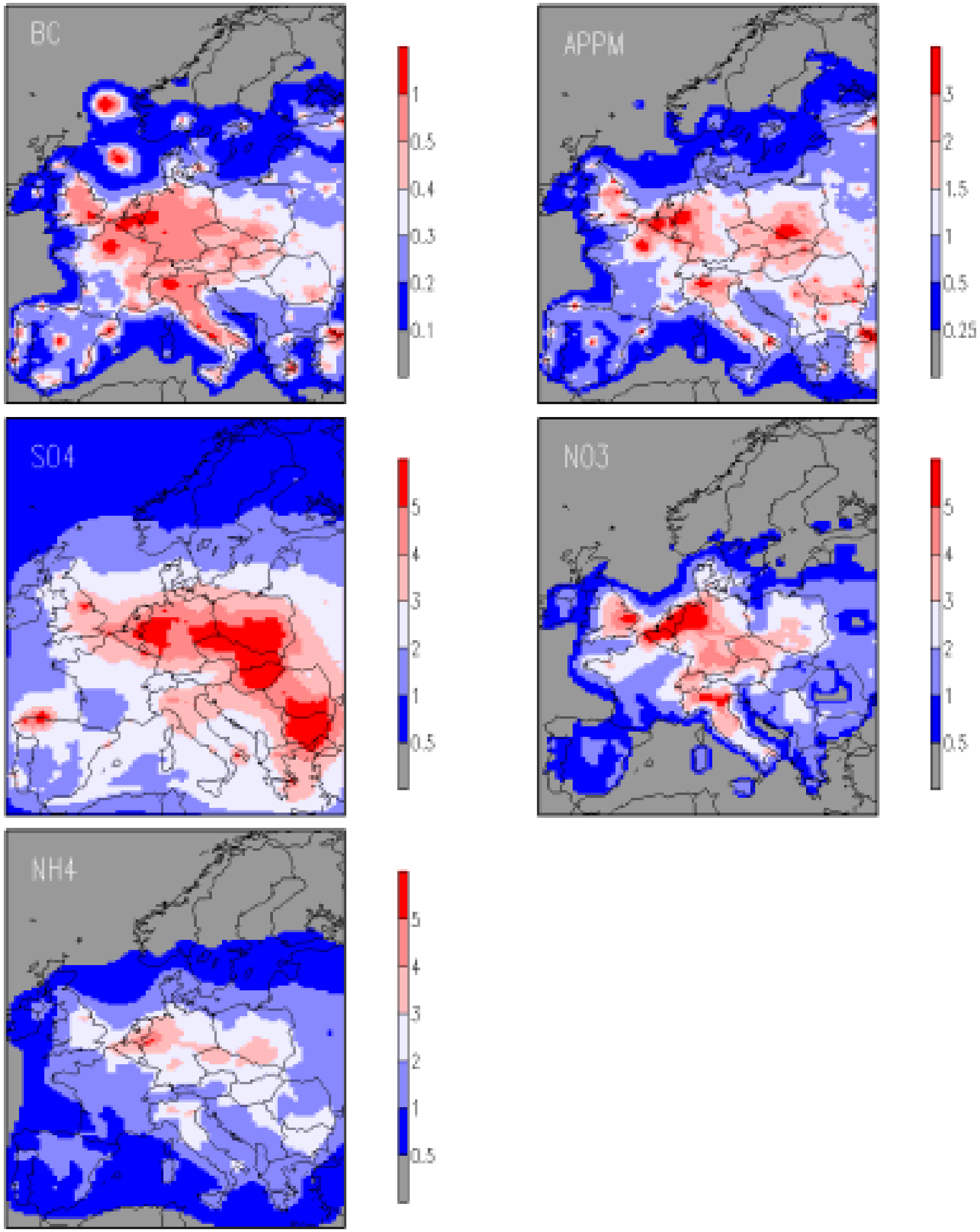


Figure 4
Annual average distribution of BC, APPM, SO_4, NO_3 and NH_4 over Europe (µg/m^3).

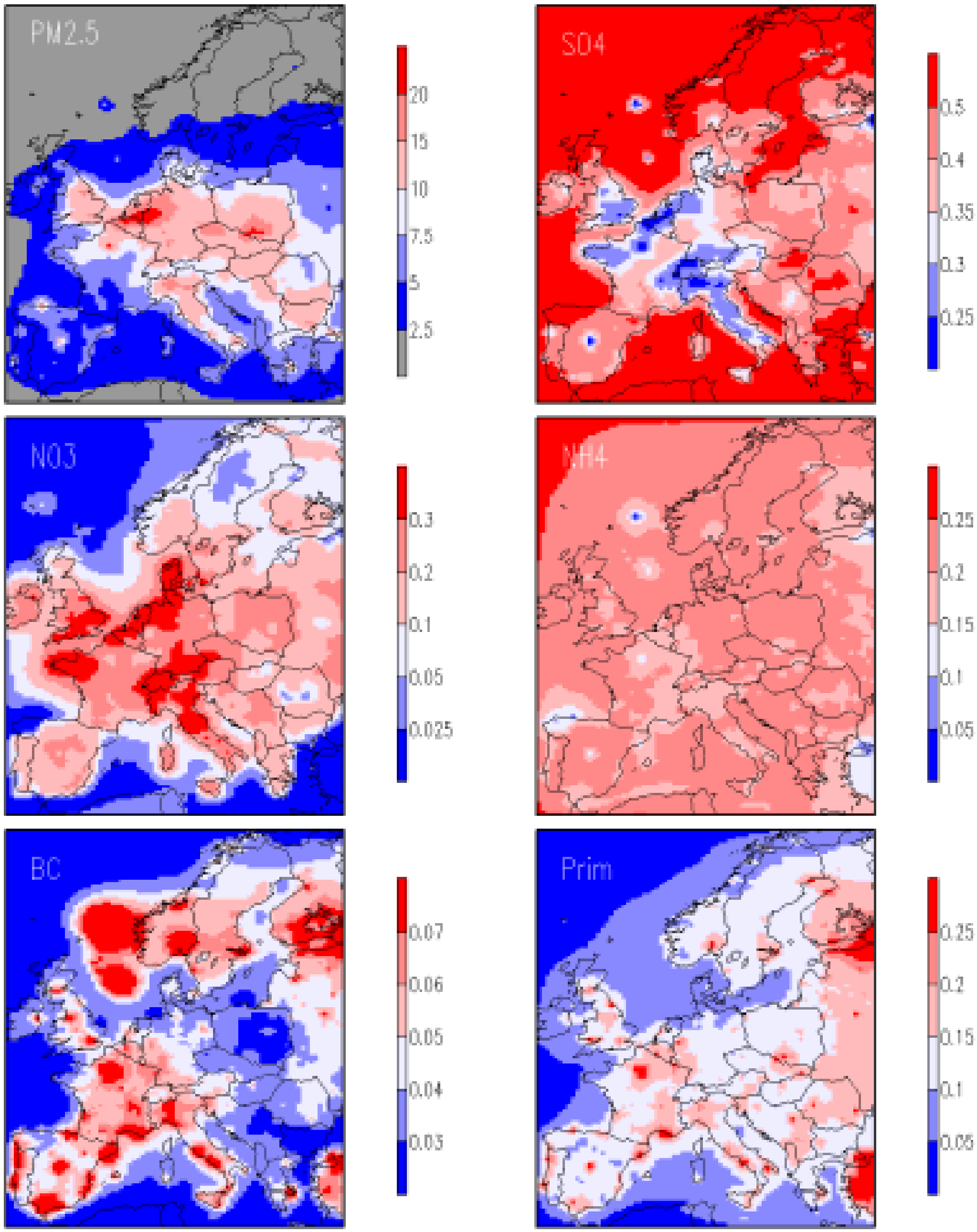
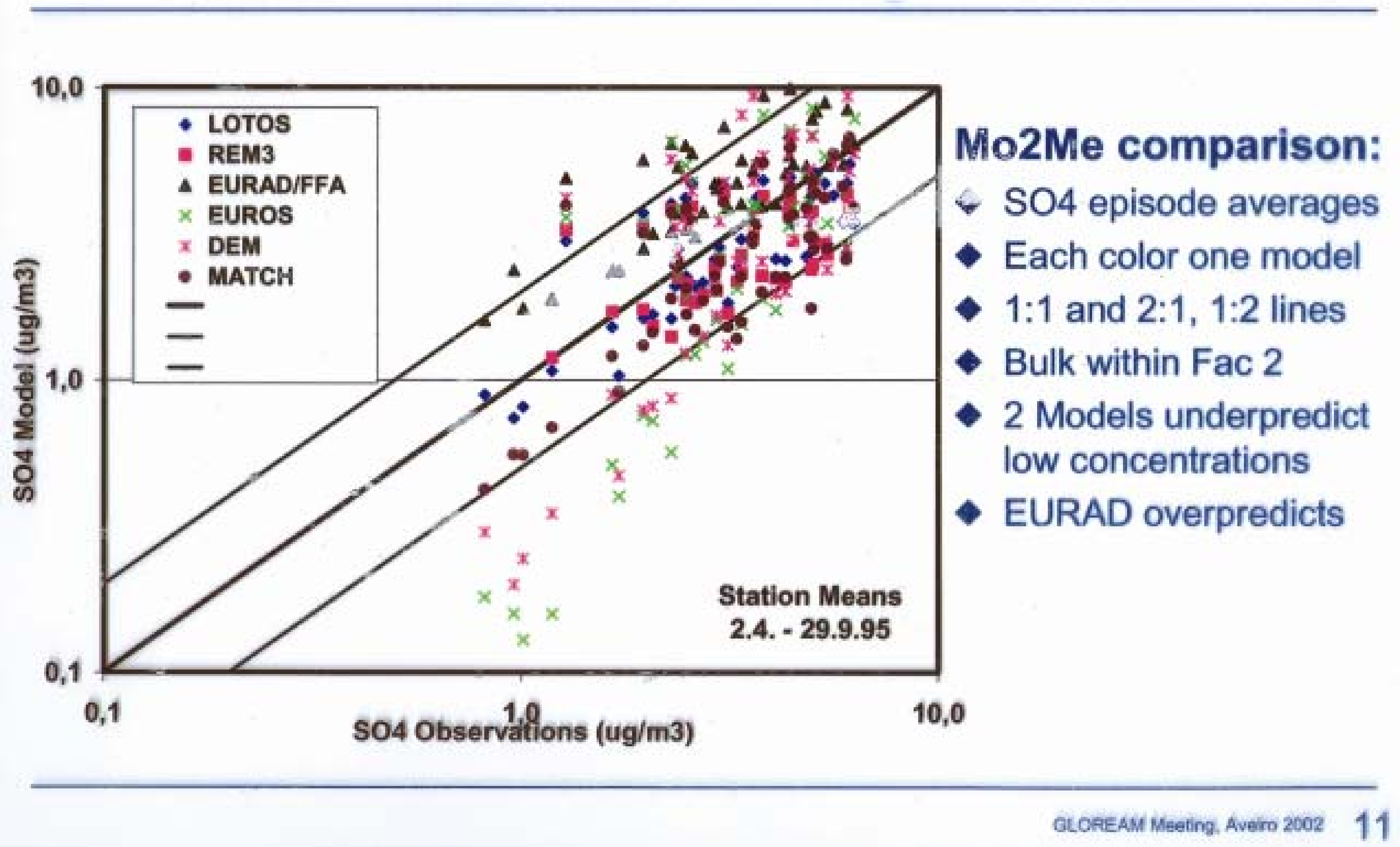


Figure 5
Annual average distribution of PM2.5 (µg/m^3) over Europe in the upper left panel and the associated fractions of BC, APPM, SO_4, NO_3 and NH_4 in the other panels.

SO$_3$ Scatter Diagram

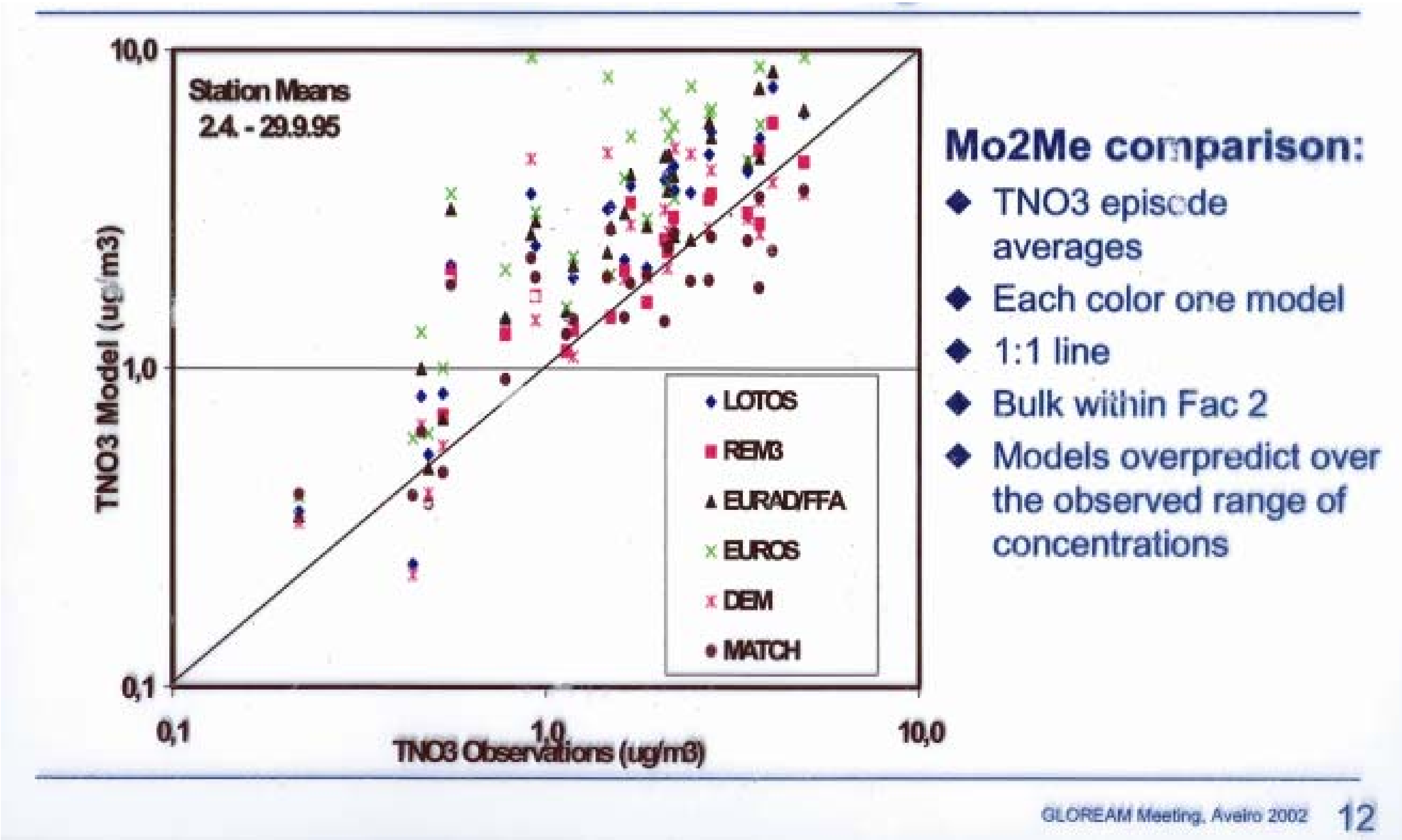


Mo2Me comparison:

- 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

TNO_3 Scatter Diagram

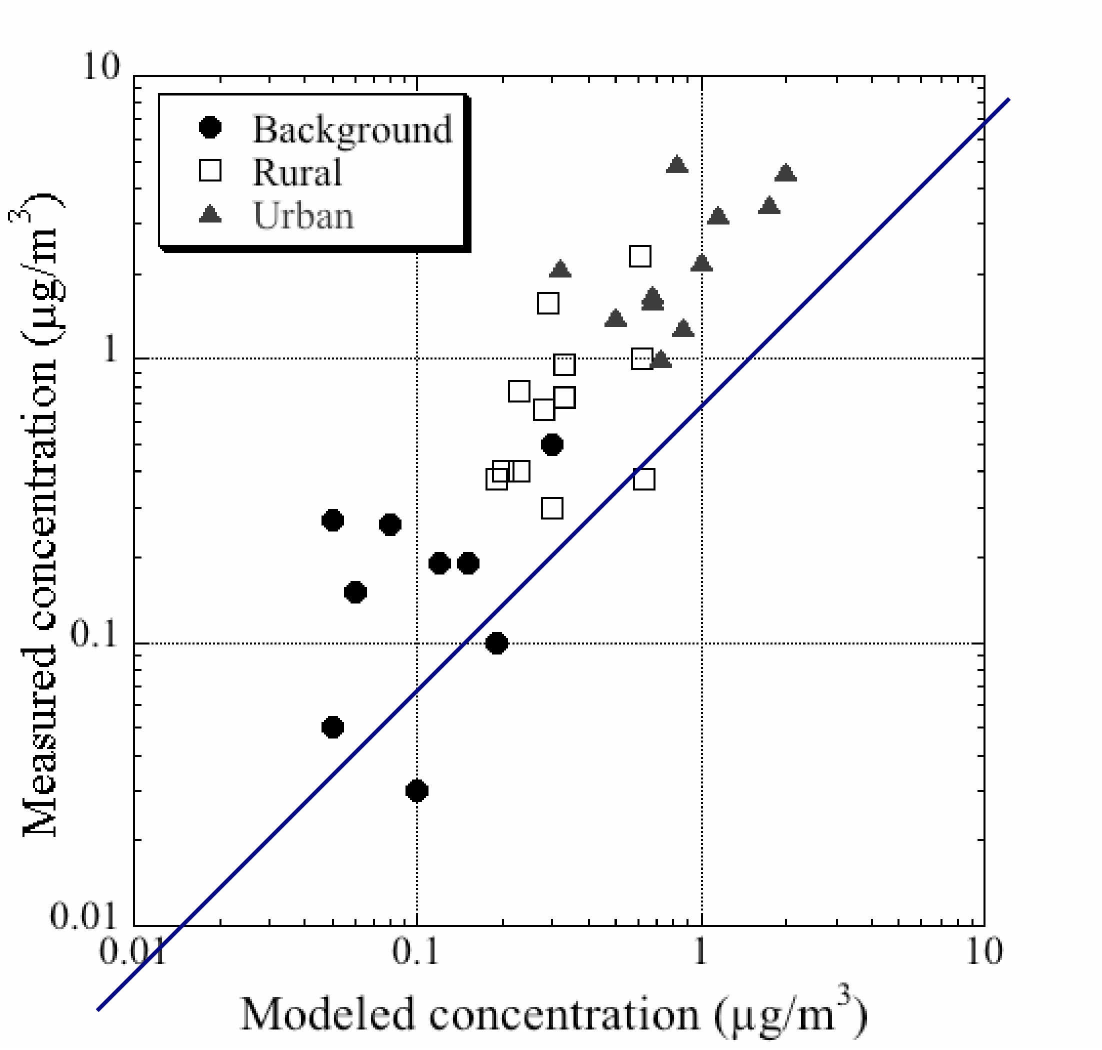


Mo2Me comparison:

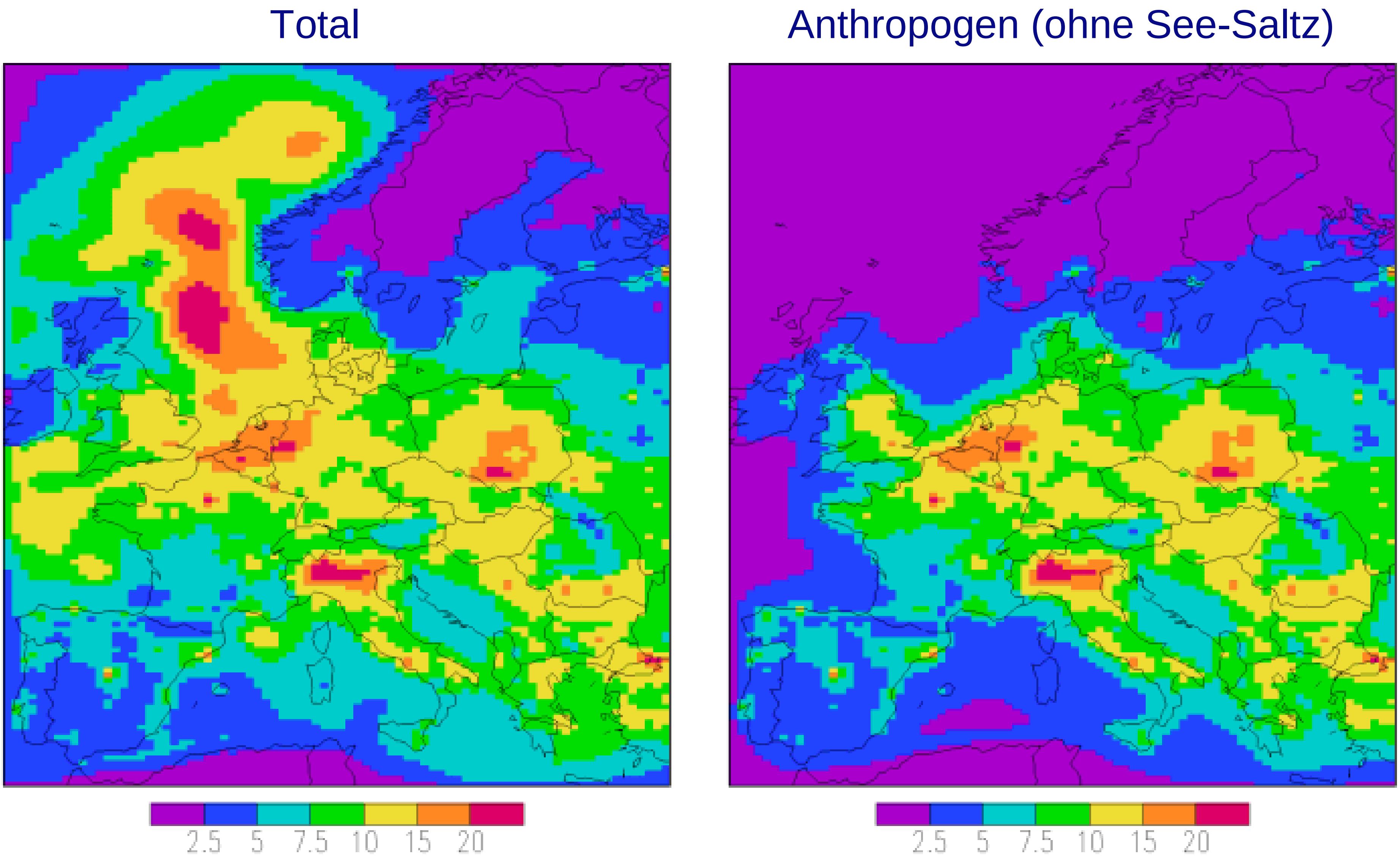
- TNO3 episode averages
- Each color one model
- 1:1 line
- Bulk within Fac 2
- Models overpredict over the observed range of concentrations

GLOREAM Meeting, Aveiro 2002 12

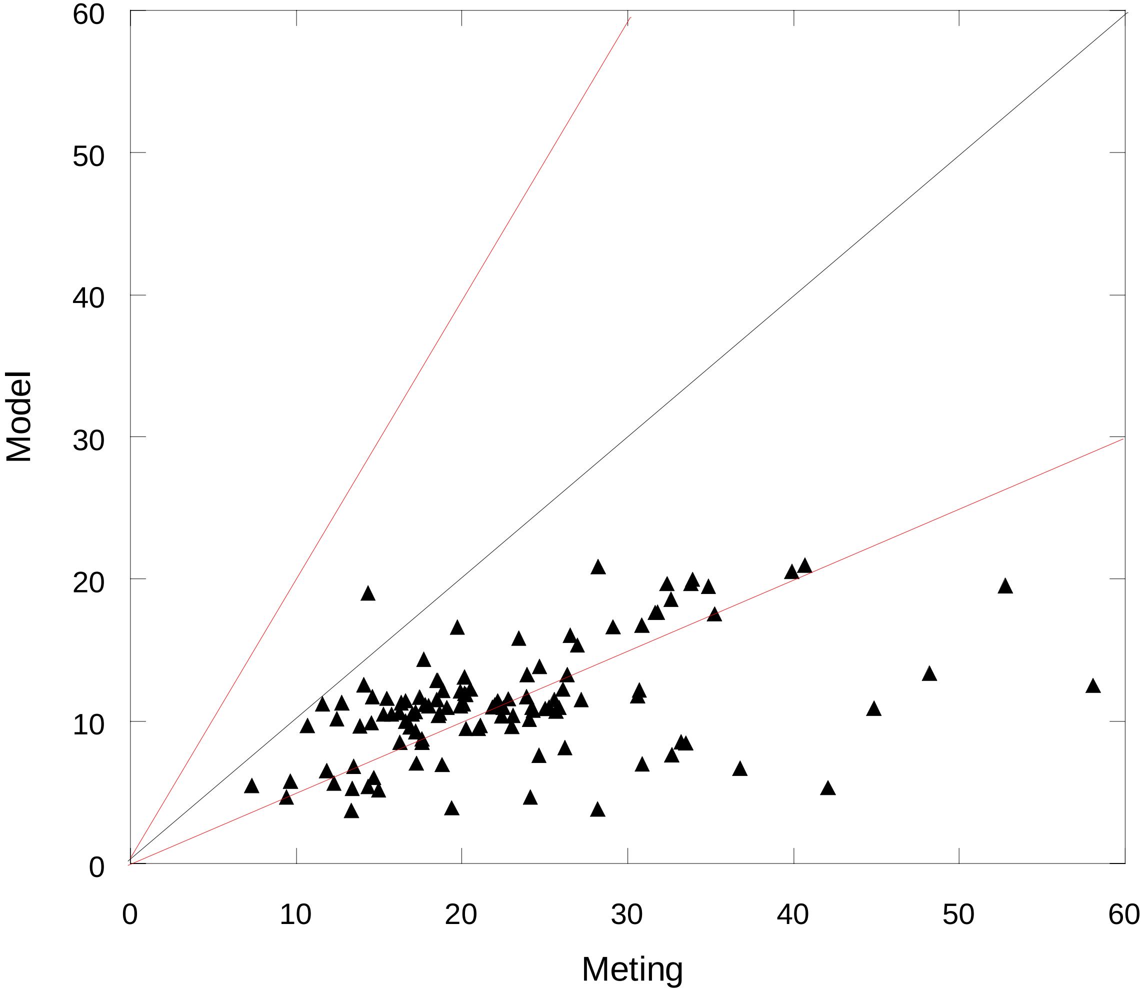
BC to measurements



Modellierte PM10 über Europa (2003)



Verifikation von Modell-Ergebnisse: PM10

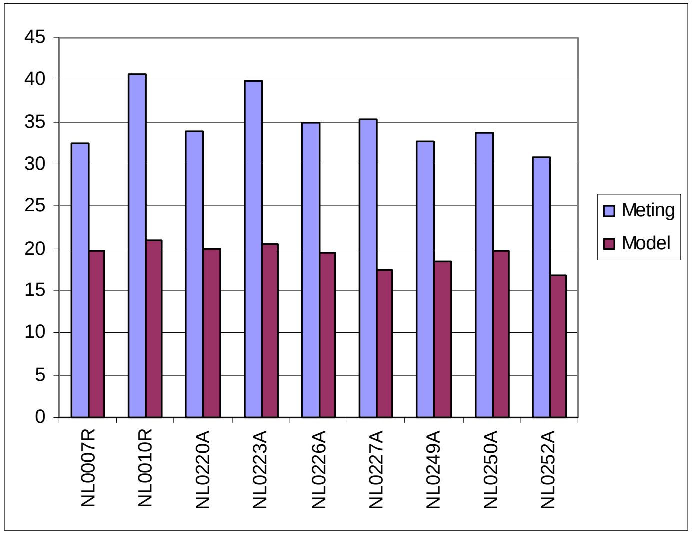


PM10 Model vs Airbase metingen

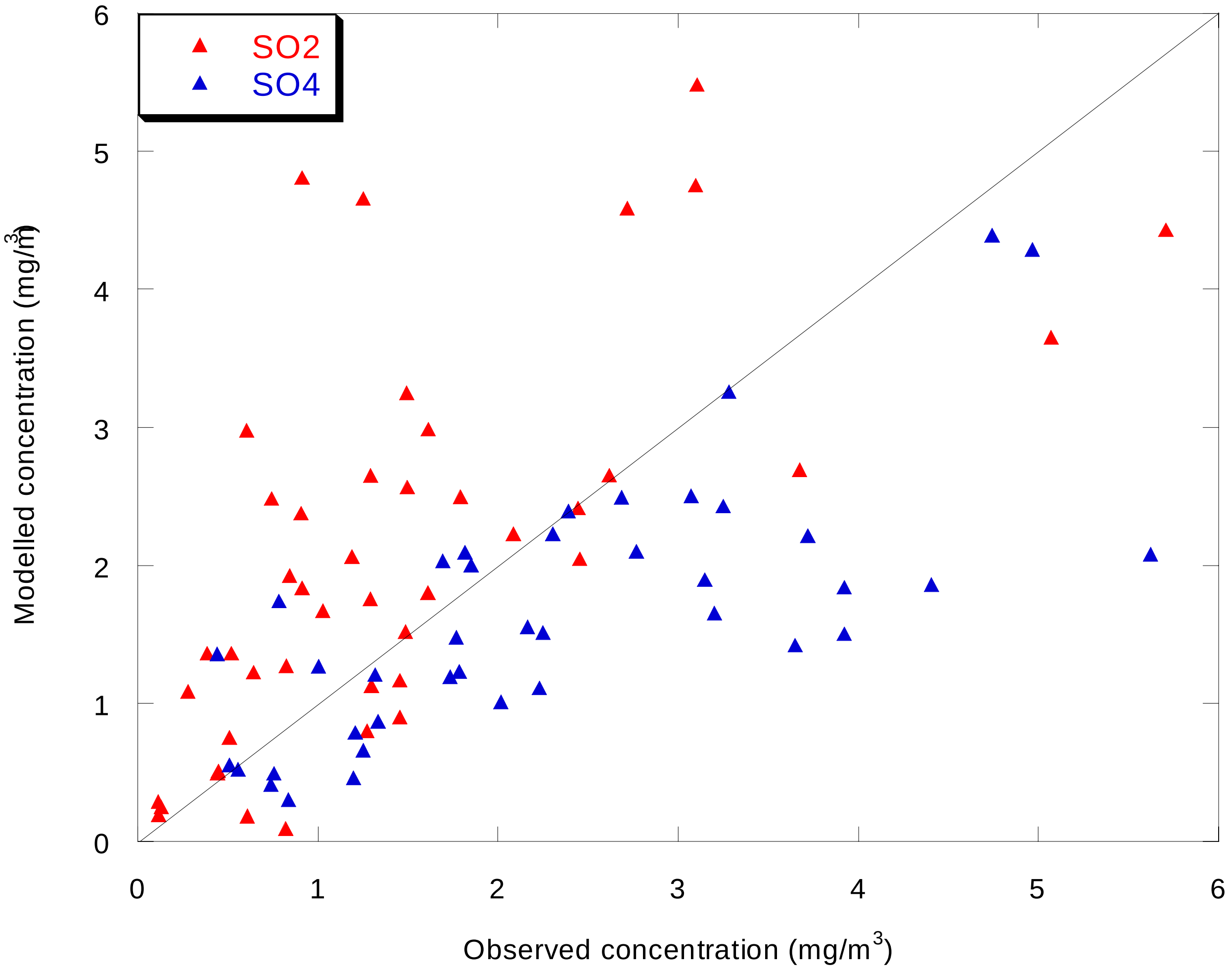
Holland:

PM10 wird 45 % unterschätzt

Korrelation: 0.52-0.62

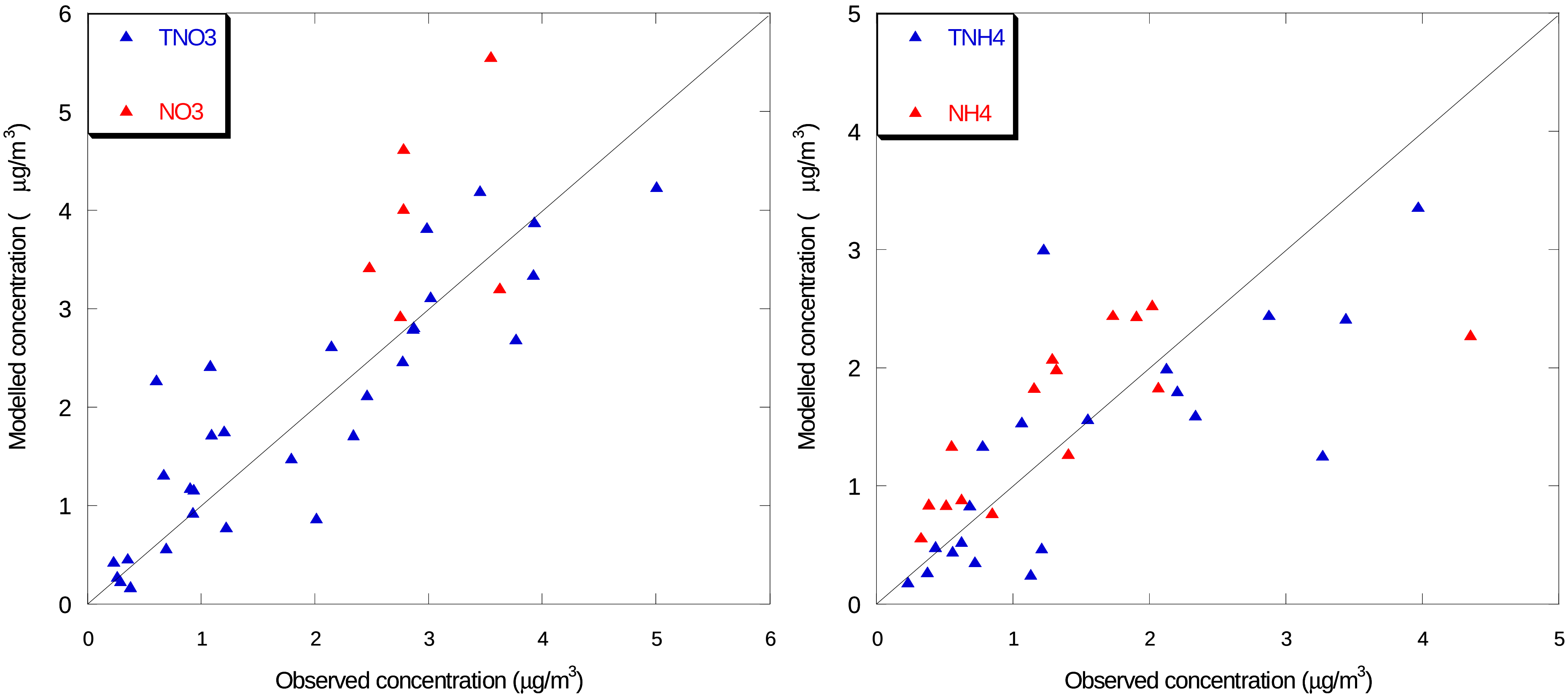


Verifikation von Modell-Ergebnisse: Sulfaat



Unsicherheit: Nicht-Lineare Trend in SO_2-SO_4 umsetzung (Wolken/Mist, heterogene Reaktion, usw

Verifikation von Modell-Ergebnisse: Nitraat en ammonium

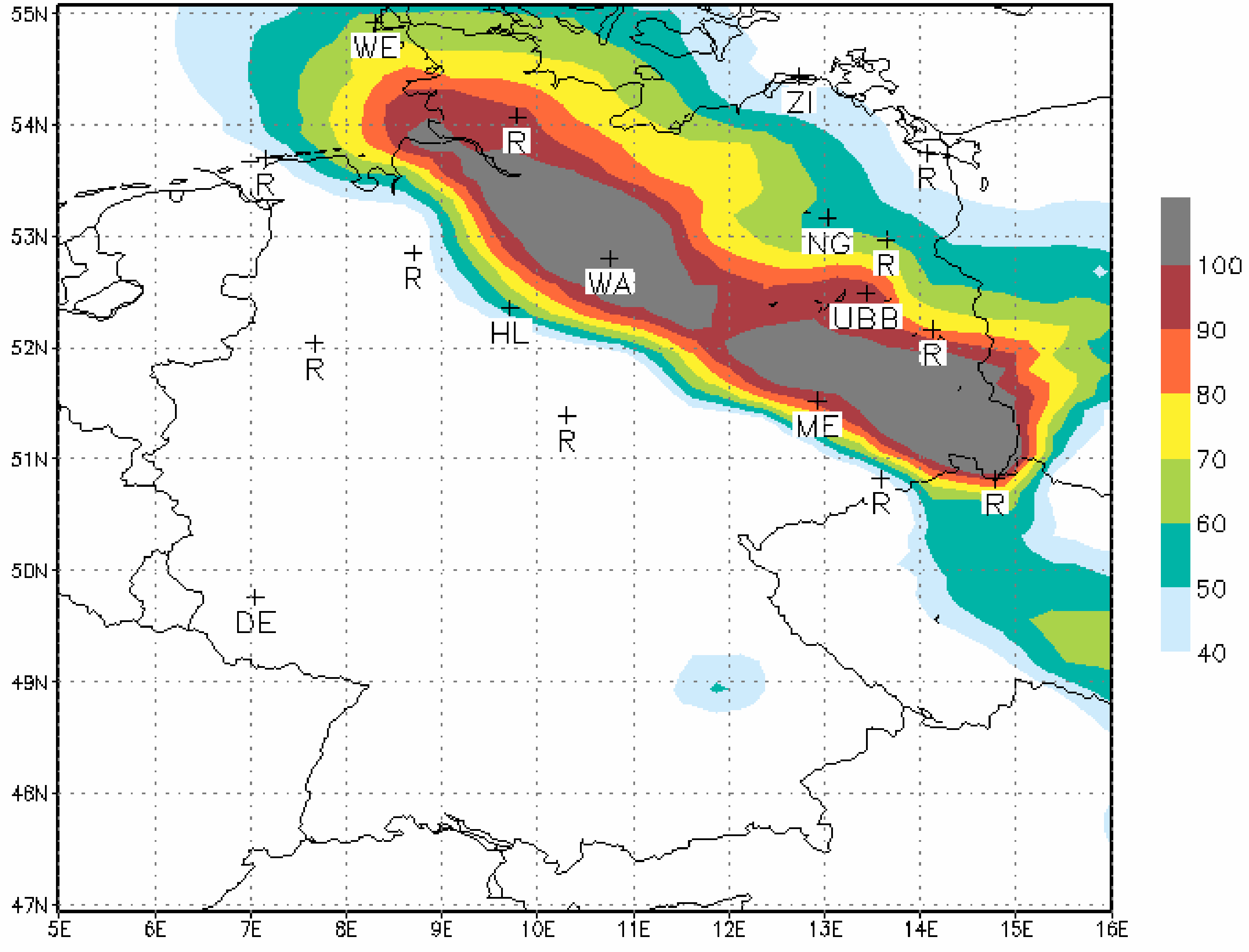


A model intercomparison study focussing on episodes of elevated PM10 concentrations

Das Ziel von das Projekt war das verstehen von die hohe gemessene PM-werte, mit Hilfe von Modellen

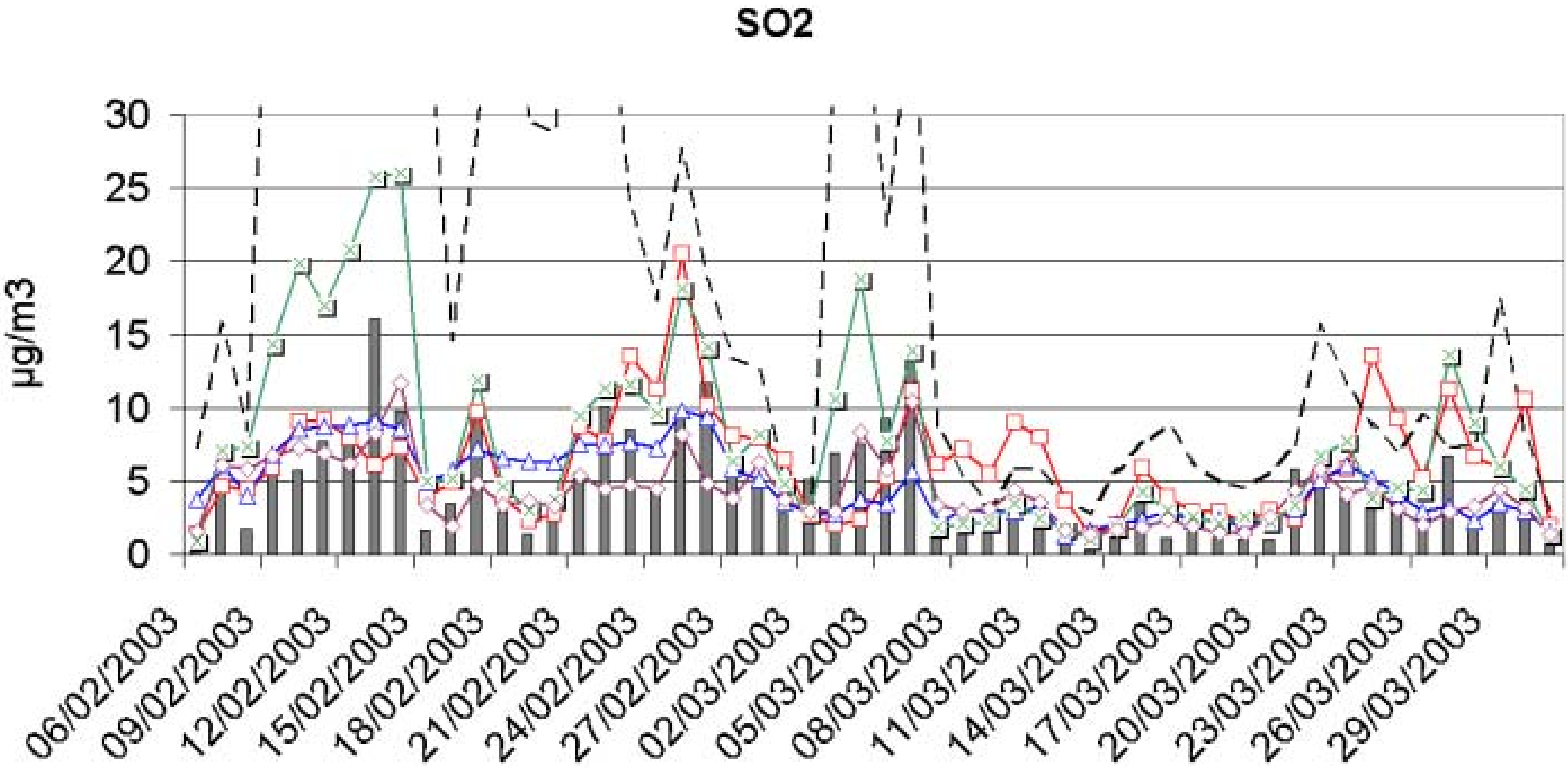
Benützte Modellen: RCG, LOTOS-EUROS, CHIMERE, EURAD, LM-MUSCAT

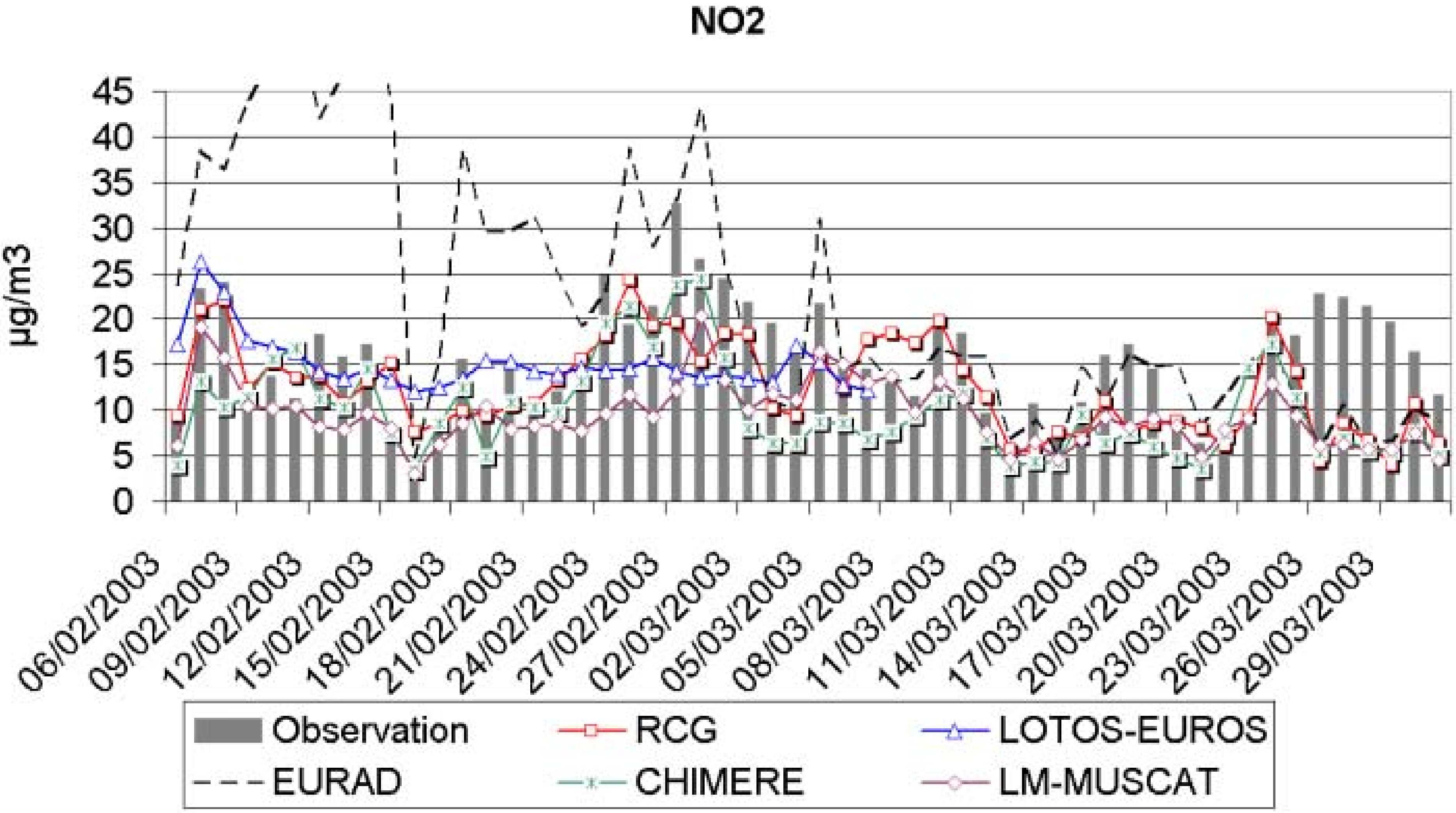
Episode von Jan-April 2003

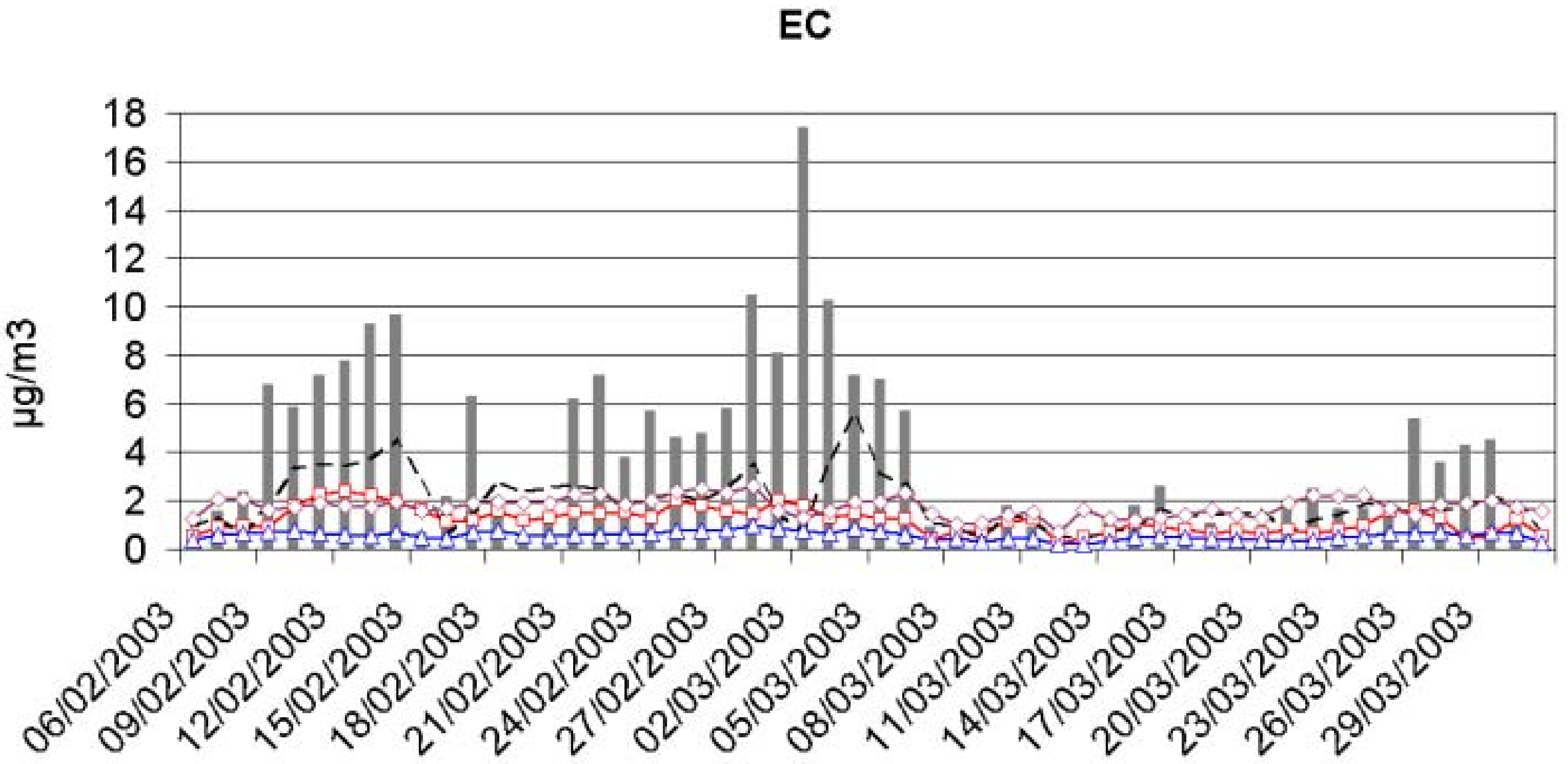


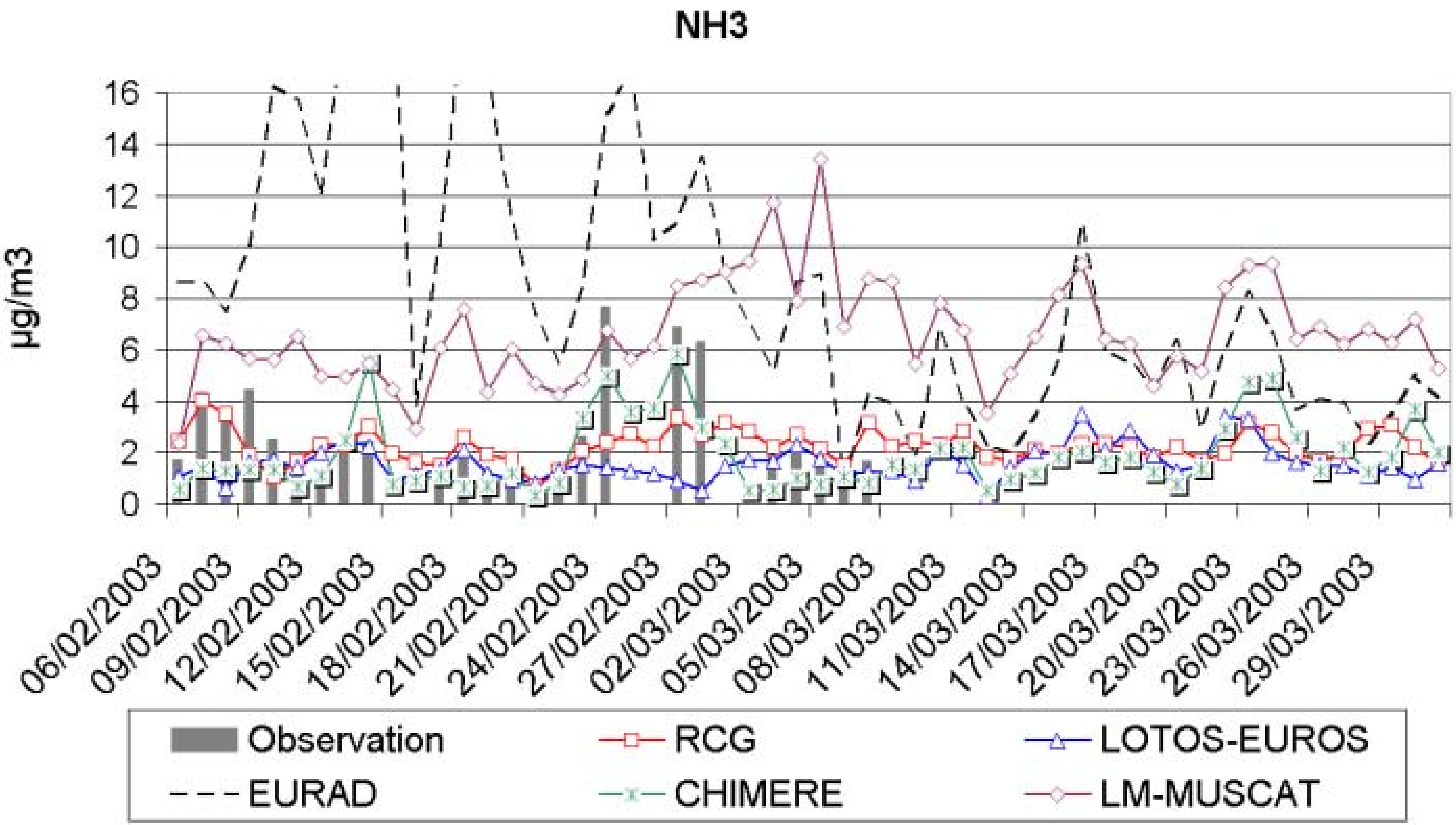
GrADS: COLA/IGES

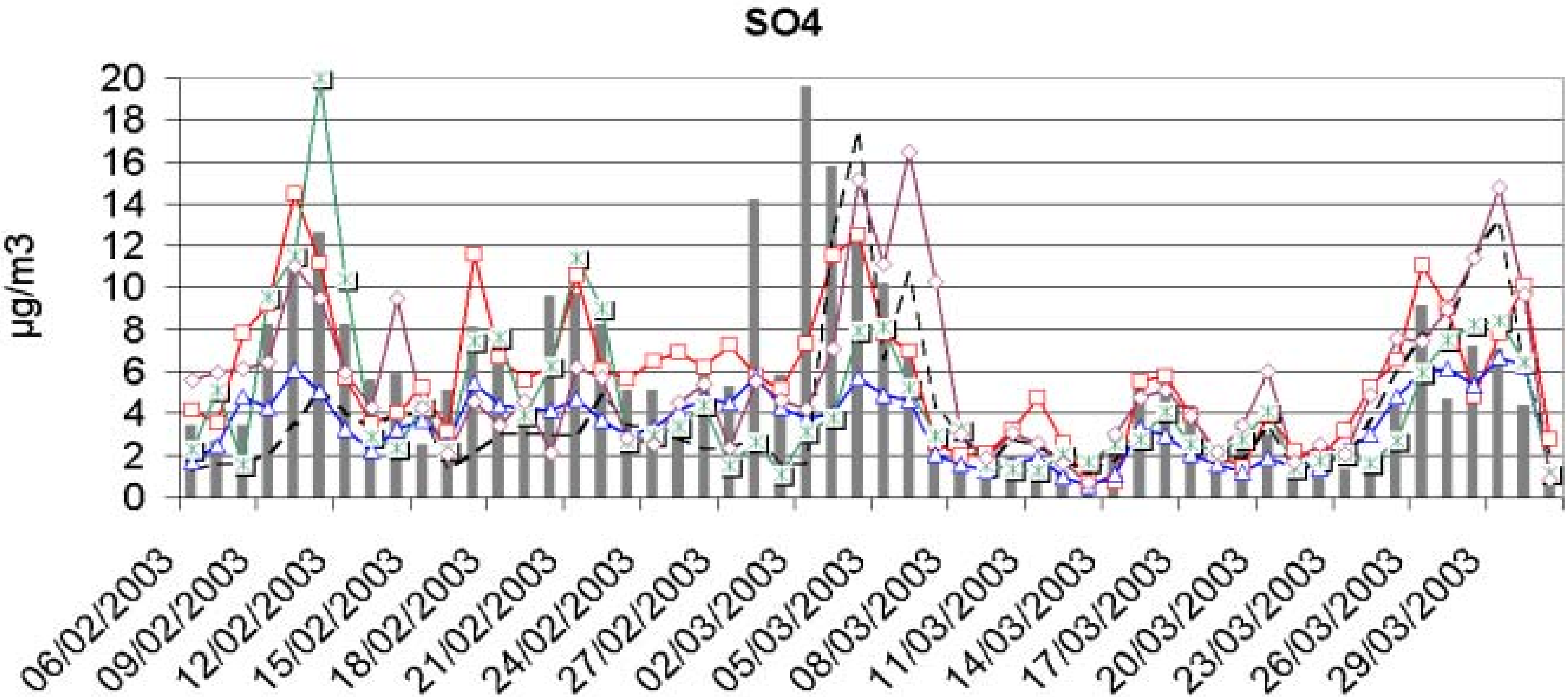
2007-08-29-14:43

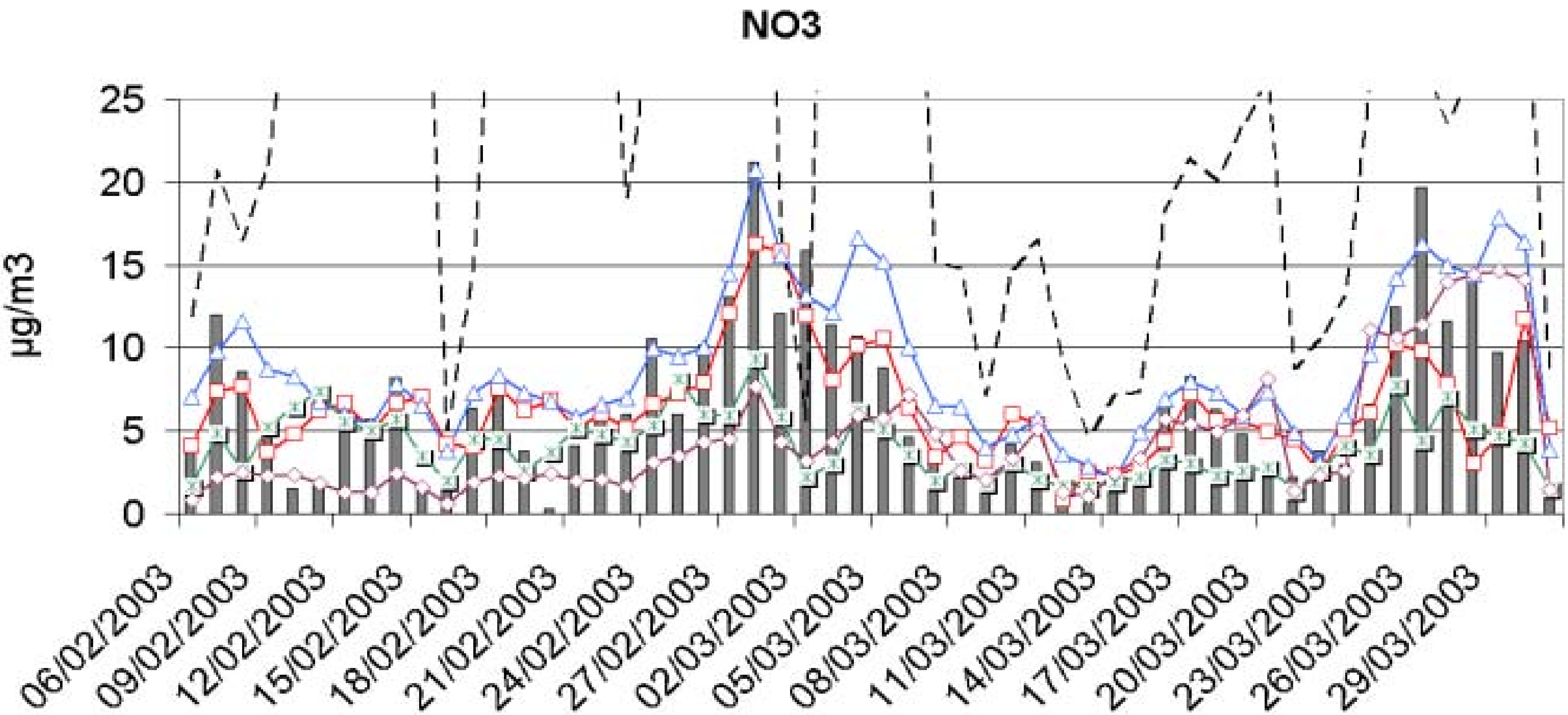

SO2
µg/m3
30
25
20
15
10
5
0
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003

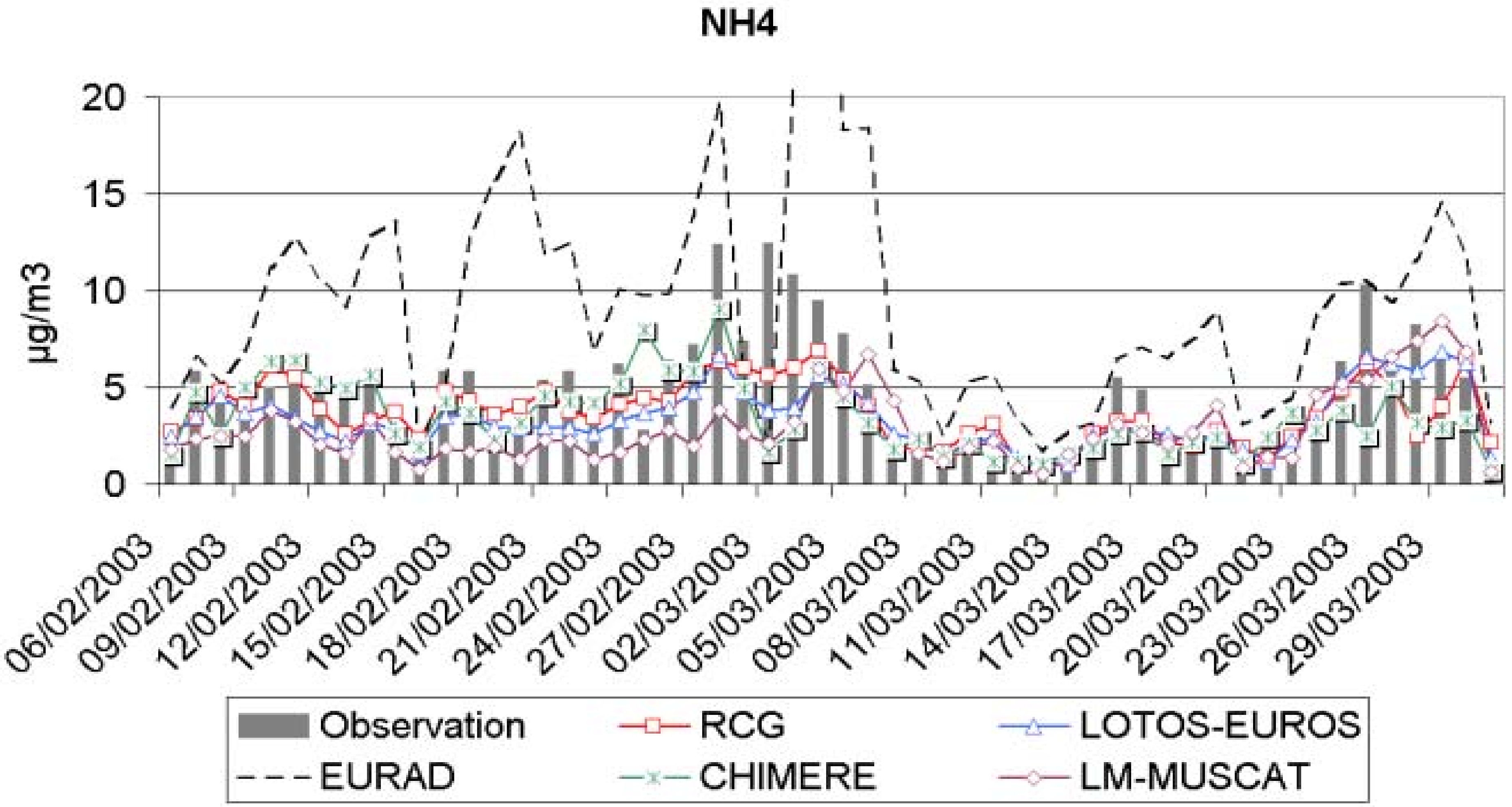

NO2
µg/m3
45
40
35
30
25
20
15
10
5
0
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003
Observation
RCG
LOTOS-EUROS
EURAD
CHIMERE
LM-MUSCAT


EC
µg/m3
0
2
4
6
8
10
12
14
16
18
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003

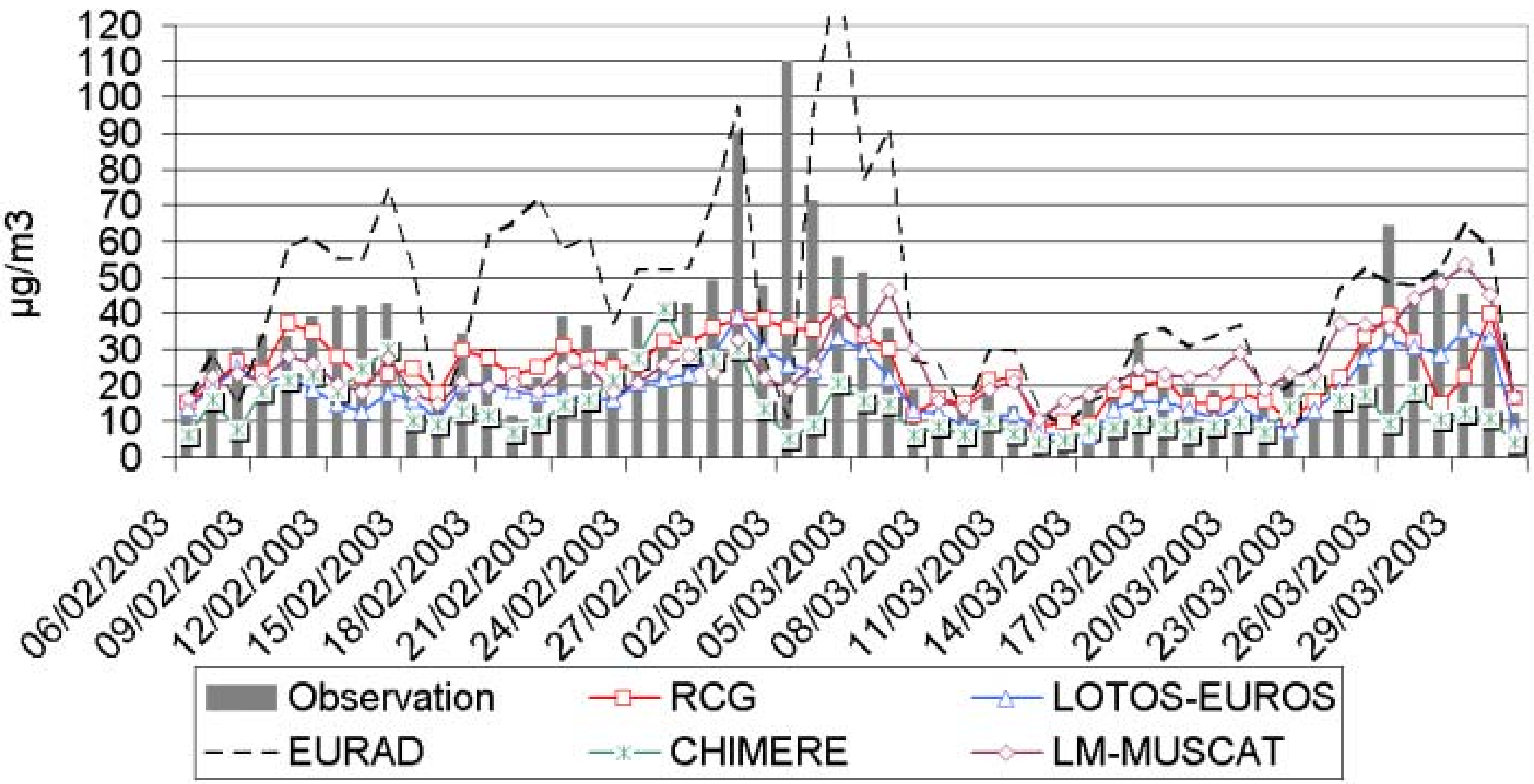

NH3
µg/m3
16
14
12
10
8
6
4
2
0
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003
Observation
RCG
LOTOS-EUROS
EURAD
CHIMERE
LM-MUSCAT

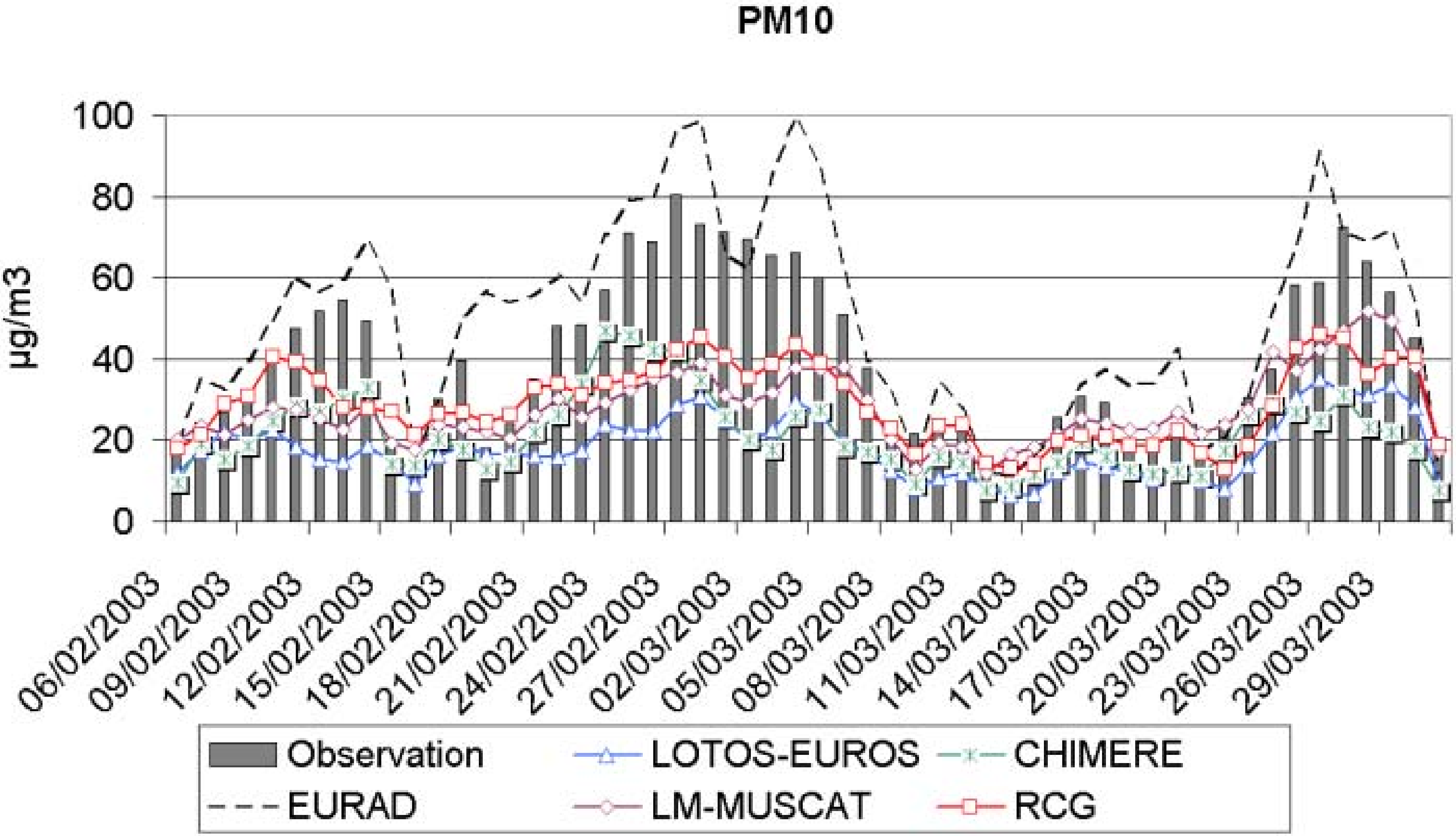

SO4
µg/m3
20
18
16
14
12
10
8
6
4
2
0
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003

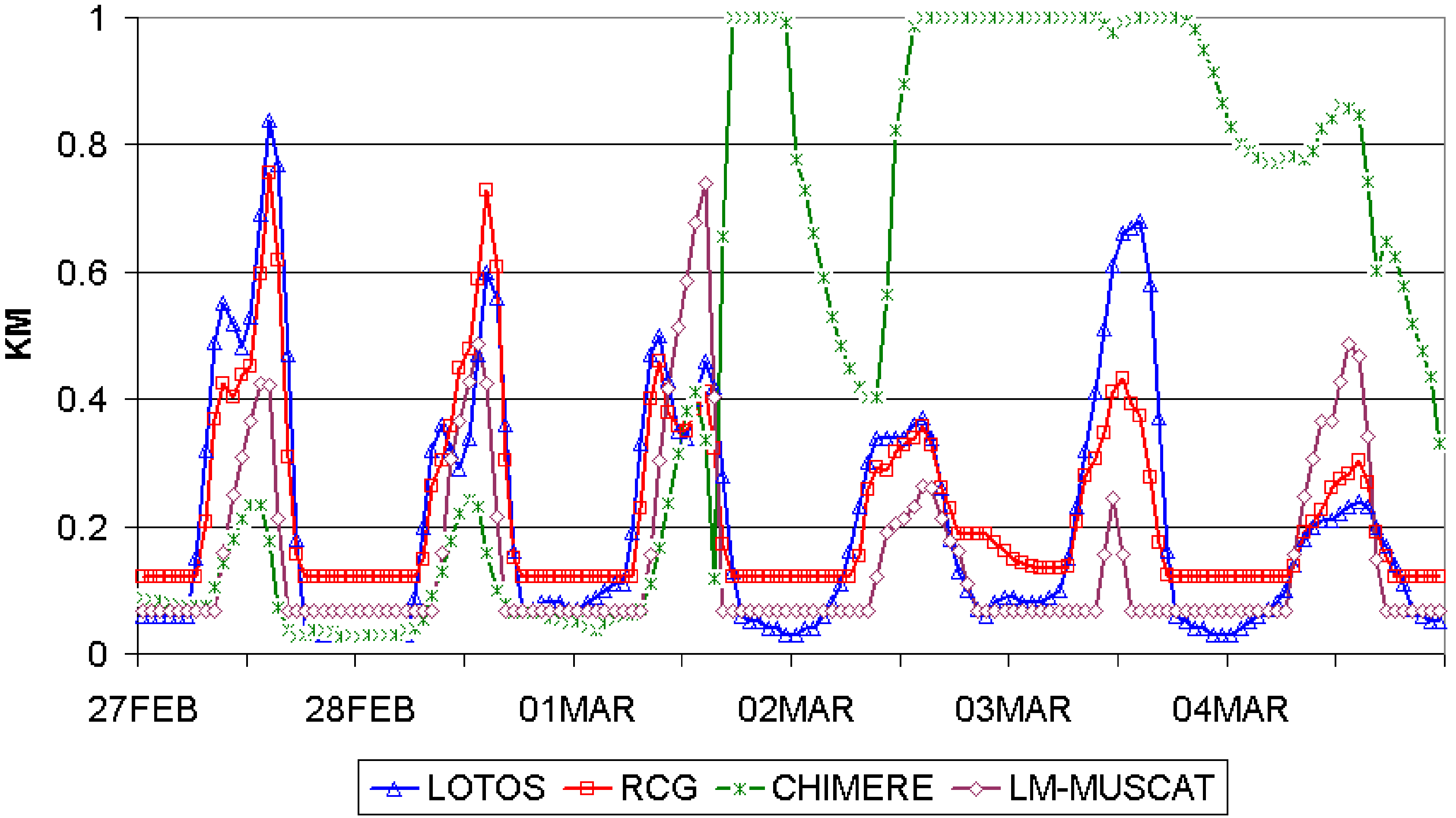

NO3
µg/m3
25
20
15
10
5
0
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003

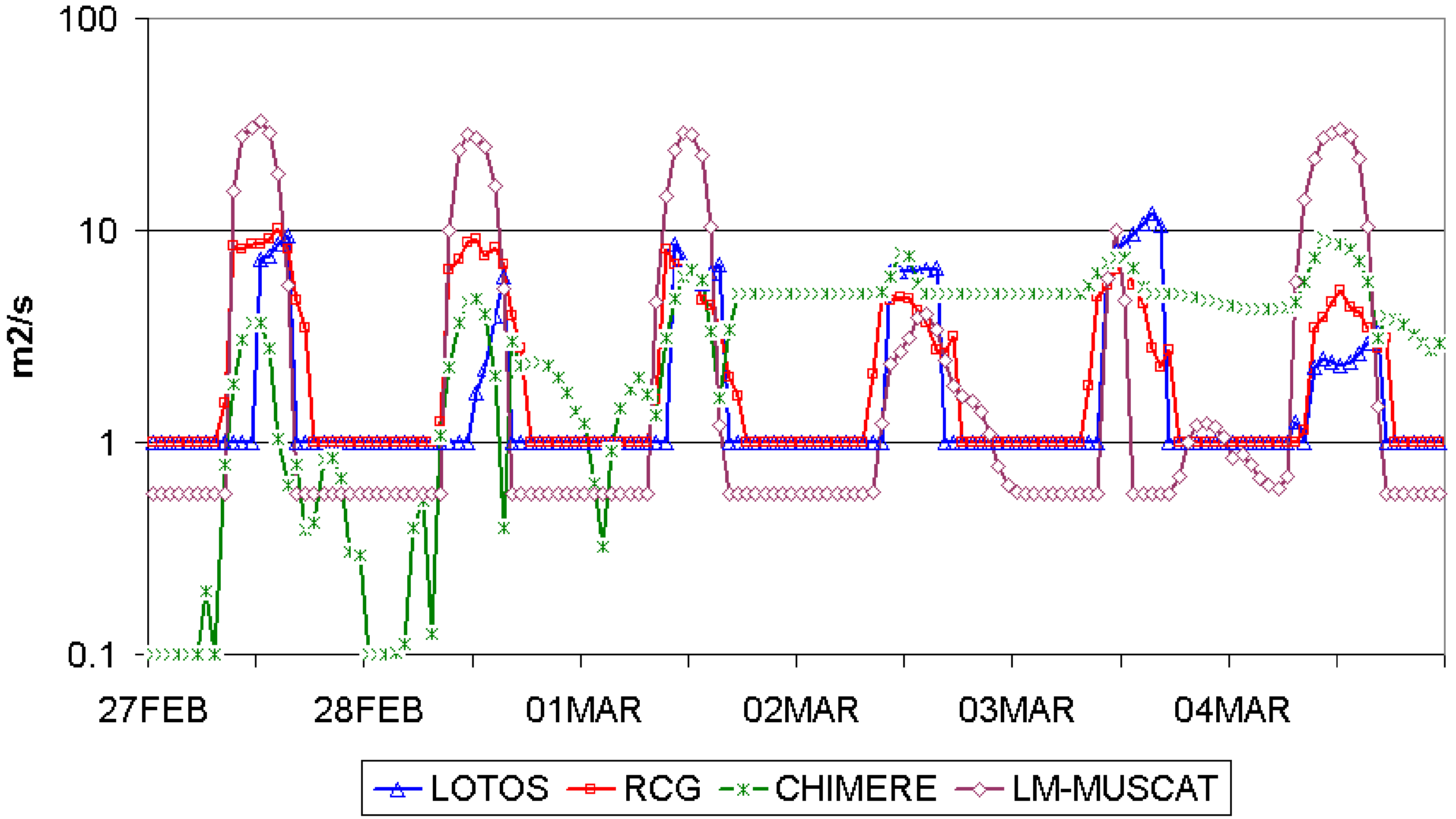

NH4
µg/m3
20
15
10
5
0
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003
Observation
RCG
LOTOS-EUROS
EURAD
CHIMERE
LM-MUSCAT

PM2.5


µg/m3
120
110
100
90
80
70
60
50
40
30
20
10
0
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003
Observation
RCG
LOTOS-EUROS
EURAD
CHIMERE
LM-MUSCAT


PM10
100
80
60
40
20
0
µg/m3
06/02/2003
09/02/2003
12/02/2003
15/02/2003
18/02/2003
21/02/2003
24/02/2003
27/02/2003
02/03/2003
05/03/2003
08/03/2003
11/03/2003
14/03/2003
17/03/2003
20/03/2003
23/03/2003
26/03/2003
29/03/2003
Observation
LOTOS-EUROS
CHIMERE
EURAD
LM-MUSCAT
RCG

KM
1
0.8
0.6
0.4
0.2
0
27FEB
28FEB
01MAR
02MAR
03MAR
04MAR
LOTOS
RCG
CHIMERE
LM-MUSCAT


100
10
1
0.1
m2/s
27FEB
28FEB
01MAR
02MAR
03MAR
04MAR
LOTOS
RCG
CHIMERE
LM-MUSCAT

Ergebnis

Das Modellieren von Anorganisch Aerosol geht gut (nicht bei EURAD)

Das Modellieren von hohe PM10 werte geht nicht gut (nur bei EURAD, aber da “right for the wrong reasons”)

Empfindlichkeit für Meteorologie ist Gross

Untersätzung von PM10 bei Modellen bei:
- Fehlende Emissionen wie Windblown Dust
- Schwierigkeiten bei Modellierung von BSOA
- Meteorologische Beschreibung bei stabiele Wetterlagen/Vertikal Austausch

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

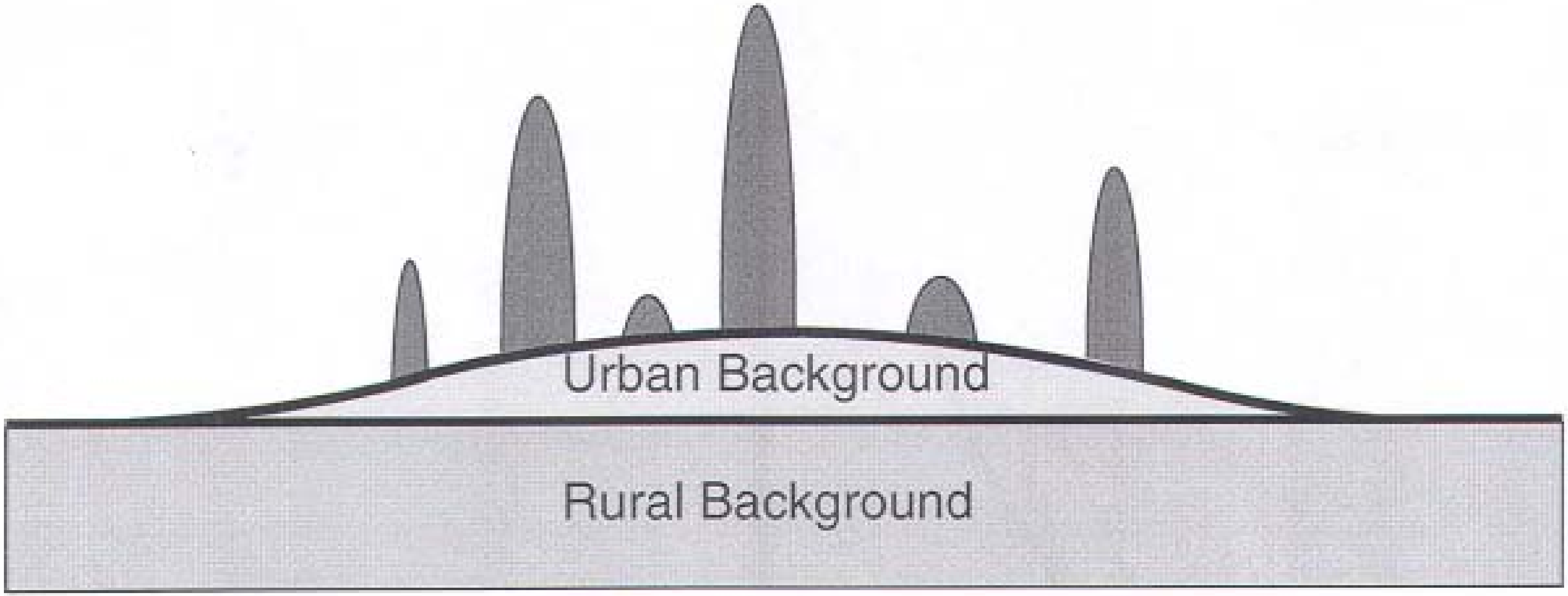
In Grossstaedten: Ueberschreitungen, auch in Berlin

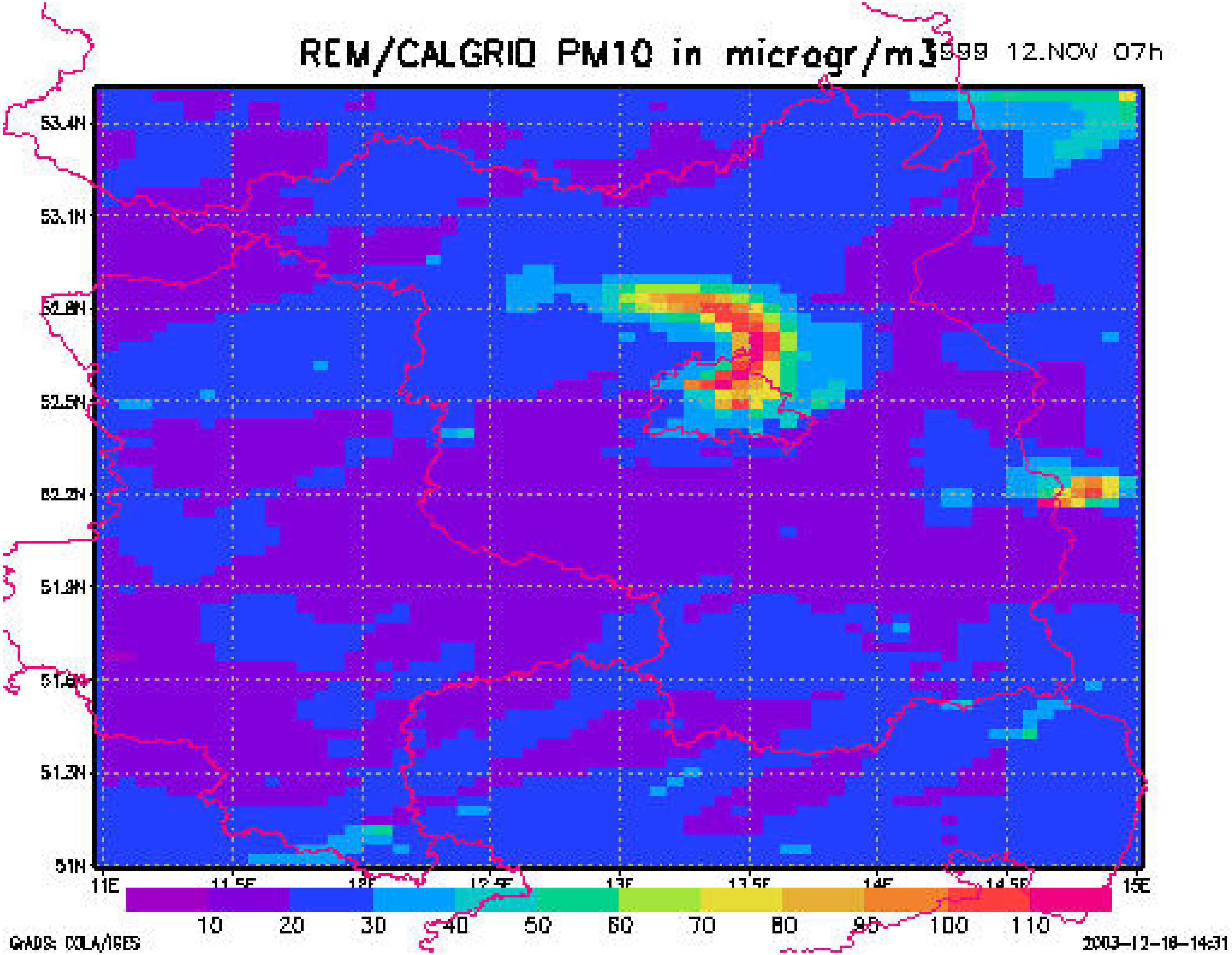
Konzentrationen in der Stadt sind bestimmt durch

Grossraeumigen Hintergrund

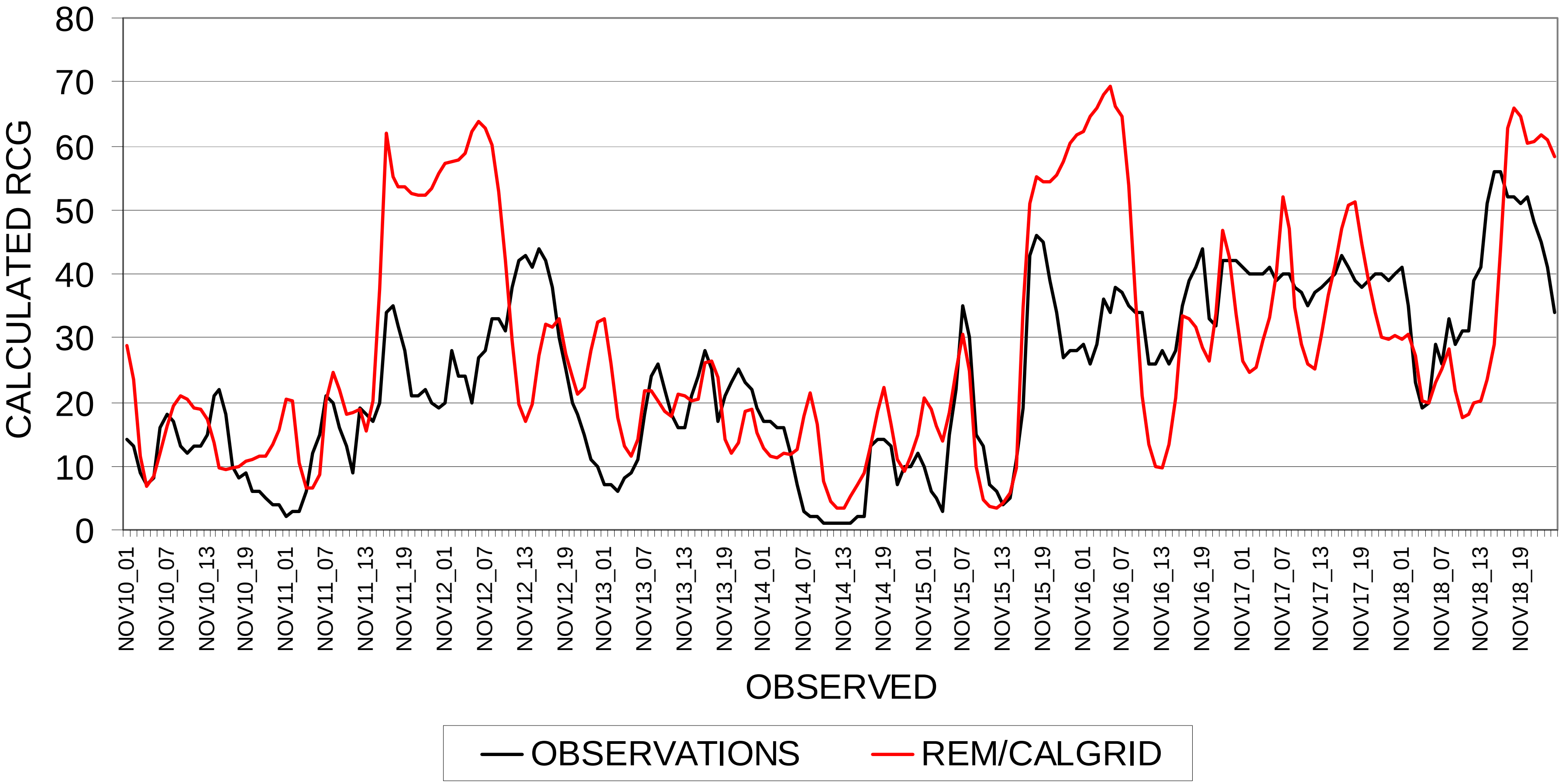
Allgemeinen Stadt-Hintergrund

Lokale Situation: Hot spots

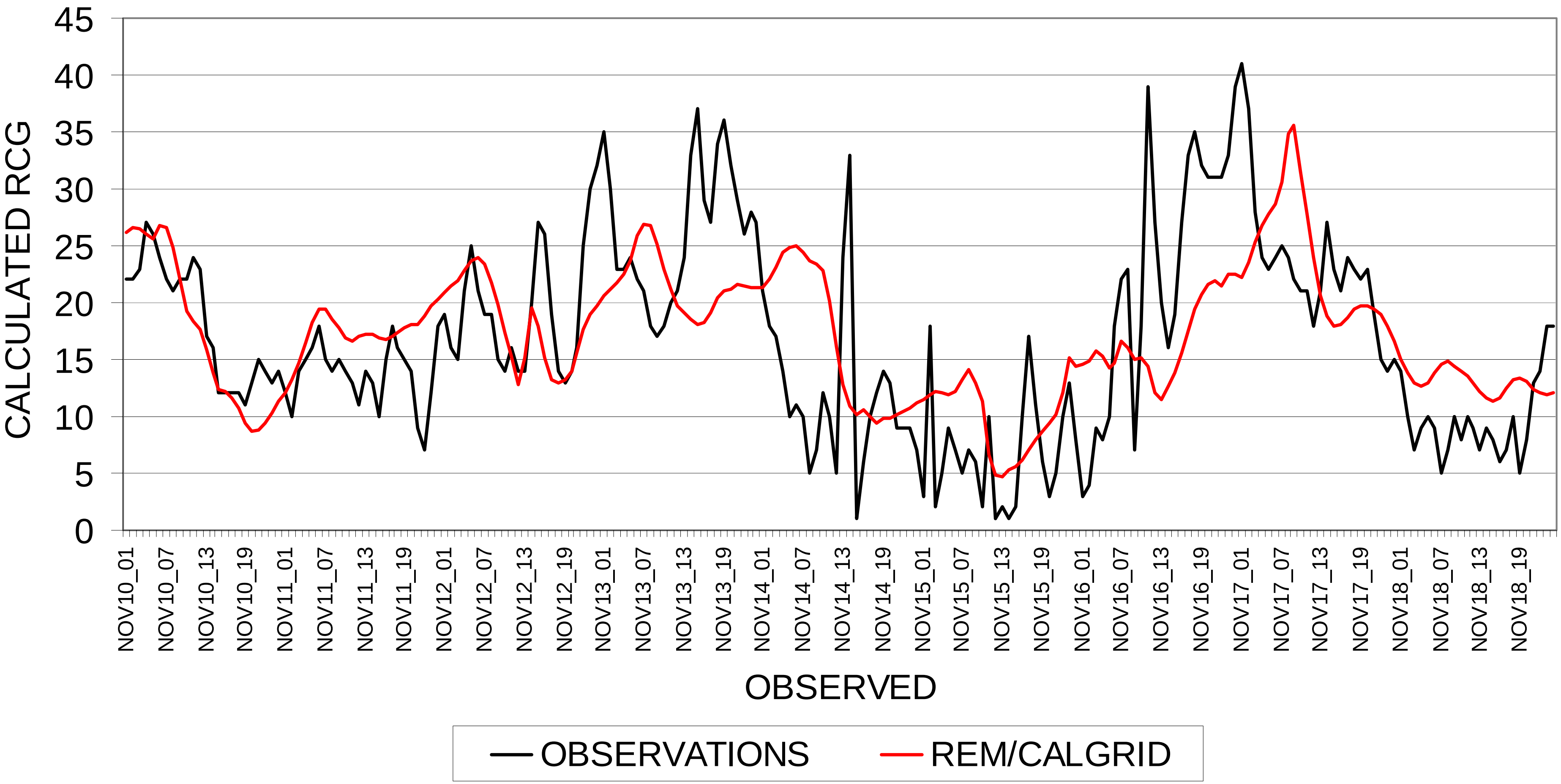

Urban Background
Rural Background


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
20
30
40
50
60
70
80
90
100
110
GrADS: COLA/IGES
2003-12-18-14:31

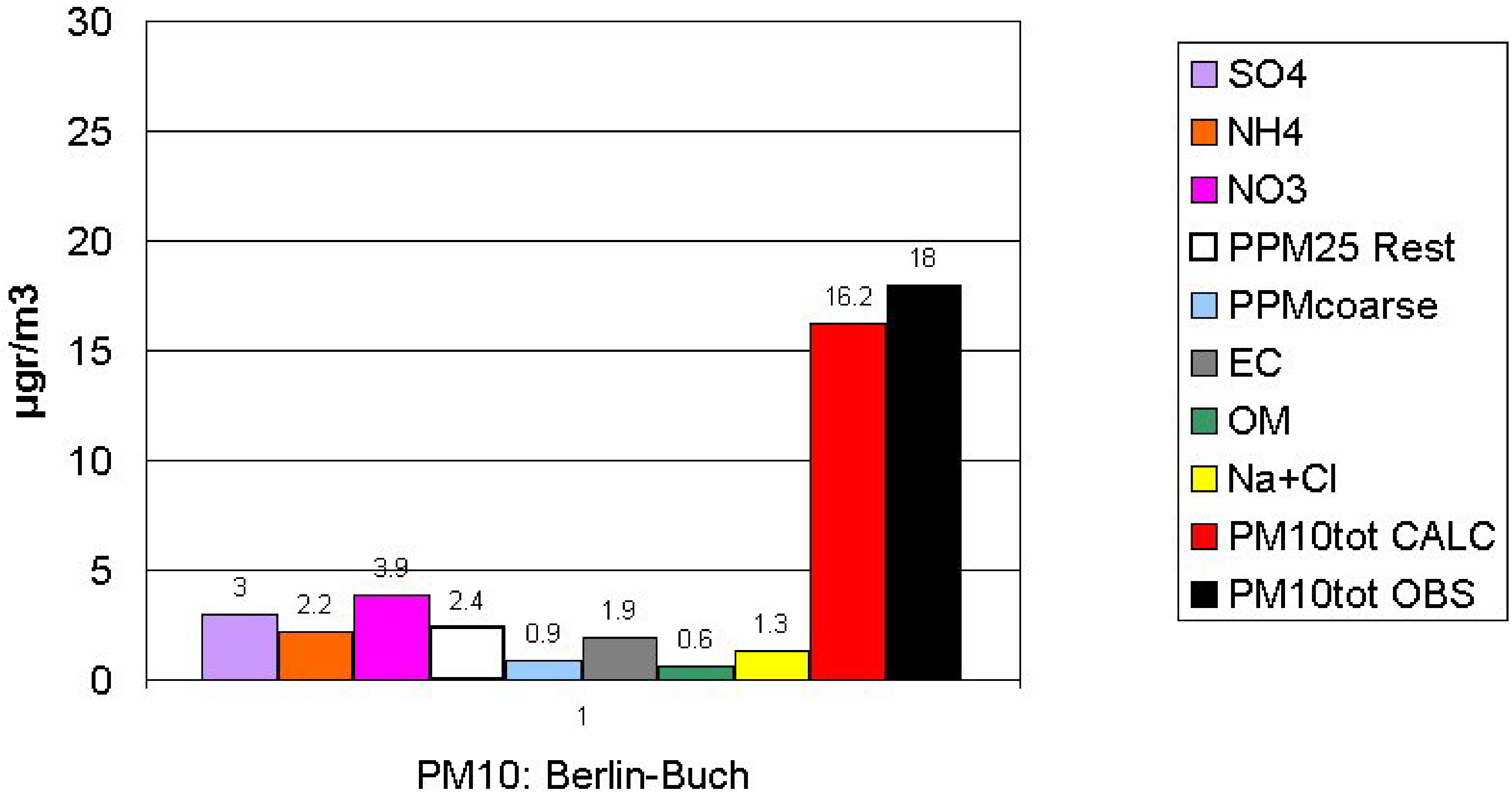
NO_2 Berlin-Buch (Hourly in microgr/m^3)



PM10 ZARTOU (Hourly in microgr/m³)



RCG: Zartau: PM10 COMPOSITION 1999



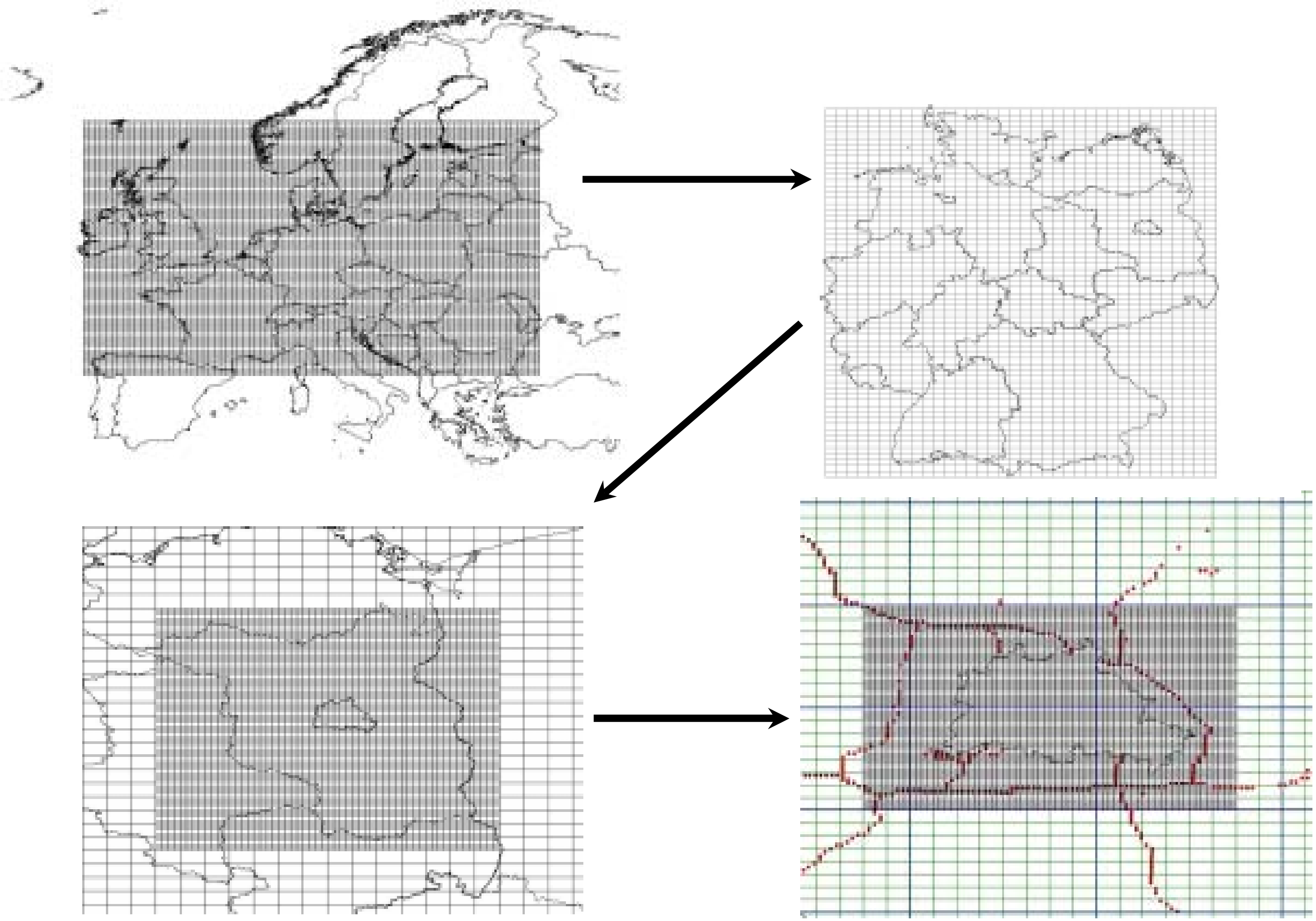
Modellierung von PM10 über Berlin

Hauptfrage

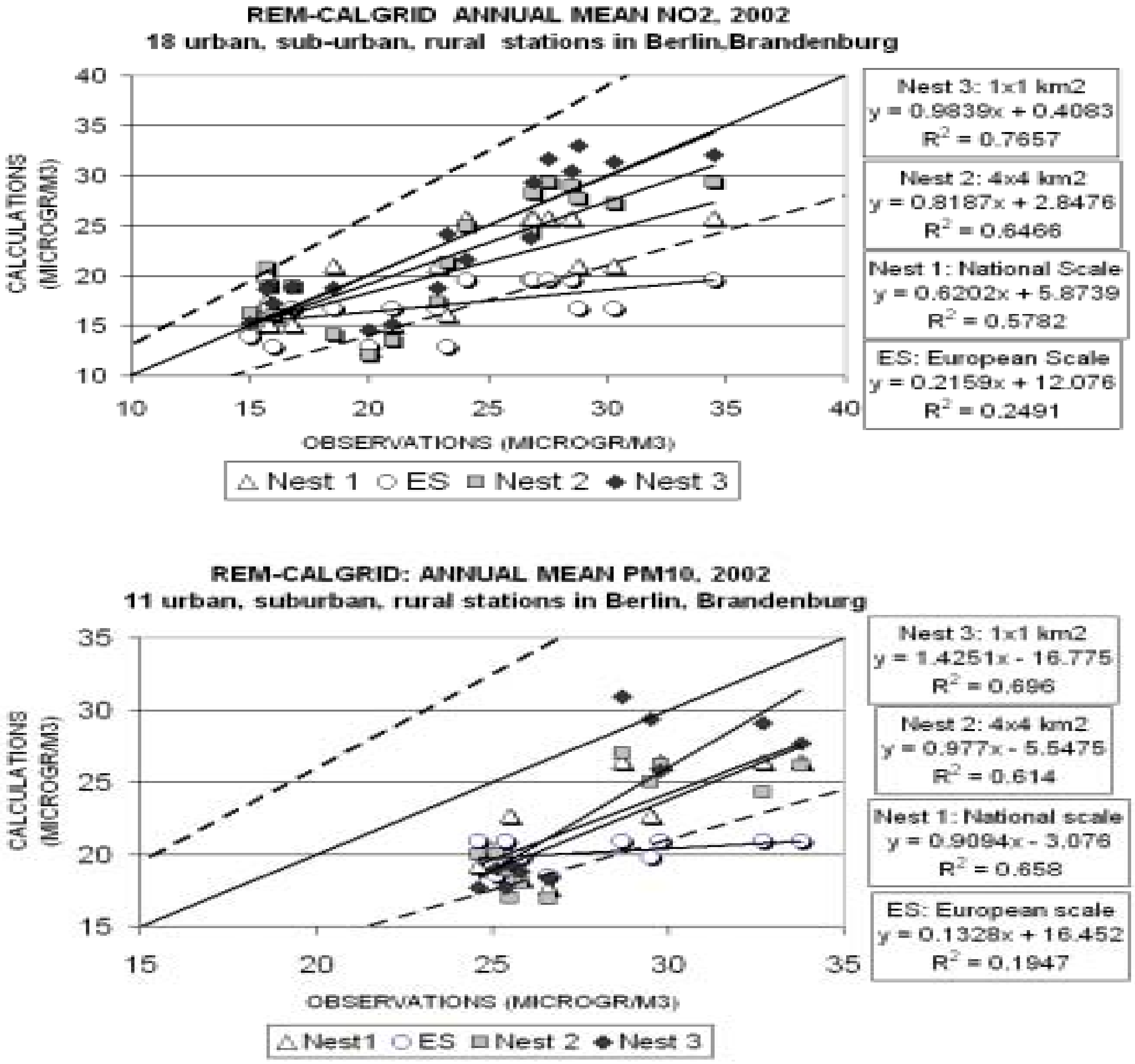
- Wie gut kann ich PM10 in Berlin modellieren?
- Wieviel von PM10 ist verursacht durch Emissionen in Berlin?

Paper

- R. Stern et al. “Analyzing the response of a chemical transport model to emission reductions utilizing various grid resolutions”, ITM, Leipzig, May 2006



RCG modelling domains. Upper left: European scale grid with resolution of 0.25° Lat., 0.5° Lon. Upper right: Nest 1, national scale (Germany) grid with resolution of 0.125° Lat., 0.25° Lon. Lower left: Nest 2, the Federal State (Brandenburg) grid with resolution of 0.03125° Lat., 0.0625° Lon., embedded in Nest 1. Lower right: Nest 3, urban grid Berlin with resolution of 0.0078125° Lat., 0.015625° Lon., embedded in Nest 2 (and Nest 1) and also showing the major “ring” motorway around Berlin.



Scatter diagram of observed and calculated NO_2 and PM10 annual means in the greater Berlin area at four scales, including regression lines and correlation coefficients. Dashed lines indicate the range of +/- 50% of the observations. For further explanations see text.

IV) Ursachen Analyse und Massnahmen in Deutschland

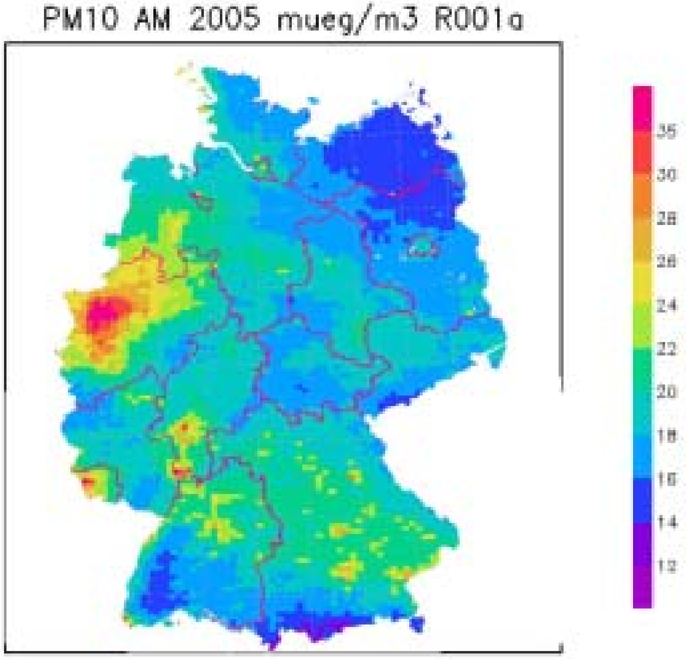
- Präsentation von PM 10 über Deutschland bei Kombination von Messungen und Modellergebnisse

- Data-assimilation ist der Kombination von Messungen und Berechnungen:
  - Passief: Kriging, Optimal Interpolation
  - Aktief: 4-D var, Ensemble Kalman Filter

- Massnahmen Analyse: UBA-project PAREST: Particle Reduction Strategies: www.parest.de

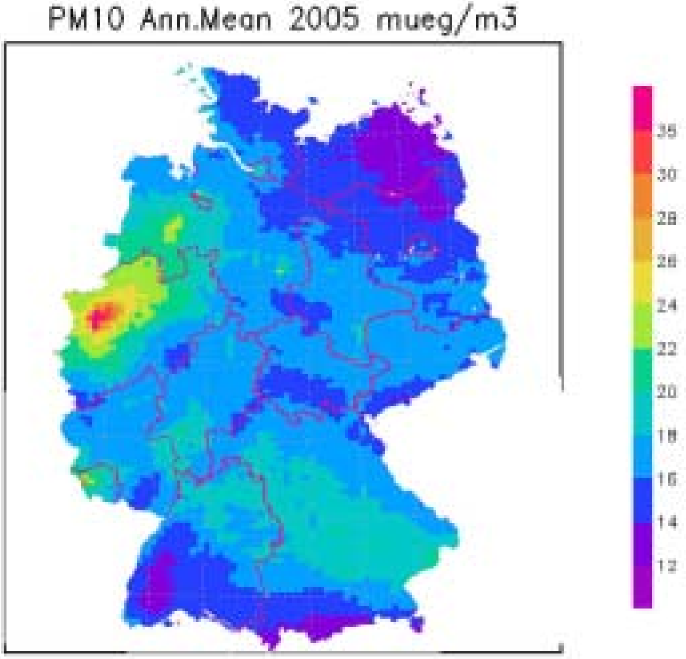
Basislauf 2005

Parest modifiziert


PM10 AM 2005 mueg/m3 R001a

2008-11-05-13:15

Parest original


PM10 Ann.Mean 2005 mueg/m3

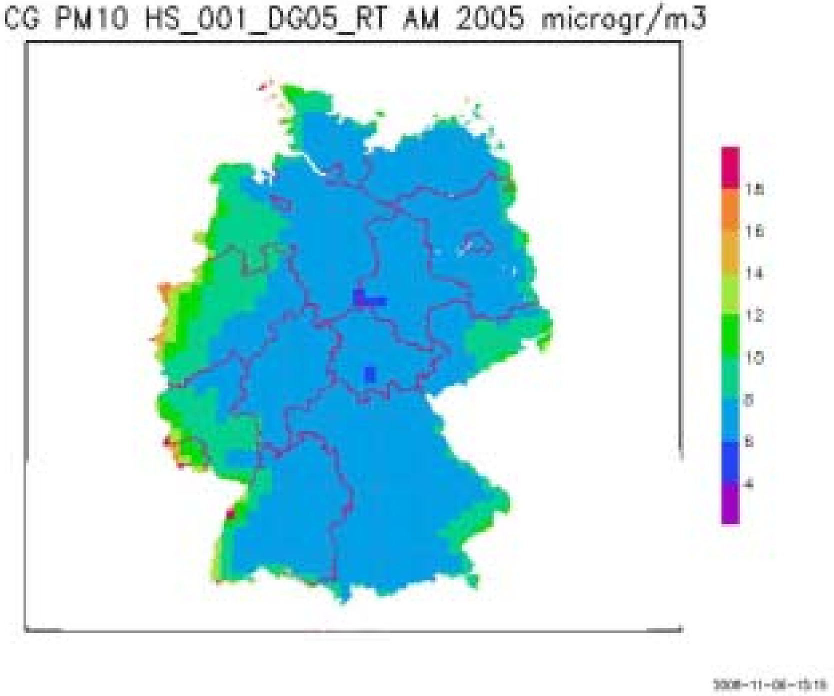
2008-11-05-13:17

Modifizierung der Parest-Emissionen führt zu einer Erhöhung der berechneten PM10-Immissionen in den Emissionsgebieten, aber: Tendenz zur Unterschätzung bleibt erhalten

R.Stern, 10. Nov. 2008

Szenario 001: keine anthropogene Emissionen in Deutschland

PM10-Jahresmittelwerte ohne deutsche Emissionen



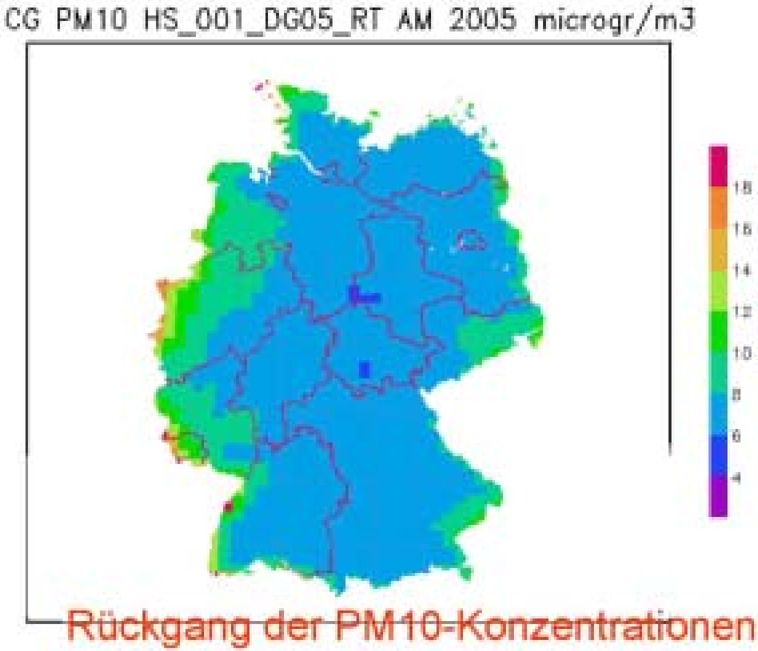
R.Stern, 10. Nov. 2008

Maximal mögliche Immissionsminderung:

Rückgang der PM10-Konzentrationen auf 6-18 µg/m3

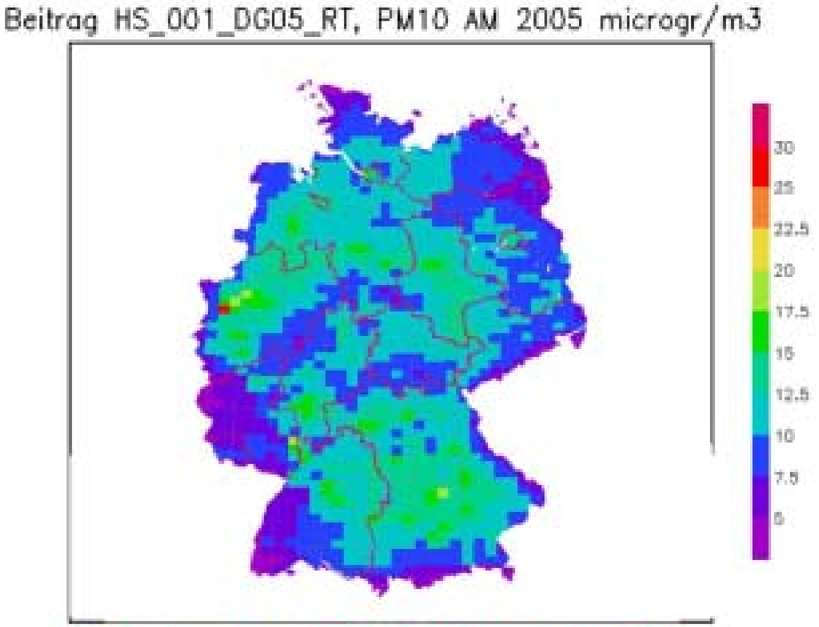
Szenario 001: keine anthropogene Emissionen in Deutschland

PM10-Jahresmittelwerte ohne deutsche Emissionen



Rückgang der PM10-Konzentrationen auf circa 6-18 µg/m3

Beitrag der deutschen Emissionen zu den PM10-Jahresmittelwerten



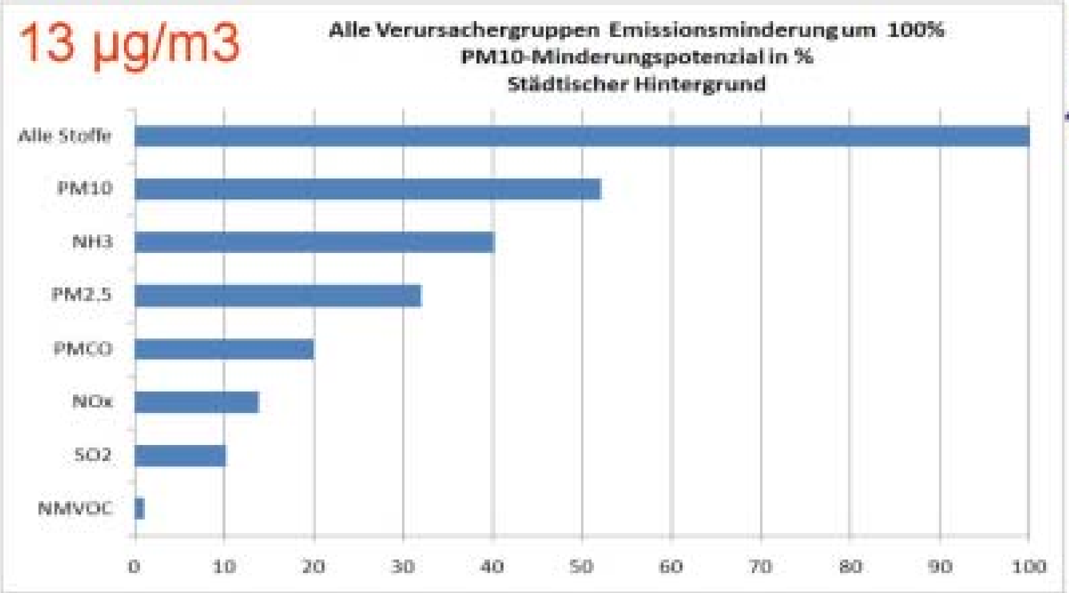
Maximales Minderungspotenzial:
Circa 5 - 25 µg/m3
Ländlicher bis städtischer Hintergrund

Rangordnung:
NH3
PM2.5
PMCO

Minderung der Emissionen **pro Stoff** um 100%,
Jeweils alle Verursachergruppen

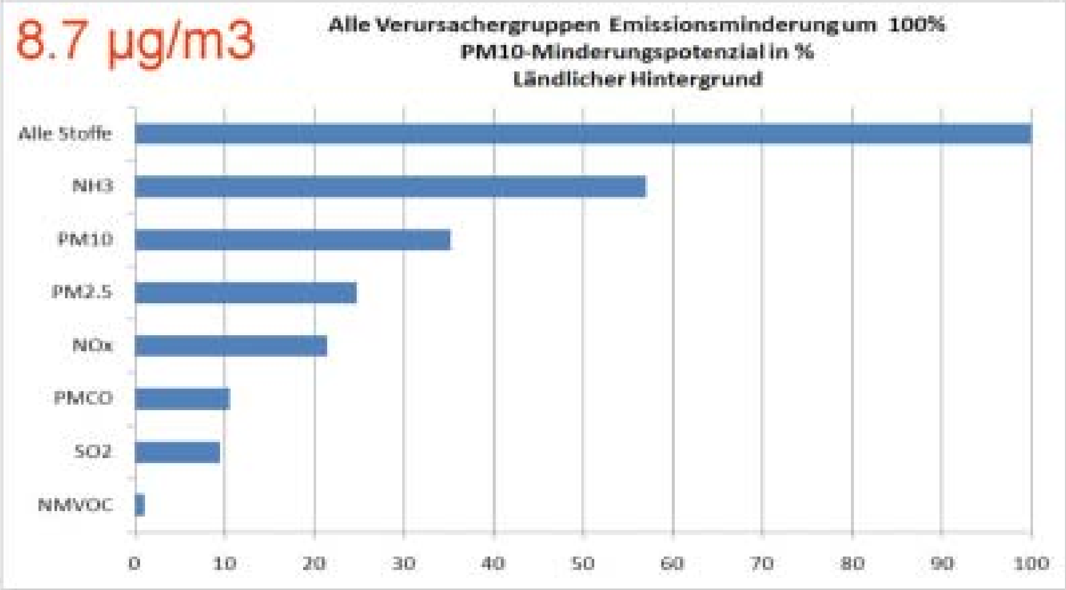
Relative Beiträge der einzelnen Stoffe zum gesamten Minderungspotenzial (Alle Stoffe: 13 µg/m3) für den städtischen Hintergrund

R.Stern, 10. Nov. 2008


13 µg/m3

Alle Verursachergruppen Emissionsminderung um 100%
PM10-Minderungspotenzial in %
Städtischer Hintergrund

Rangordnung:
NH3
PM2.5
PMCO


8.7 µg/m3

Alle Verursachergruppen Emissionsminderung um 100%
PM10-Minderungspotenzial in %
Ländlicher Hintergrund

Rangordnung:
NH3
PM2.5
NOx

R.Stern, 10. Nov. 2008

Zusammenfassung III:

Stoffbezogene Minderungseffektivität

	-100% pro Stoff	-25% pro Stoff
Städtischer Hintergrund	NH3: 40%	PM2.5: 8%
max. Minderungspotenzial	PM2.5: 32%	PMCO: 5%
13 µg/m3	PMCO: 20%	NH3: 5%
	Alle: 100%	Alle: 22%
Ländlicher Hintergrund	NH3: 57%	NH3: 6%
max. Minderungspotenzial	PM2.5: 25%	PM2.5: 6%
9 µg/m3	Nox: 21%	Nox: 3%
	Alle: 100%	Alle: 20%

Bei realistischen Minderungsraten (in ganz D) haben im

Städtischen Hintergrund: *PM2.5*

Ländlichen Hintergrund: *NH3 und PM2.5*

das größte Minderungspotenzial

R.Stern, 10. Nov. 2008

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 :

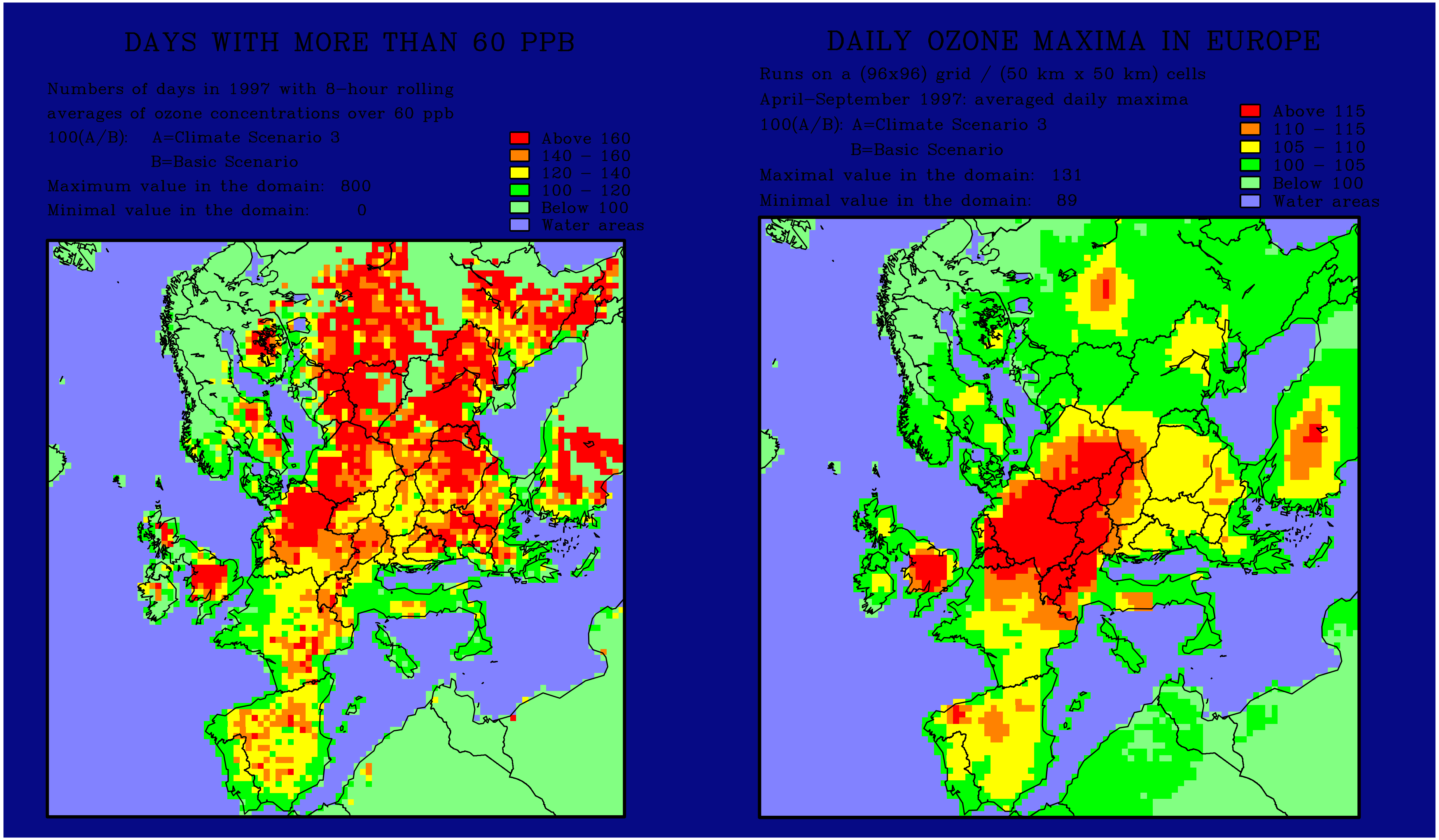
Missing emission-sources : Wind-blown dust
Road abrasion
Tyres and brakes

Resuspension : Treatment of Agricultural Soil

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 ???

DEM with climate change



DAYS WITH MORE THAN 60 PPB

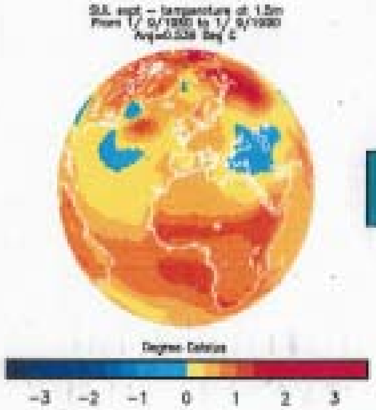
Numbers of days in 1997 with 8–hour rolling averages of ozone concentrations over 60 ppb
100(A/B): A=Climate Scenario 3
B=Basic Scenario
Maximum value in the domain: 800
Minimal value in the domain: 0

DAILY OZONE MAXIMA IN EUROPE

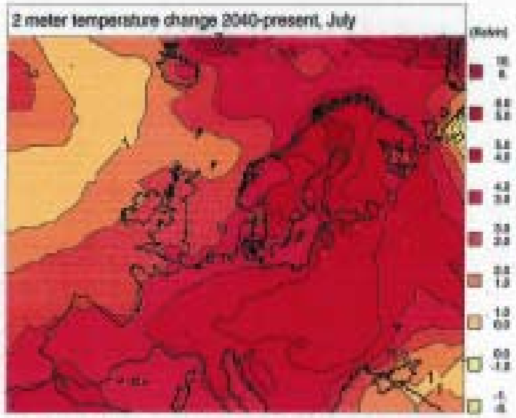
Runs on a (96x96) grid / (50 km x 50 km) cells
April–September 1997: averaged daily maxima
100(A/B): A=Climate Scenario 3
B=Basic Scenario
Maximal value in the domain: 131
Minimal value in the domain: 89

Impact of climate change on regional air pollution budgets

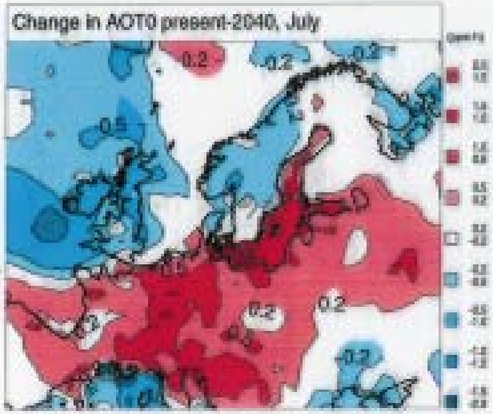
A contribution to subproject GLOREAM, Joakim Langner and Robert Bergström, Swedish Meteorological and Hydrological Institute,
SE-601 76 Norrköping, Sweden, joakim.langner@smhi.se, robert.bergstrom@smhi.se



AOGCM simulations, Hadley Centre, UKMO



Dynamical downscaling using RCA1, Rossby Centre, SMHI



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

SMHI
Research and Development
www.smhi.se

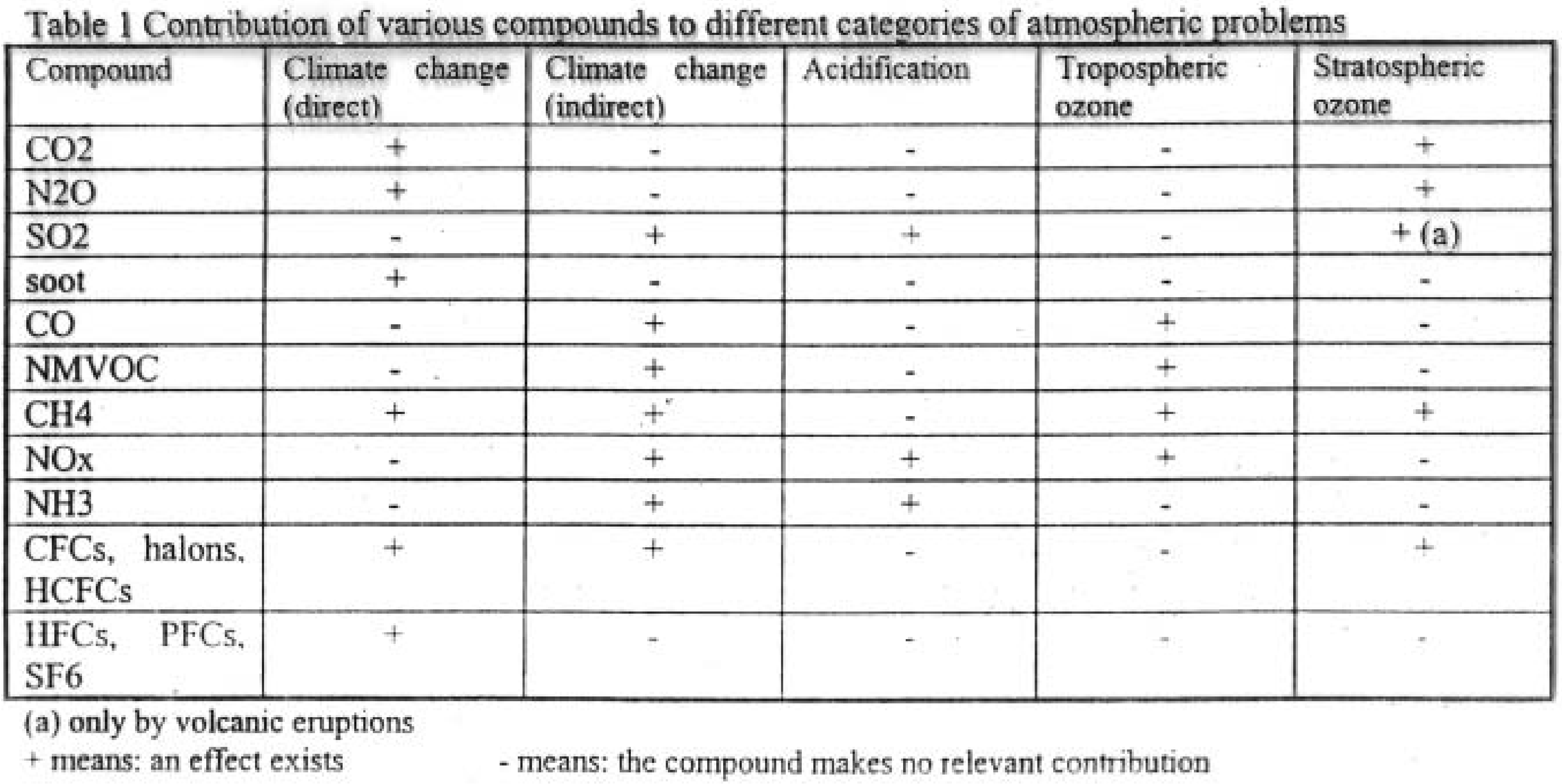


Table 1 Contribution of various compounds to different categories of atmospheric problems

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

Climate Change is not only due to CO_2

Importance

- of Tropospheric ozone
- of aerosols

Radiative Forcing Components

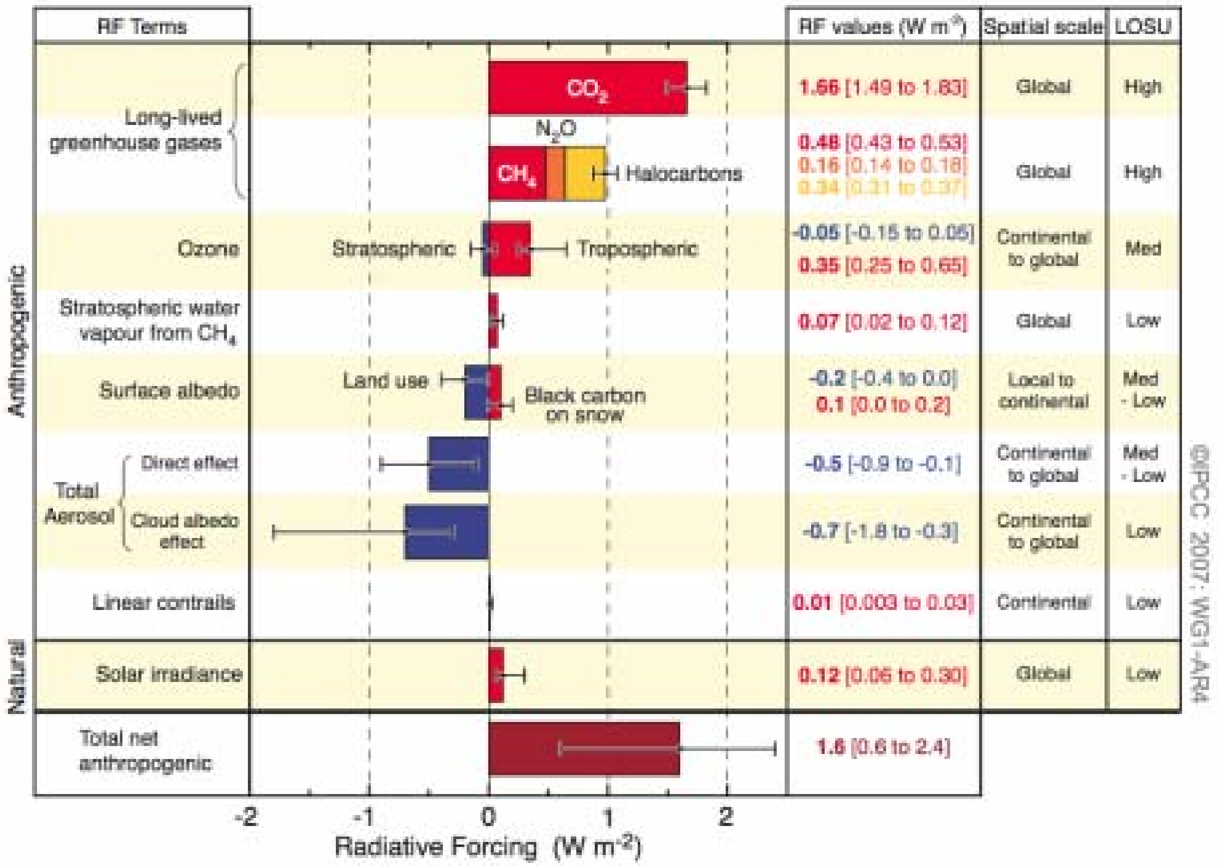


FIGURE SPM-2. Global-average radiative forcing (RF) estimates and ranges in 2005 for anthropogenic carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and other important agents and mechanisms, together with the typical geographical extent (spatial scale) of the forcing and the assessed level of scientific understanding (LOSU). The net anthropogenic radiative forcing and its range are also shown. These require summing asymmetric uncertainty estimates from the component terms, and cannot be obtained by simple addition. Additional forcing factors not included here are considered to have a very low LOSU. Volcanic aerosols contribute an additional natural forcing but are not included in this figure due to their episodic nature. Range for linear contrails does not include other possible effects of aviation on cloudiness. {2.9, Figure 2.20}

Aerosols are also relevant for Climate Change

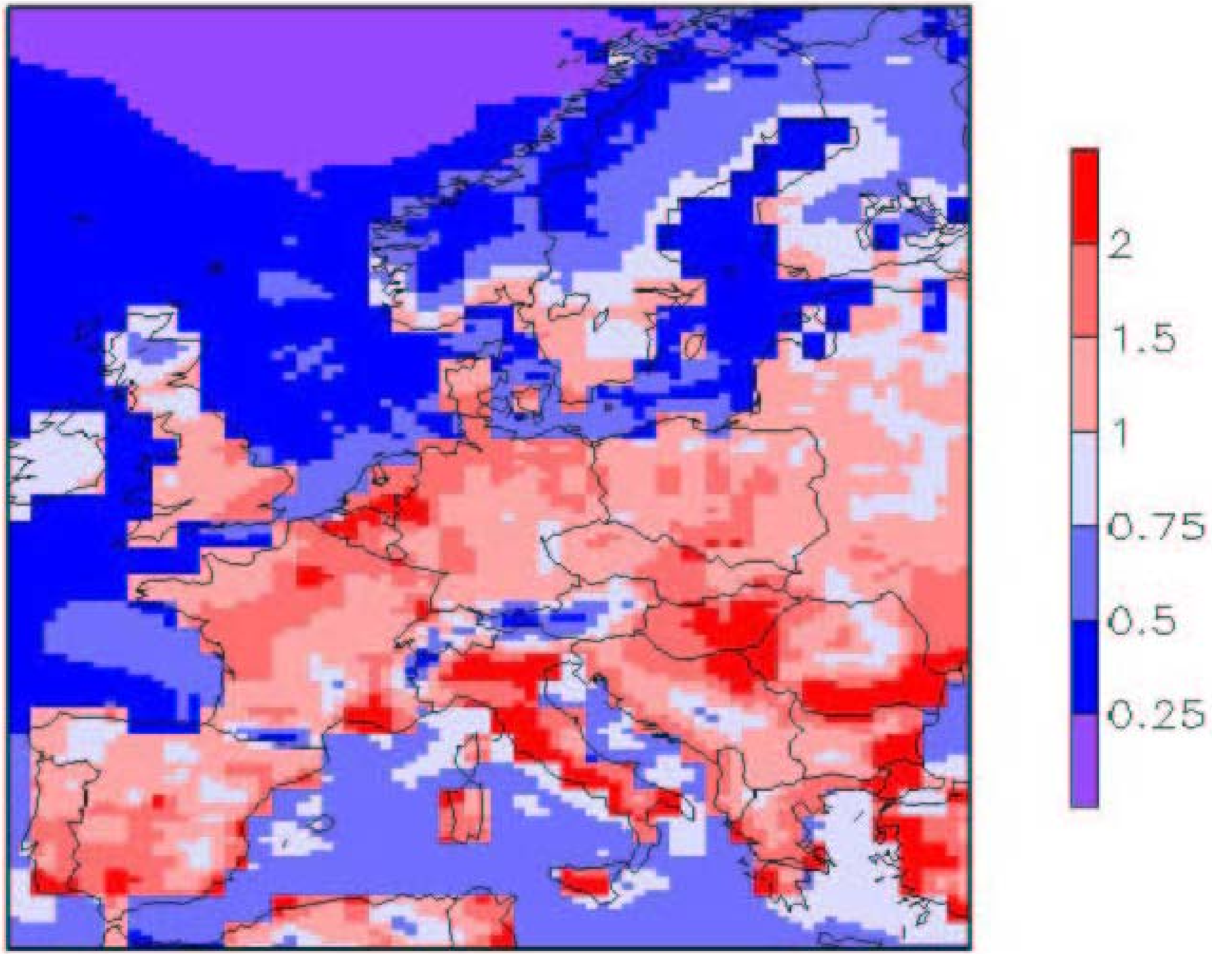
Most aerosols are cooling (reflection)

Estimate over Europe ~ -2 W/m^2

Black Carbon is warming (absorption)

Estimate over Europe ~ +1 W/m^2

Modelling Black Carbon over Europe



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.

Four areas of current research

- Data assimilation
- Ensemble approach
- Impact of climate change on air quality, and vice versa
- Use of satellite observations for air quality and climate

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”

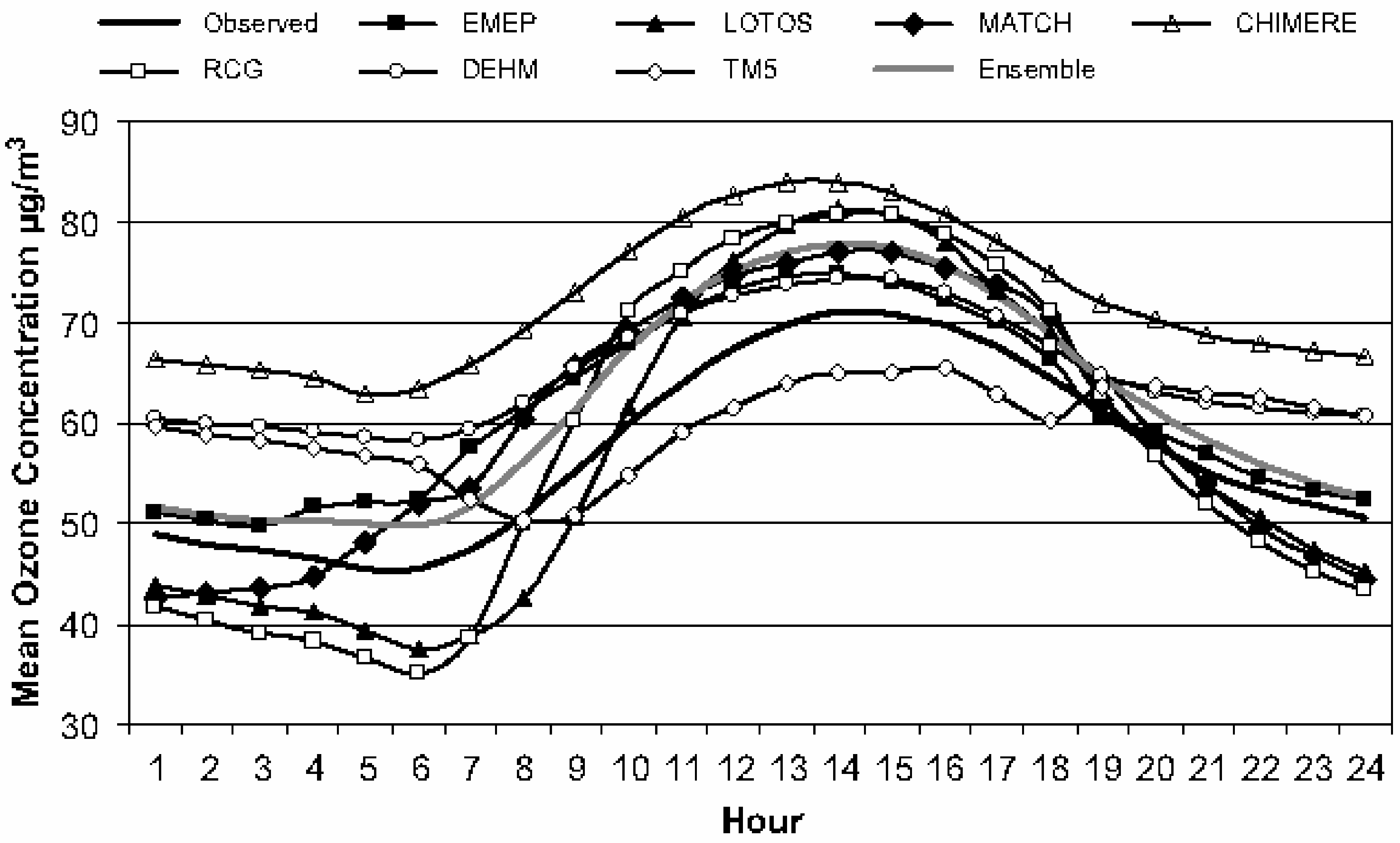
Air Pollution Modelling and its Application XIV

Kluwer/Plenum, 2001

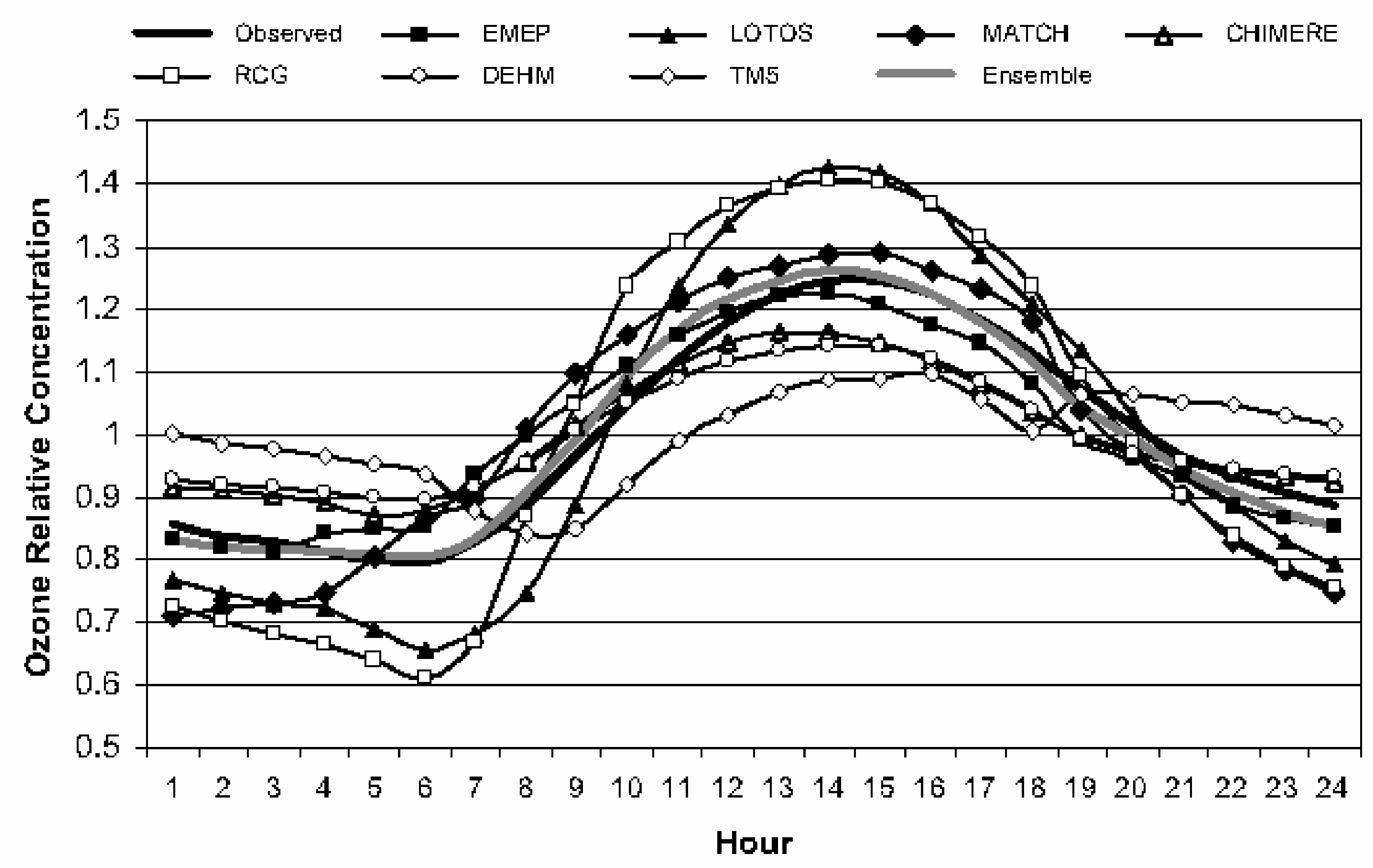
Preliminary results of applying Kalman filtering for combining observed and modelled ozone concentrations over Europe

Ensemble using different CTM's to determine the spread of models

- Example for O_3 using EMEP, RCG, MATCH, LOTOS-EUROS, CHIMERE, TM-5, DEHM
- Loon, van M. *et al* "Evaluation of long-term ozone simulations from seven regional air quality models and their ensemble" Accepted Atm. Env. 2007
- Ensemble is a method to determine uncertainty
- (Science florishes by uncertainty, policy freeces by uncertainty)



Yearly mean diurnal cycle of ozone, in $\mu g.m^{-3}$, as a function of hour, for all models, averaged over all monitoring stations.

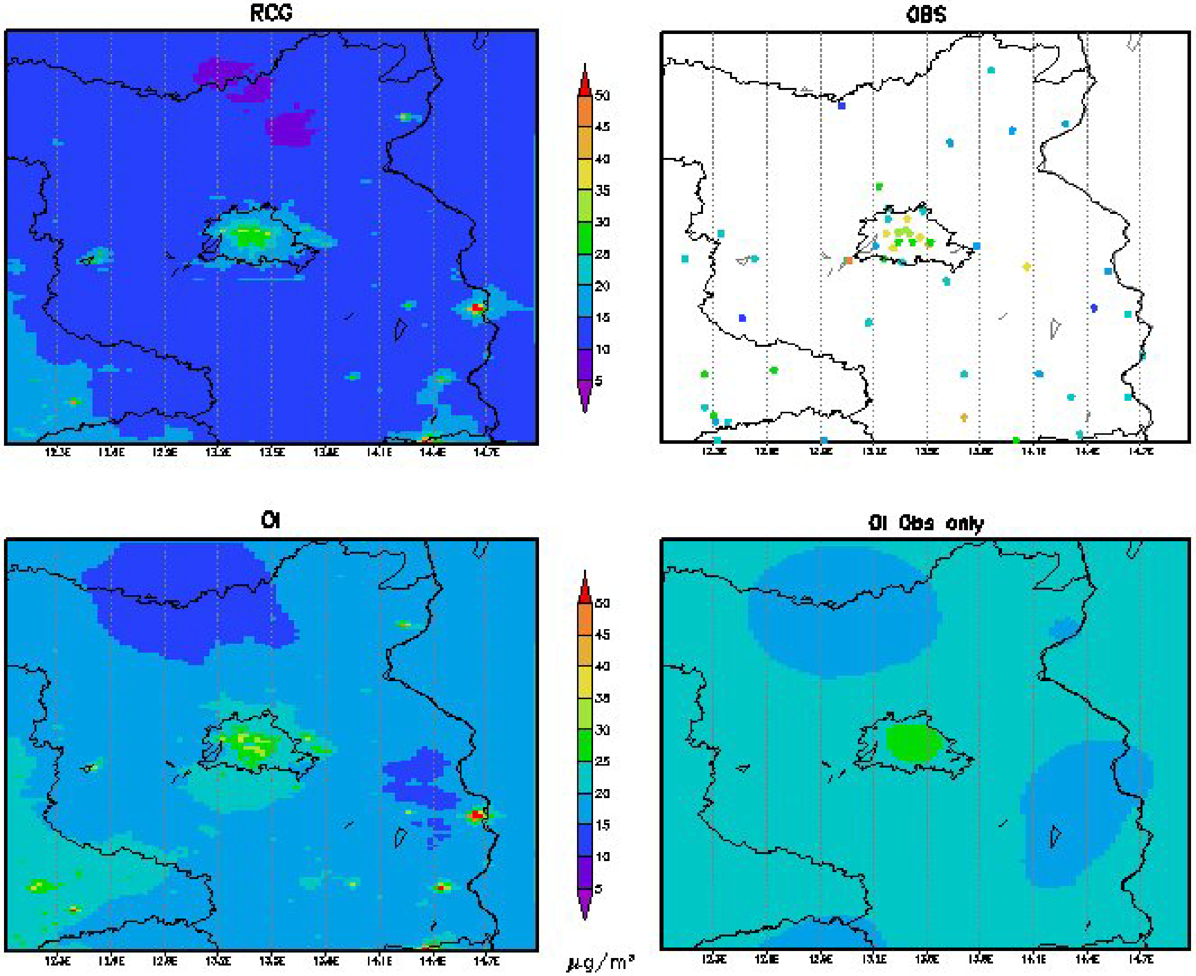


Yearly mean diurnal cycle of ozone, in $\mu g.m^{-3}$, as a function of hour, for all models, averaged over all monitoring stations, relative to the average of each data set. In order to obtain values in this figure, values of Figure 1 are divided by their Average over hours for each model.

Schlussbemerkungen

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

PM10 MEAN 1999 BERLIN/BRB



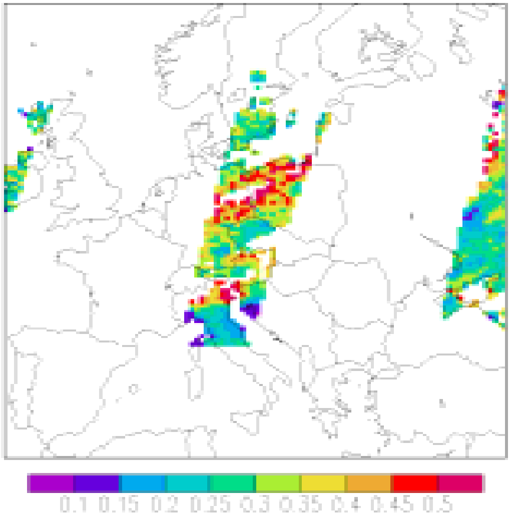
Jahresmittelwert der PM10-Konzentration für Berlin\Brandenburg aus der kleinräumigen Modellrechung (links, oben), der OI-Methode aus Modell und Beobachtung (links unten) und der Beobachtung (rechts oben) und der OI-Methode ausschließlich aus Messungen für das Jahr 1999.

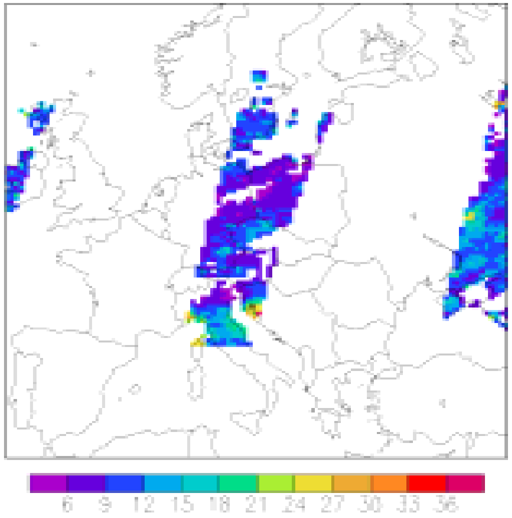
Data assimilatie AOD en PM in LOTOS-EUROS

23-5-2000

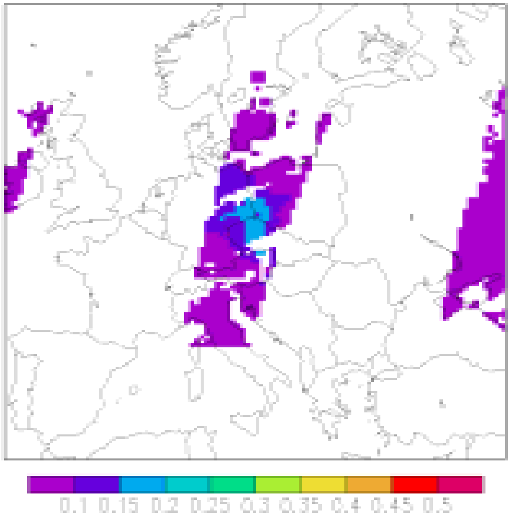
Exp 2.

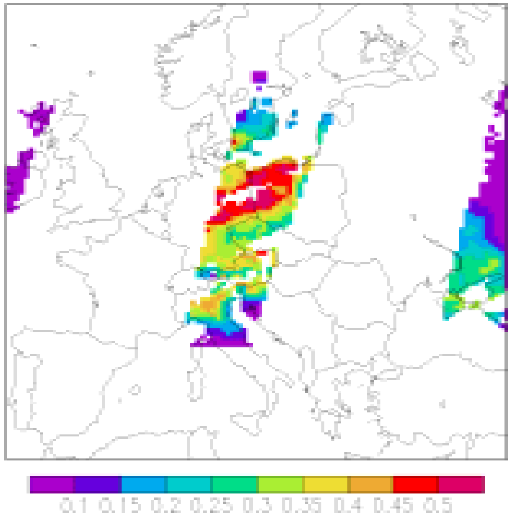
Retrieved





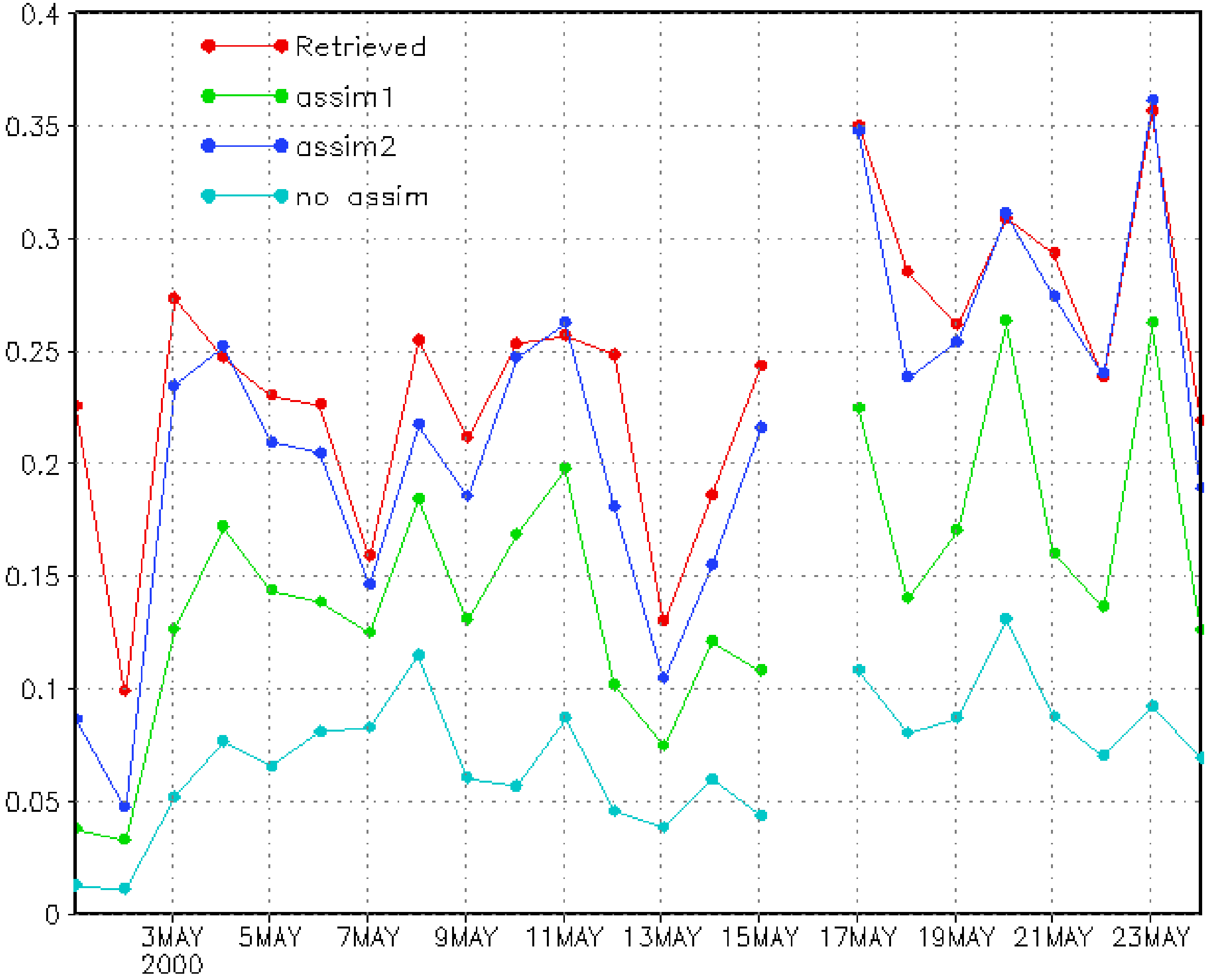
Model





geässimileerd

Validatie AOD → systeem werkt!



Diplomthemen/Batchelor-Masters (1)

- Weitere Modell-Evaluierung REM-CALGRID (RCG)
- Budget Analyse PM über Berlin mit RCG (Dr. Arbeit Andreas Kerschbaumer)
- Verbesserung Depositions Modul in RCG
- Prognoseverifizierung für PM10 und PM2.5
- Statistische Auswertung PM10 usw im Vergleich zu Meteorologische Grössen

Diplomthemen/Batchelor-Masters (2)

- Verwendung von Wolkenanalyse, Wolken Top und -Basis, Einbau in TRAMPER
- Source/Receptor Statistik für Pollenmessungen, Einbau in RCG
- Verbesserung Aerosol-Modellierung, mit TNO
- Data Assimilation, mit TNO
- Analyse Satelliet-Data für Luftqualität, mit TNO

Diplomthemen/Batchelor-Masters (3)

- Analyse von Seesalzmessungen (in Deutschland)
- Seesalzmodellierung mit RCG
- Modellierung Basische Kationen (TNO)

Danke für die Interesse !!!