4. Tropospheric Chemistry of Gas Phase

Prepared by J. Staehelin, IAC*ETH*
email: Johannes.Staehelin@env.ethz.ch
(including pictures provided by A.S.H. Prevot (PSI))

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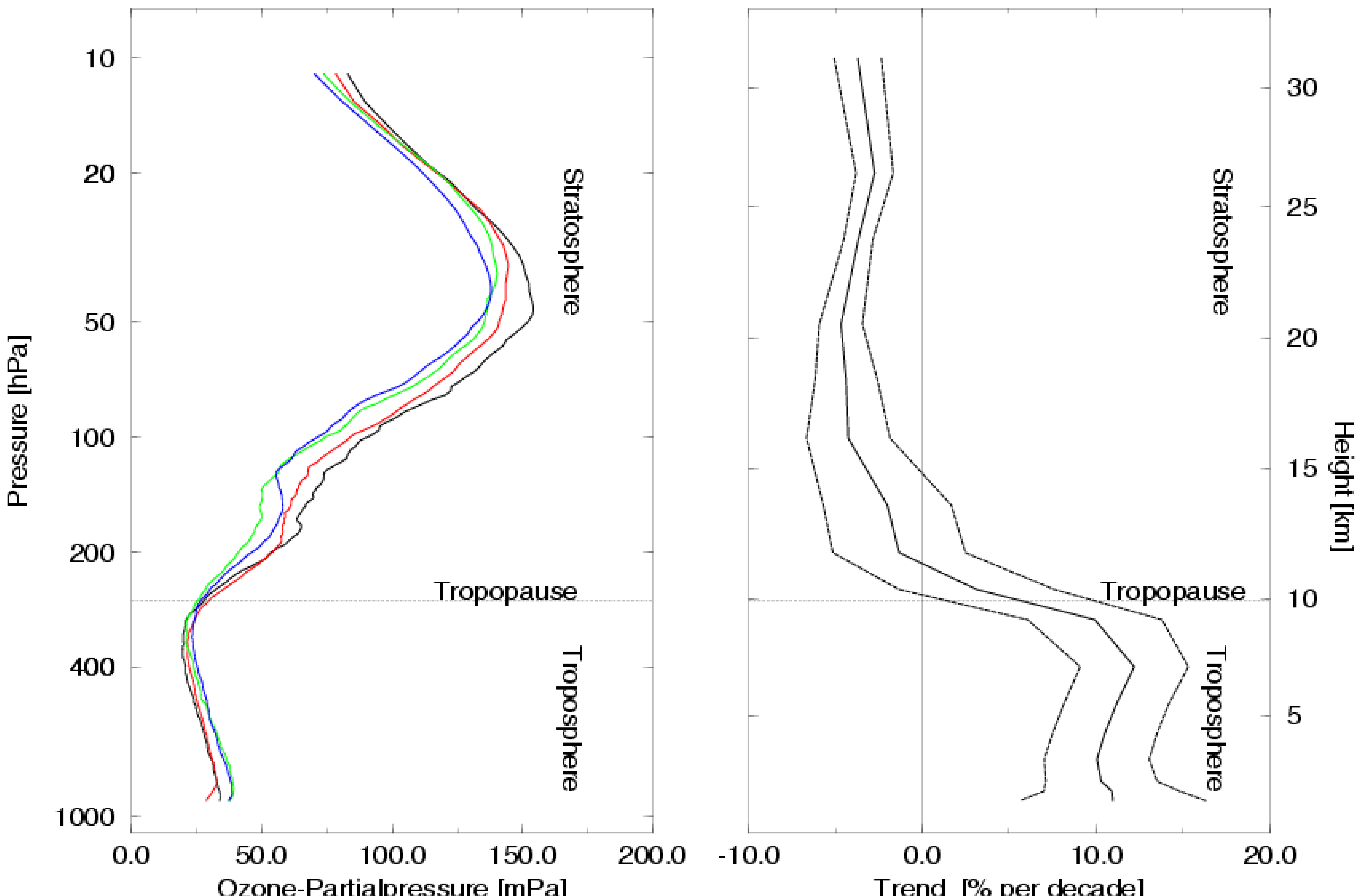
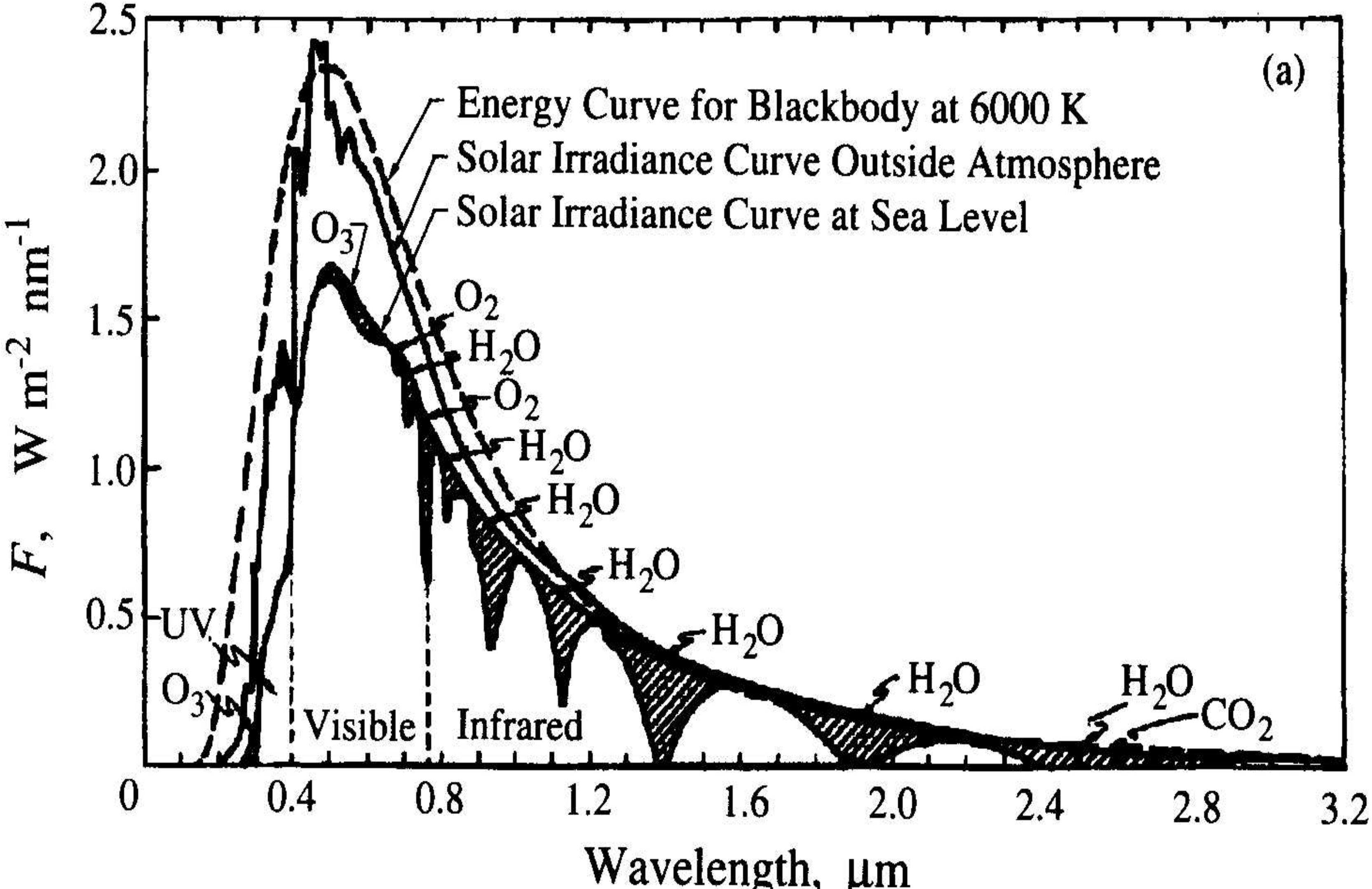
4.1. Introduction: Atmospheric ozone changes

Ozone balloon measurements of Payerne (Switzerland)



Solar spectrum outside the atmosphere and at Earth's surface



Reaction system: Radical chain reaction

Initiation: Formation of reactive radicals by photochemical reactions

$CFCl_3 \xrightarrow{h\nu} Cl\cdot + ...$ $\lambda < 230$ nm

Propagation, radical chain: Conversion of reactive radicals (e.g. stratoshperic ozone depletion):

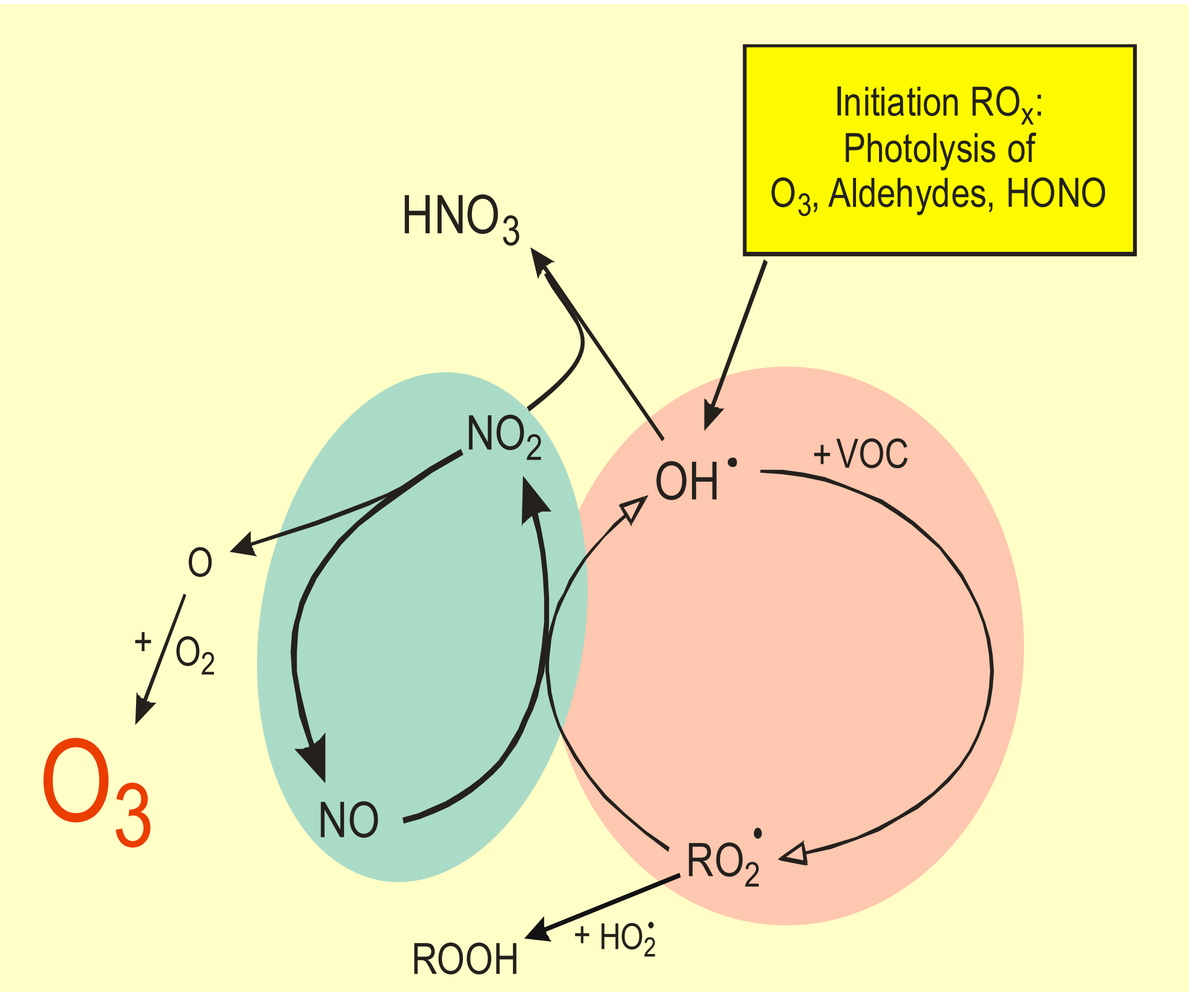
$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$

$ClO\cdot + O \rightarrow Cl\cdot + O_2$

Termination: Formation of nonradical species from two radicals (sink of reactive radicals)

$ClO\cdot + NO_2\cdot \rightarrow ClONO_2$

4.2. Photooxidant formation



Two coupled radical chain reactions:
NO_x (green): NO, NO_2
RO_x (red): OH·, HO_2·, RO·, RO_2·

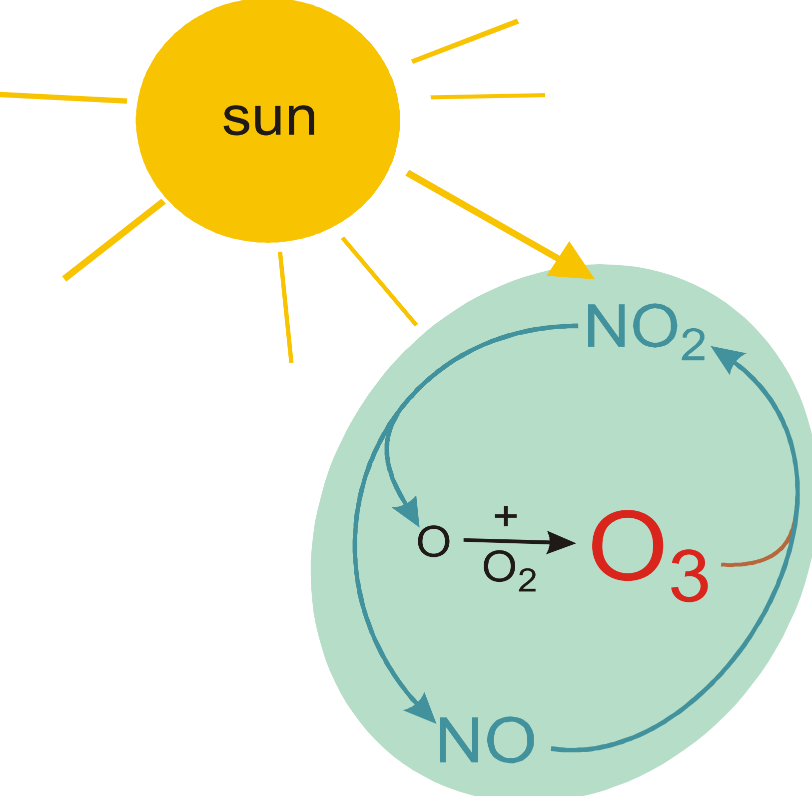
4.2.1. NO_x

Photostationary state

NO_x ($NO+NO_2$)

fast equilibrium

$Ox = NO_2 + O_3$



$$NO_2 \xrightarrow{h\nu} NO + O$$

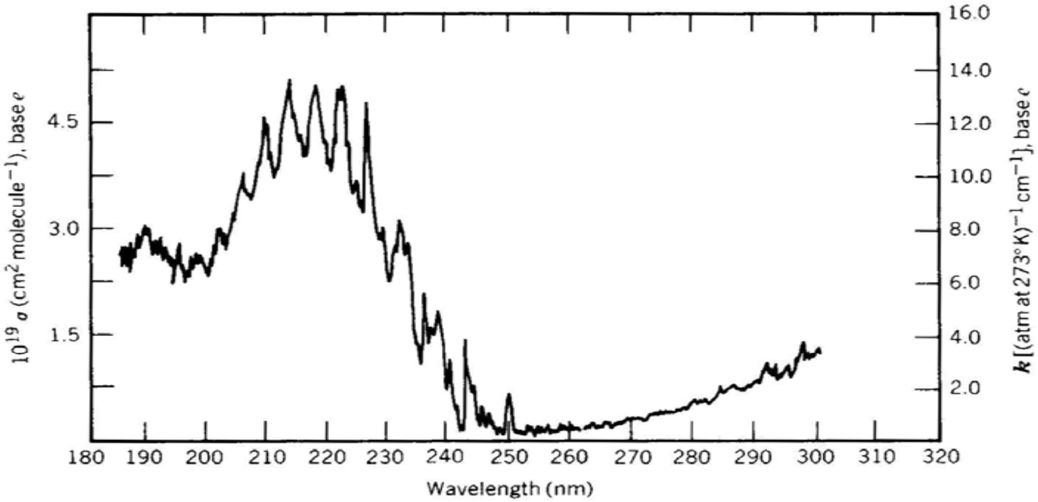
$$O + O_2 \ (+M) \longrightarrow O_3 \ (+M)$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

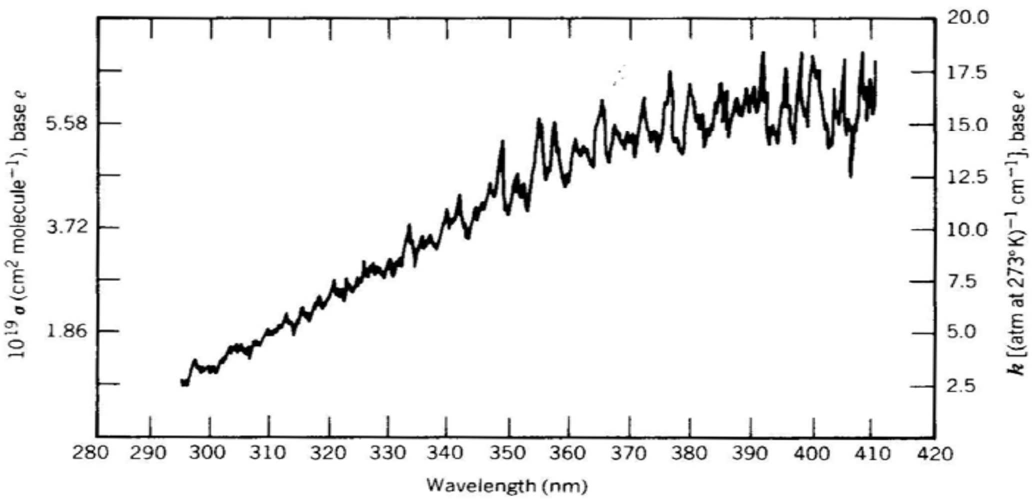
photostationary state:

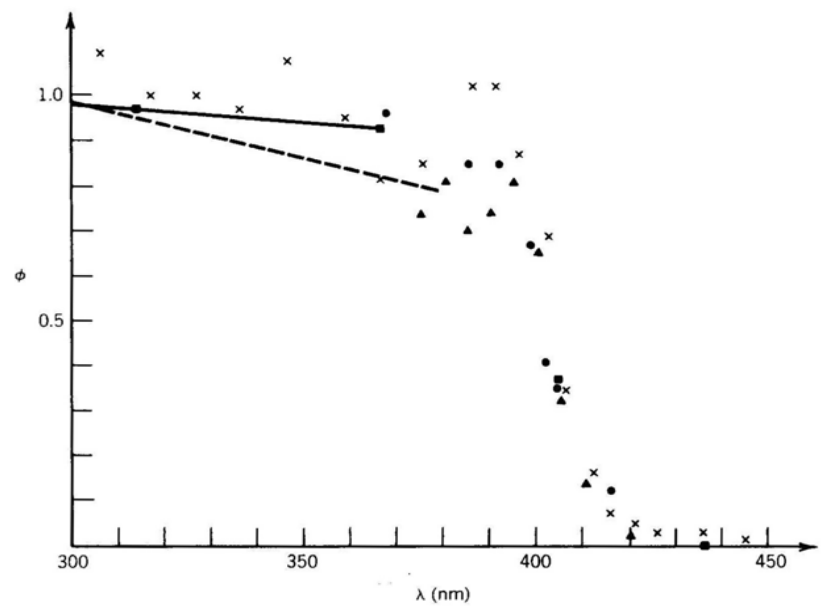
$$K = \frac{JNO_2}{k} = \frac{[NO]\,[O_3]}{[NO_2]}$$

UV-spectrum and quantum yields of NO_2



(a)

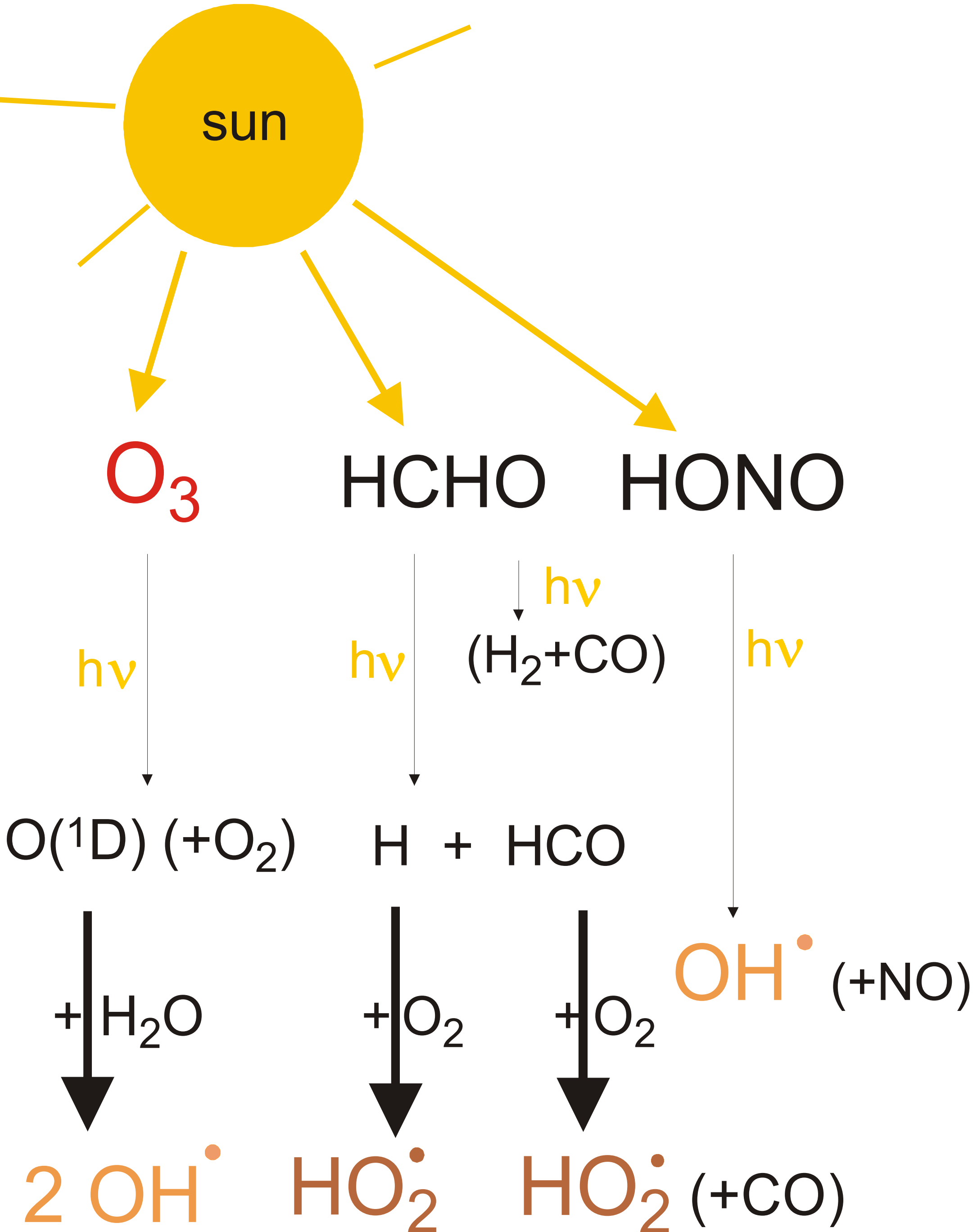




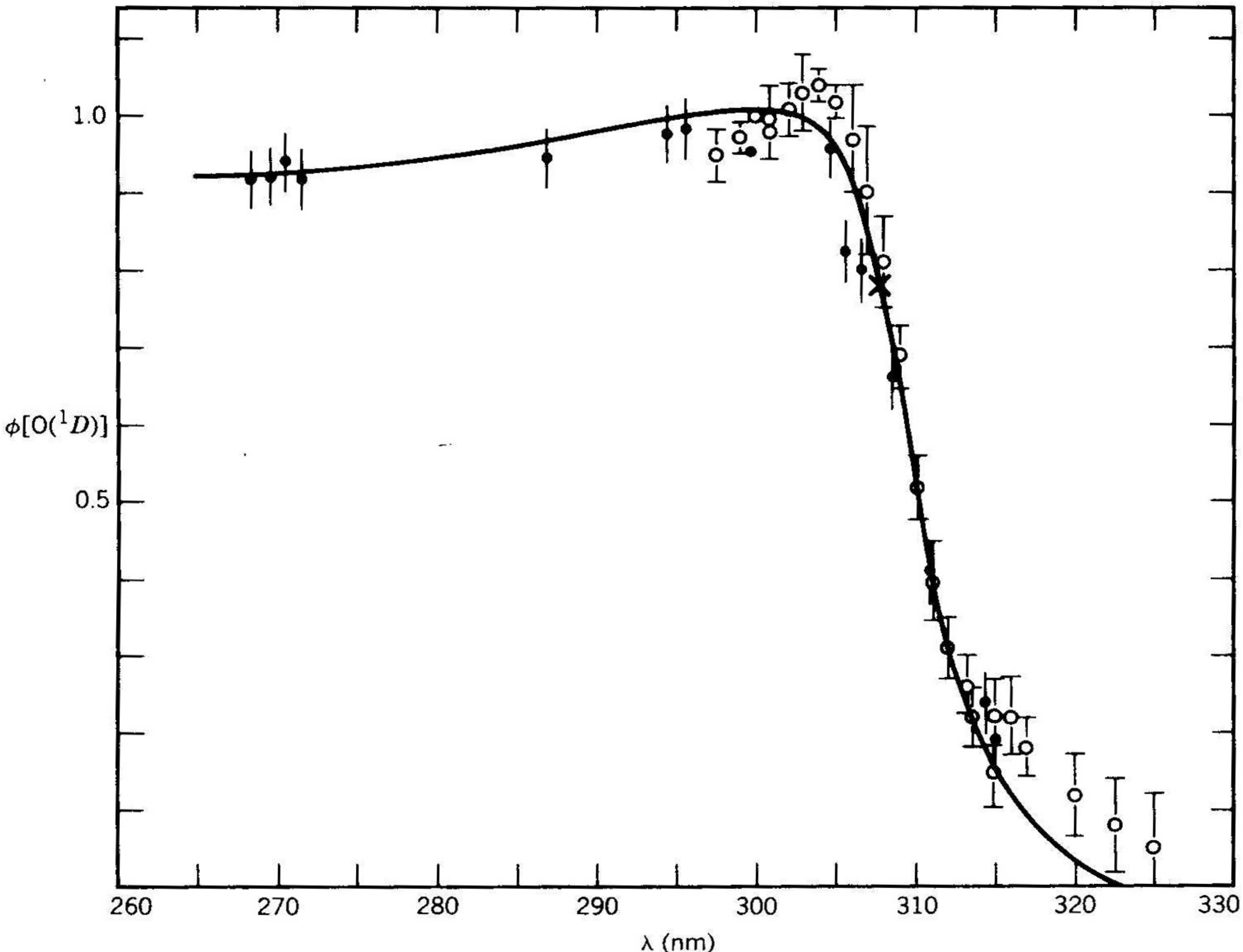
4.2.2. RO_x-radical chain: **Initiation:**

formation of HO_x-radicals by photolysis

OH: „cleansing agent“ of troposphere, „oxidation capacity“



Quantum yield for $O(^1D)$
($O_3 \xrightarrow{h\nu} O(^1D)$)



Propagation exemplified by ethane
(Volatile Organic Compound (VOC))

RO_x radical chain , e.g.

$$CH_3\text{-}CH_3 + OH^\bullet \longrightarrow CH_3\text{-}CH_2^\bullet + H_2O$$

$$CH_3\text{-}CH_2^\bullet + O_2 \xrightarrow{+M} CH_3\text{-}CH_2\text{-}O_2^\bullet$$

$$NO + CH_3\text{-}CH_2\text{-}O_2^\bullet \longrightarrow NO_2 + CH_3\text{-}CH_2\text{-}O^\bullet$$

$$CH_3\text{-}CH_2\text{-}O^\bullet + O_2 \longrightarrow CH_3\text{-}CHO + HO_2^\bullet$$

$$NO + HO_2^\bullet \longrightarrow NO_2 + OH^\bullet$$

$$CH_3\text{-}CH\text{-}O + OH^\bullet \longrightarrow CH_3\text{-}CO^\bullet + H_2O$$

$$CH_3\text{-}CO^\bullet + O_2 \xrightarrow{+M} CH_3\text{-}COO_2^\bullet$$

$$CH_3\text{-}COO_2^\bullet + NO_2 \rightleftharpoons \underset{\text{PAN}}{CH_3\text{-}CO_3\text{-}NO_2}$$

Termination by NO_x

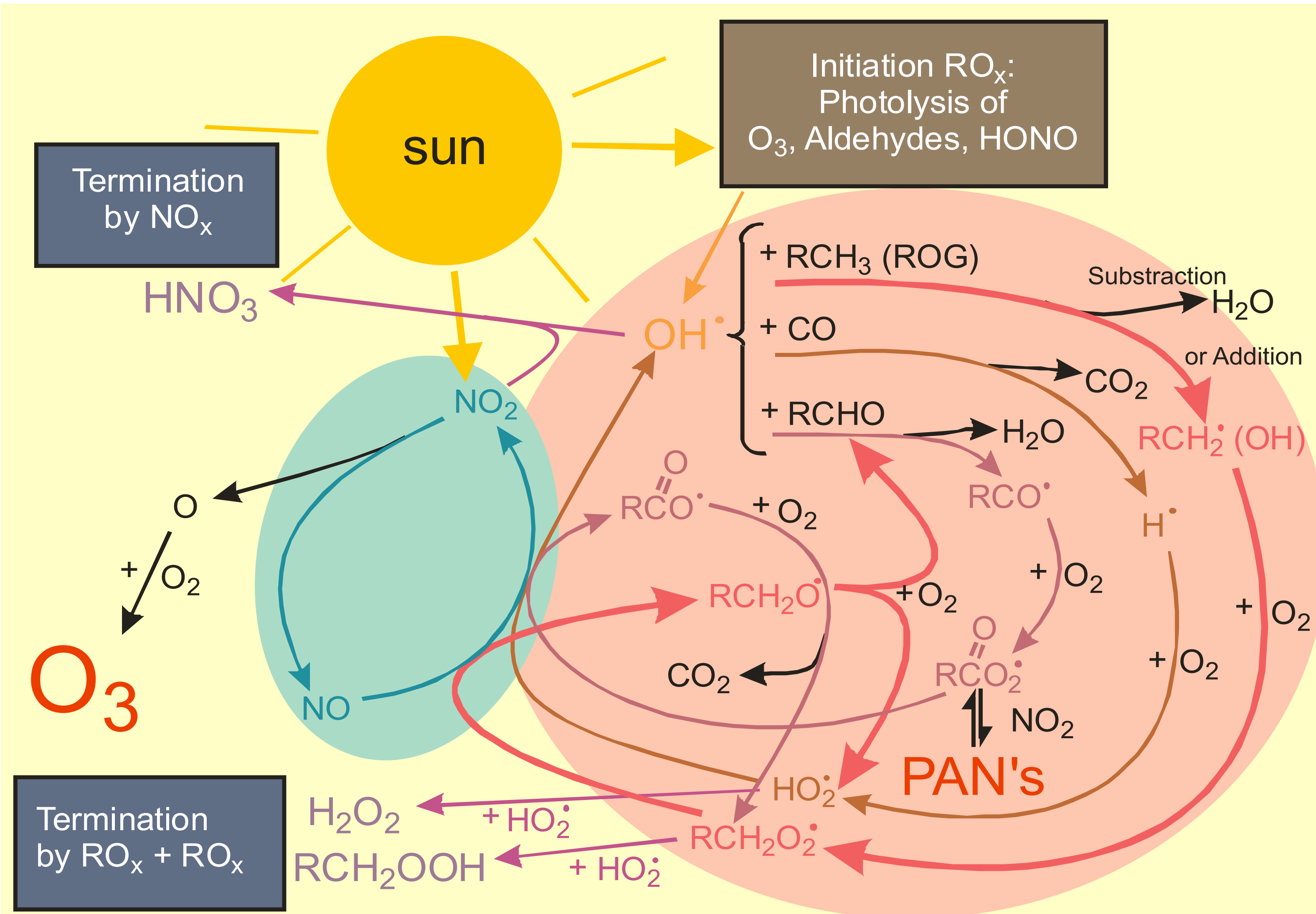
$$OH^{\bullet} + NO_2 \xrightarrow{+\,M} HNO_3$$

Termination by RO_x + RO_x

$$HO_2^{\bullet} + HO_2^{\bullet} (+ H_2O) \longrightarrow H_2O_2 + O_2 \; (+ H_2O)$$

$$RCH_2\text{-}O_2^{\bullet} + HO_2^{\bullet} \longrightarrow RCH_2\text{-}OOH + O_2$$

Overview of photochemistry in the polluted planetary boundary layer



Ozone destruction (if NO less than 10 ppt) exemplified by CO

$CO + OH \rightarrow CO_2 + H$

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

If NO less than 10 ppt (for PBL)

$HO_2 + O_3 \rightarrow OH + 2O_2$

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

(if NO more than 10ppt (for PBL):

$HO_2 + NO \xrightarrow{h\nu} OH + NO_2$

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

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

$\Sigma: CO + 2O_2 \rightarrow CO_2 + O_3$

Terms

$NO_x = NO + NO_2$ reactive species

$NO_y = \underbrace{NO + NO_2}_{NO_x} + \underbrace{HNO_3 + PAN + \text{org. nitrates} + ..}_{\text{products}}$

$NO_z = NO_y - NO_x = HNO_3 + PAN + \text{org. nitrates} + ..$

photooxidation products: O_3, NO_z

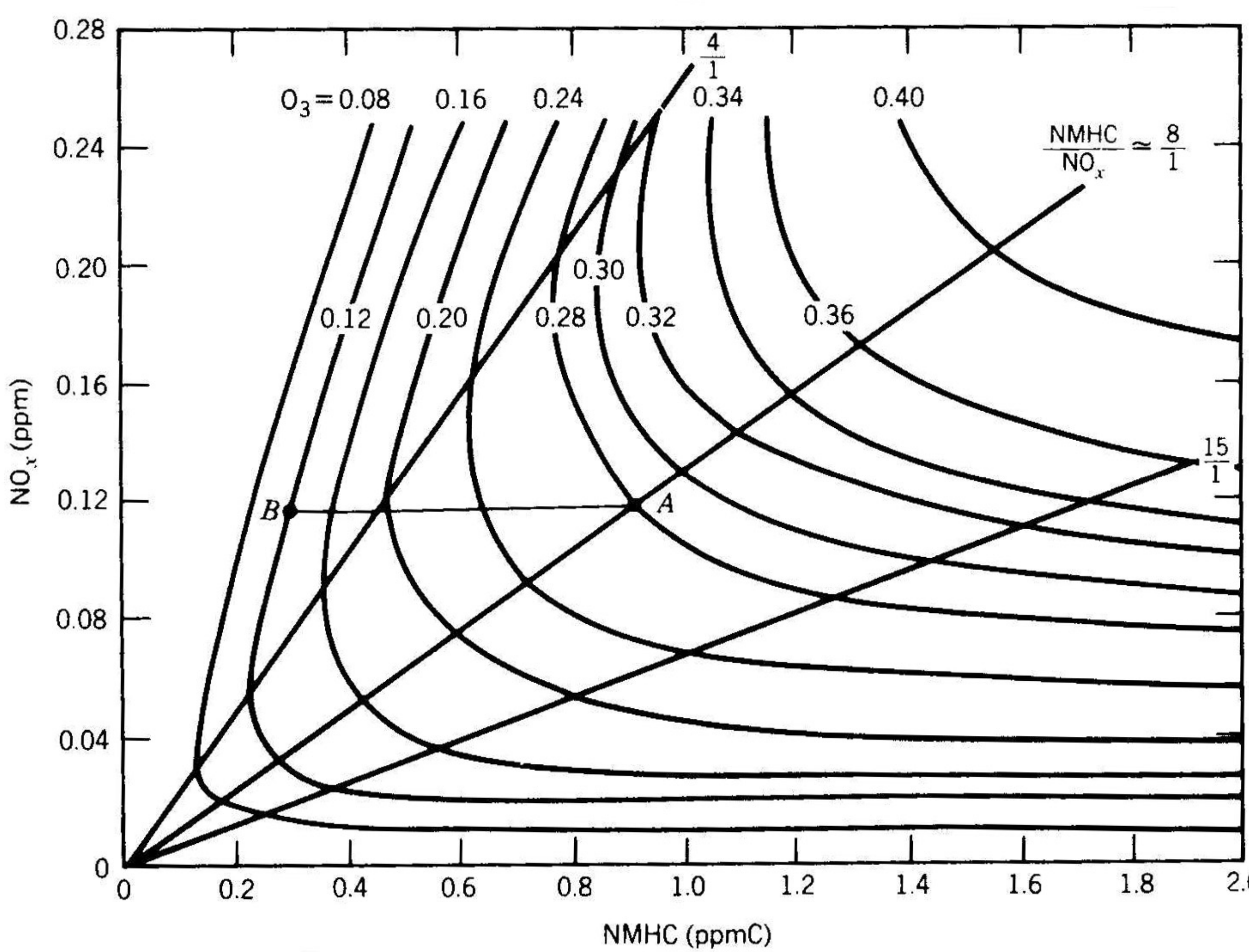
$$O_3 \sim NO_z$$

Summary

- OH very reactive: Oxidation agent of most gaseous pollutants in tropospheric air
- In presence of NO_x (NO larger than 10 ppt): Photooxidant formation (O_3, PAN, HNO_3, etc.)
- In case of very clean condition (NO smaller than 10 ppt in PBL): Ozone destruction
- Organic chemistry more complex

  (e.g. alkene + O_3: additional source of HO_x)
- Ozone precursors (NO_x, Volatile Organic Compounds (VOC) and CO: Anthropogenic or biogenic origin)

4.3. Limitation regimes: EKMA diagram



Limitation regimes, urban plumes

1. fast: *photostationary state*
2. *VOC-limitation*: O_3 production increases with VOC concentration (decreases with increasing NO_x)
3. *Transition regime*: Maximum ozone production
4. *NO_x-limitation*: Ozone production increases with NO_x concentration
5. *Ozone destruction*

4.4. Oxidation during night

NO_3: strong absorption in visible,

strong oxidant during night

$NO_2 + O_3 \rightarrow$ **NO_3** $+ O_2$

$NO_3 \xrightarrow{h\nu} NO_2 + O_2$ ($\lambda < 650$ nm)

$NO_3 \xrightarrow{h\nu} NO + O_2$

Fast: $NO_3 + NO \rightarrow 2\ NO_2$

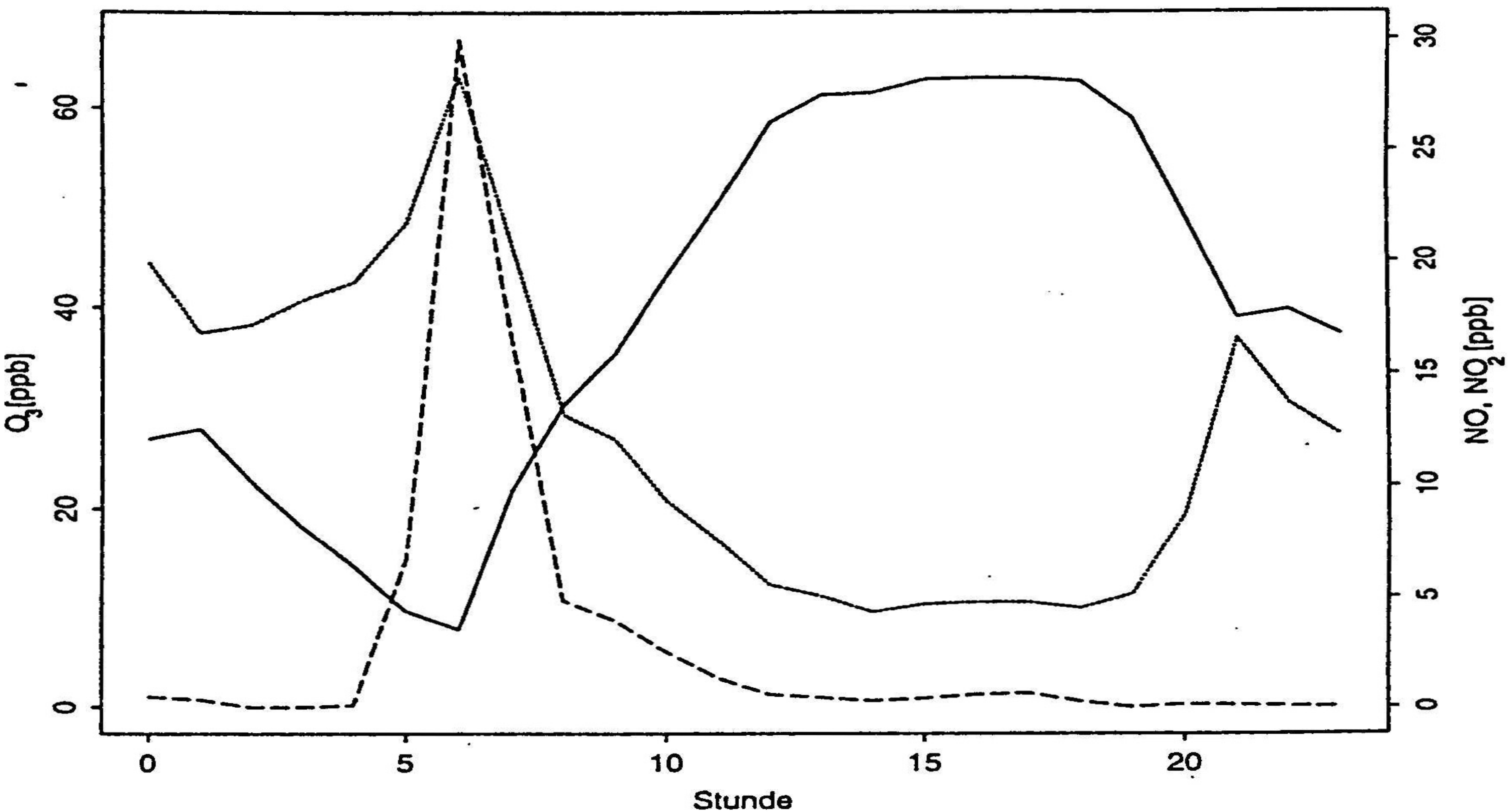
$NO_3 + NO_2\ (+M) \leftrightarrow N_2O_5\ (+M)$

NO_3 (N_2O_5) loss by heterogeneous processes

RH + NO_3 $\rightarrow \cdot R + HNO_3$ ($\rightarrow HO_x$ radicals)

RCHO + NO_3 $\rightarrow \cdot RCO + HNO_3$

4.5. Trace gas concentrations in ambient air: Diurnal variation of NO_x and O_3



Winter smog or London Smog

- Compounds: primary pollutants: SO_2, NO_x(NO_2), particulates (PM10)
- Enhanced concentrations during inversion episodes, higher concentrations during winter

Wichtige Grenzwerte der Schweizerischen Luftreinhalteverordnung (in $\mu g/m^3$)

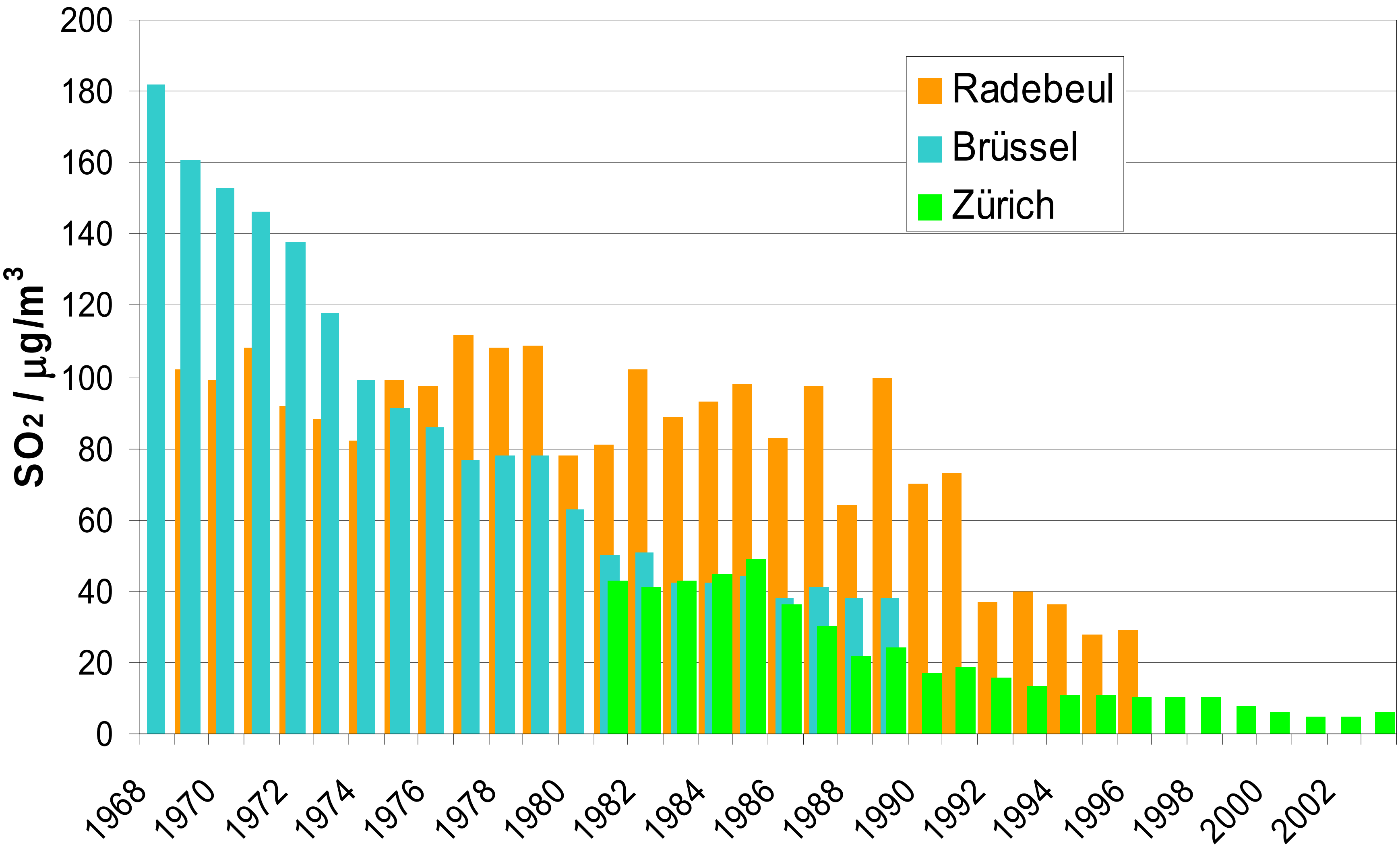
Luftschadstoff	PM_{10} [1)]	SO_2	NO_2	O_3	(CO)
Jahresmittel	20	30	30		
Wert darf maximal 1 mal jährlich überschritten werden	50 [2)]	100 [2)]	80 [2)]	120 [3)]	(8 mg/m^3 [2)])
Maximaler Wert für 95% der 1/2-h-Mittelwerte eines Jahres		100	100		
Maximaler Wert für 98% der 1/2-h-Mittelwerte eines Monats				100	

[1)] In der revidierten Luftreinhalteverordnung, die am 1. März 1998 in Kraft gesetzt wurde

[2)] Bezieht sich auf 24-h-Mittelwert

[3)] Bezieht sich auf 1-h-Mittelwert

4.6. Long-term changes in air pollution: sulfur dioxide



Conventions to reduce air pollutant emissions in Europe

1972: UN Conference on the Human Environment, Stockholm, 1972

1976: EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe): focus for cooperative European monitoring with support from the United Nations Environment Programme (UNEP)

United Nations Economic Commission for Europe (UNECE):

1979: Geneva Convention on Long-Range Transboundary Air Pollution

in force: 1983: Present Parties: European countries , USA and Canada and several others

$\underline{SO_2}$:

- ***Helsinki Protocol, 1985***, on Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 per cent
- ***Oslo Protocol, 1994,*** on Further Reduction of Sulphur Emissions

$\underline{NO_x}$:

- ***Sofia Protocol, 1988***, Concerning the Control of Emissions of Nitrogen Oxides and their Transboundary Fluxes

VOC:

- ***Geneva Protocol, 1991***, on Reduction of VOCs or their transboundary fluxes by at least 30% by 1999, relative to a base year between 1984 and 1989

CORINAIR: COoRdination of INformation on AIR emissions

EMEP/CORINAIR Atmospheric Emission Inventory Guide book

Anthropogenic emission inventories: w,w,w,w

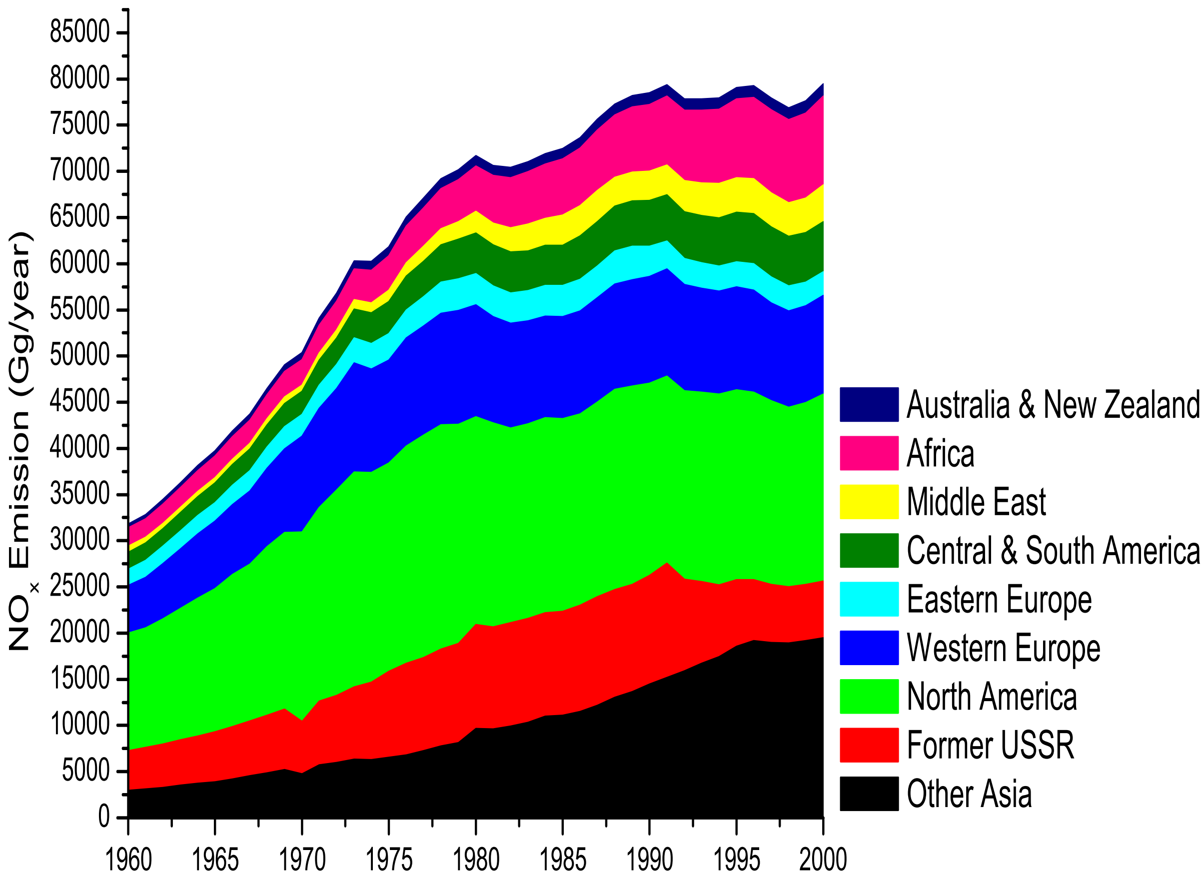
Emission rate = EF x activity

Activity rate: from statistical data (e.g. driven kilometer from vehicles, etc.)

EF: e.g. emission of NO_x per diven kilometer

- What: which compound
- Why: activity
- Where: location of emission
- When: time of emission

Fossil fuel related groundbased NO_x emissions

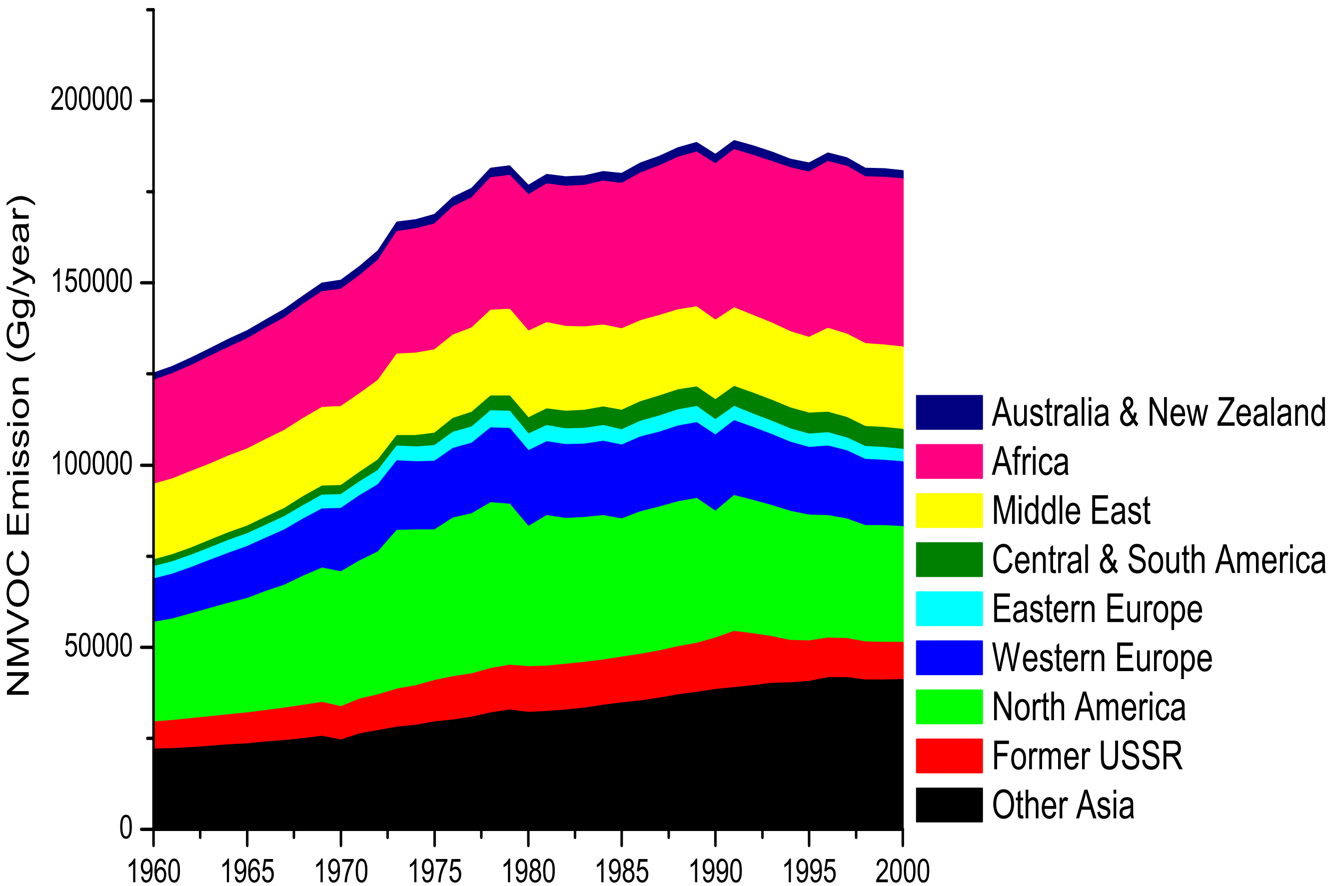


From TEAM (TNO emission assessment model) model using fossil fuel consumption data from IEA (International Energy Agency)

Em = Ac x Technology Penetration Factor x EF

(TPF: only one for OECD and non-OECD coutries)

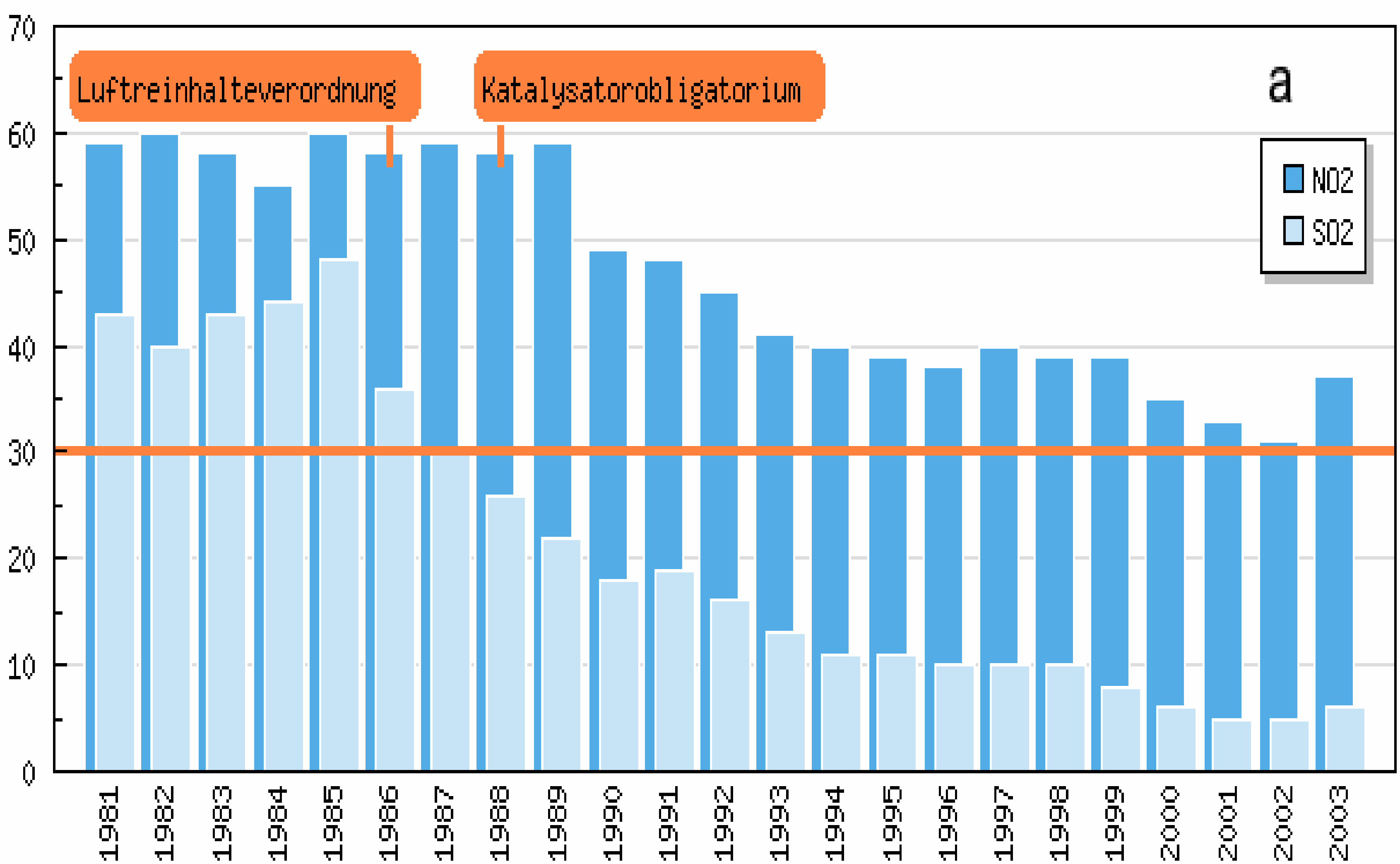
Fossil fuel related ground-based VOC-emissions (from TEAM)



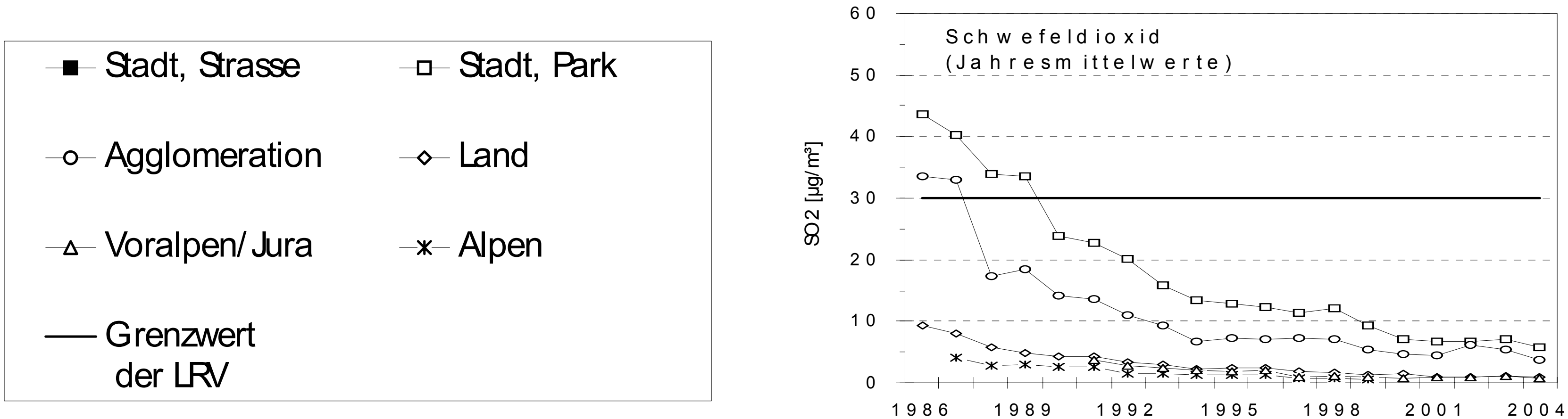
Emission change in % 1990-1999 (EMEP, Vestreng et al., 2001)

	NO_x	VOC
Switzerland	- 36	- 41
Austria	- 12	- 32
Germany	- 39	- 47
Italy	- 23	- 25
France	- 18	- 28

Concentrations at Kasernenhof Zürich (NABEL: Nationales Beobachtungsnetz für Luftfremdstoffe, operated by EMPA)



Changes in Swiss anthropogenic emissions (http://www.umwelt-schweiz.ch/buwal/de/fachgebiete/fg_luft/quellen/uebersicht/index.html) and ambient air concentrations of SO_2 (NABEL, Luftbelastung 2004, Schriftenr. 388, 2005)



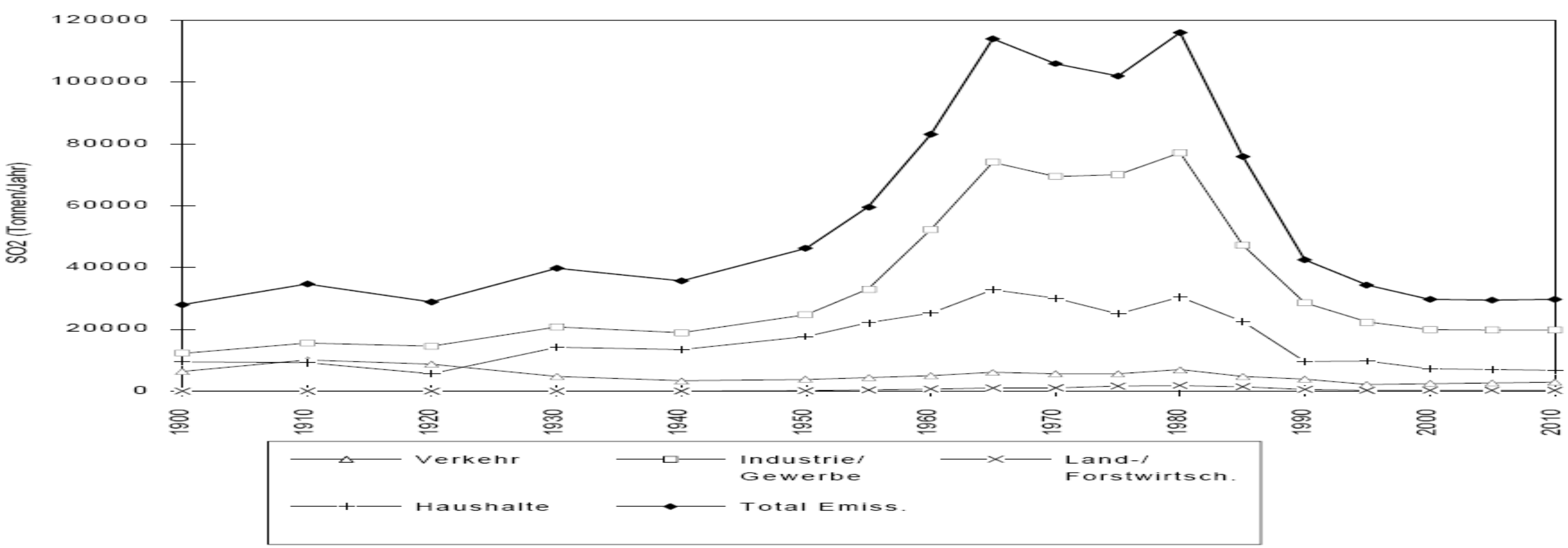
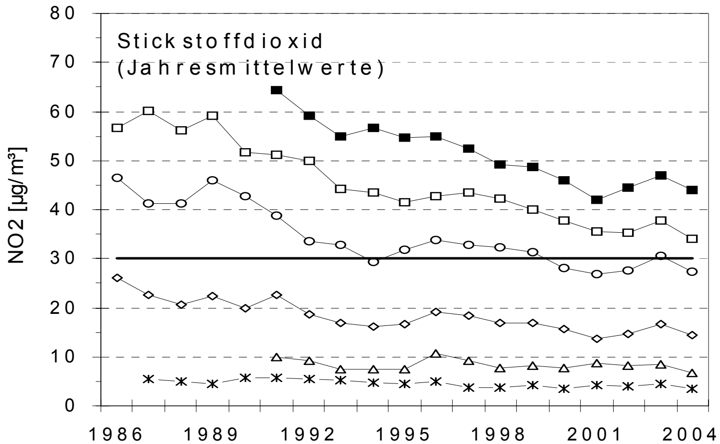
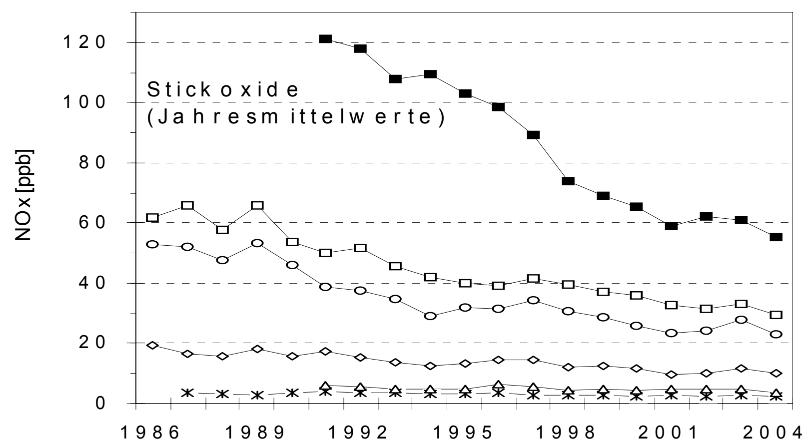


Fig. 4.1 Schwefeldioxid-Emissionen 1900 - 2010

Changes in Swiss anthropogenic emissions and ambient air concentrations of NO_x





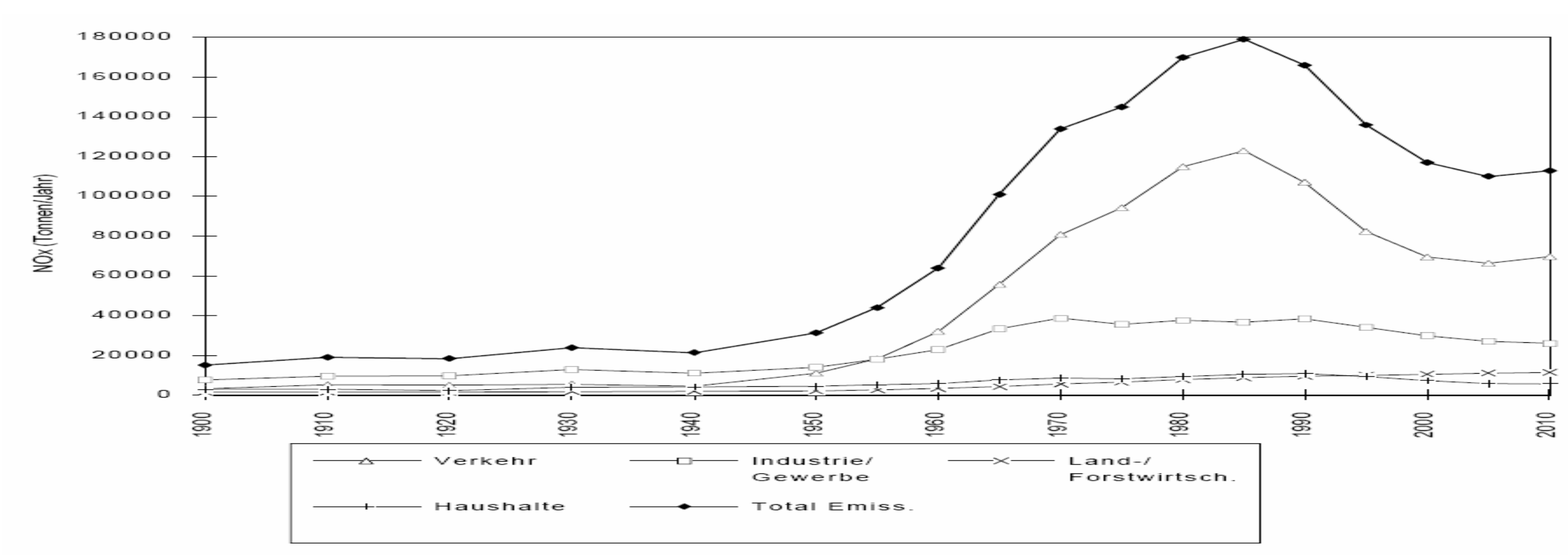
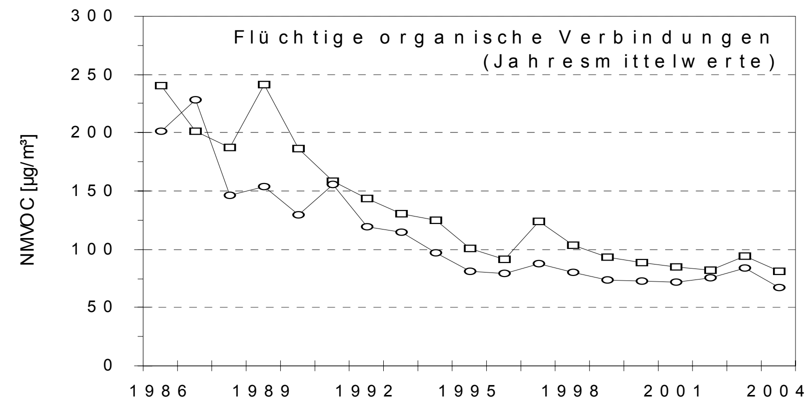


Fig. 4.2 Stickoxid-Emissionen 1900 - 2010

Changes in Swiss anthropogenic emissions and ambient air concentrations of t-NMVOC



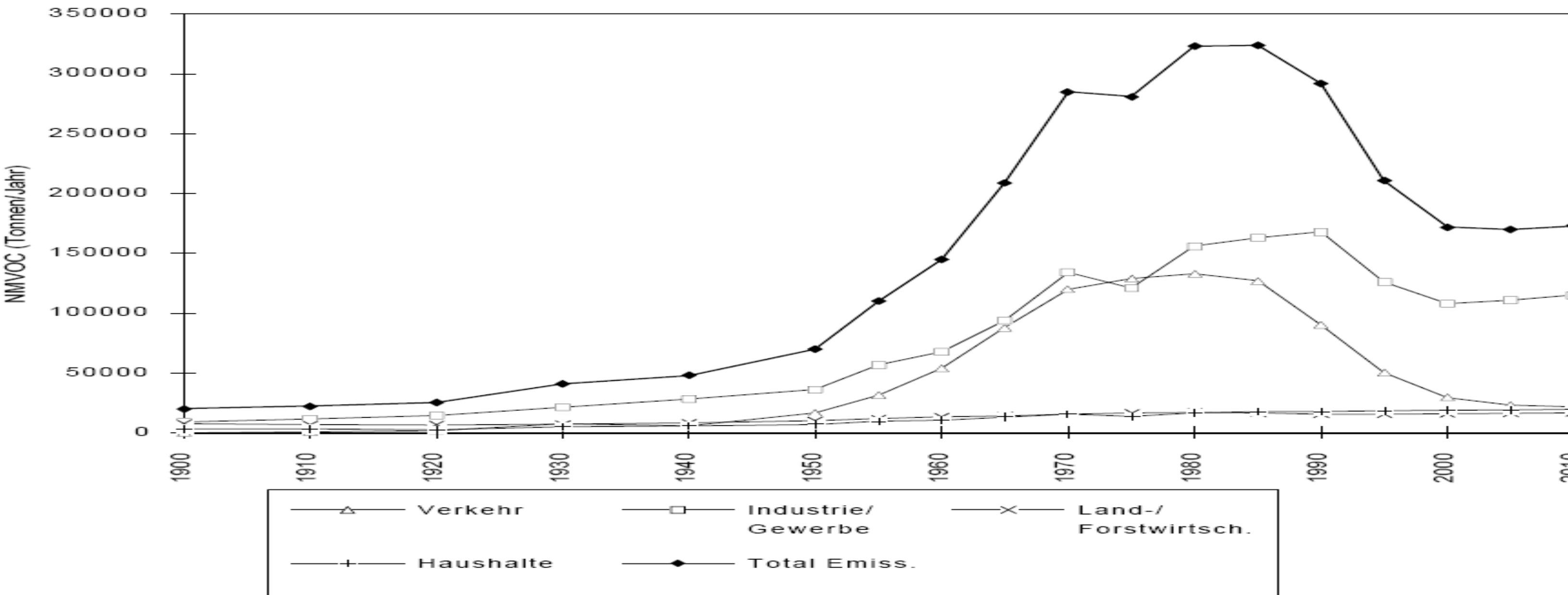


Fig. 4.3 NMVOC-Emissionen 1900 - 2010

Ozone changes in the Los Angeles area (Grosjean, 2003)

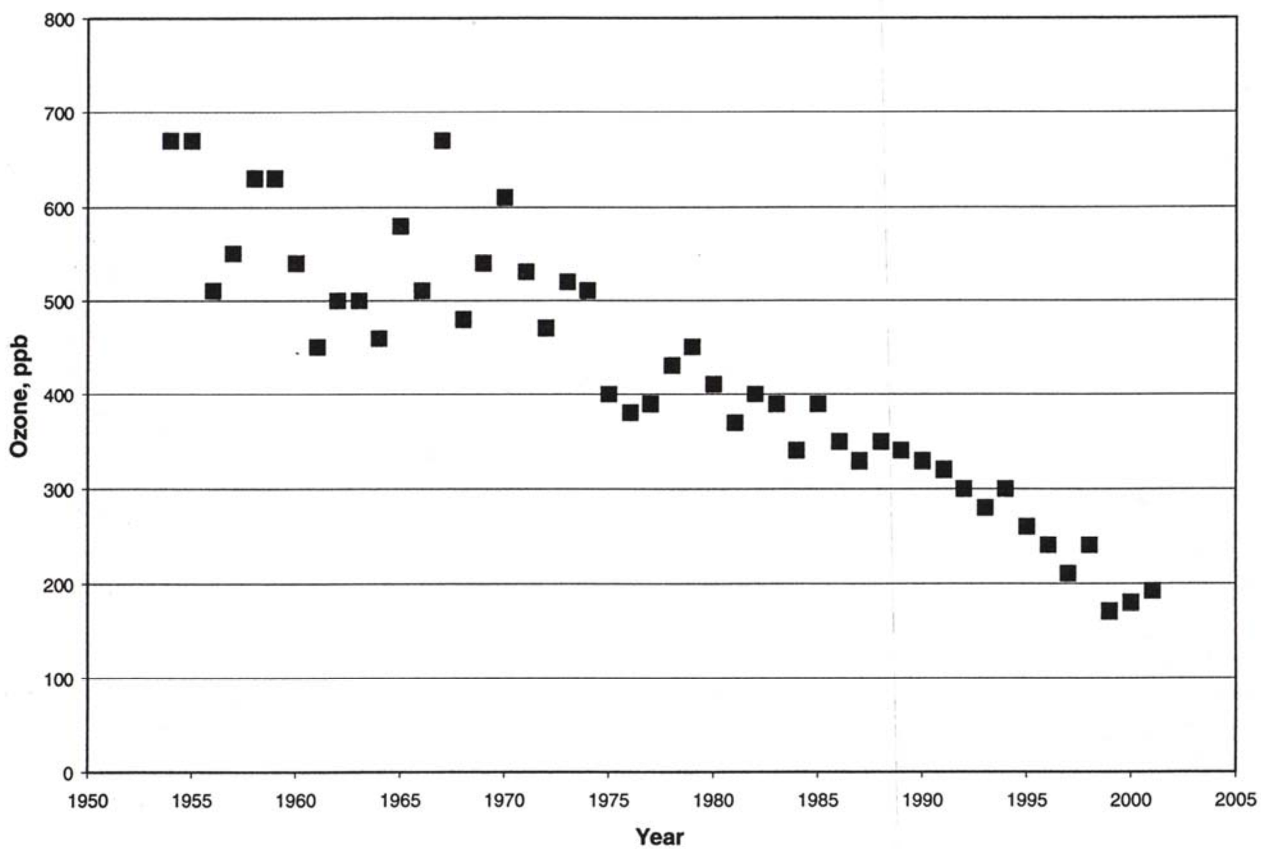


Fig. 2. Peak concentrations of ozone in the California South Coast Air Basin, 1955–2001 (constructed from South Coast Air Quality Management District, 1985 and www.aqmd.org).

(Surface) ozone concentrations from Arosa

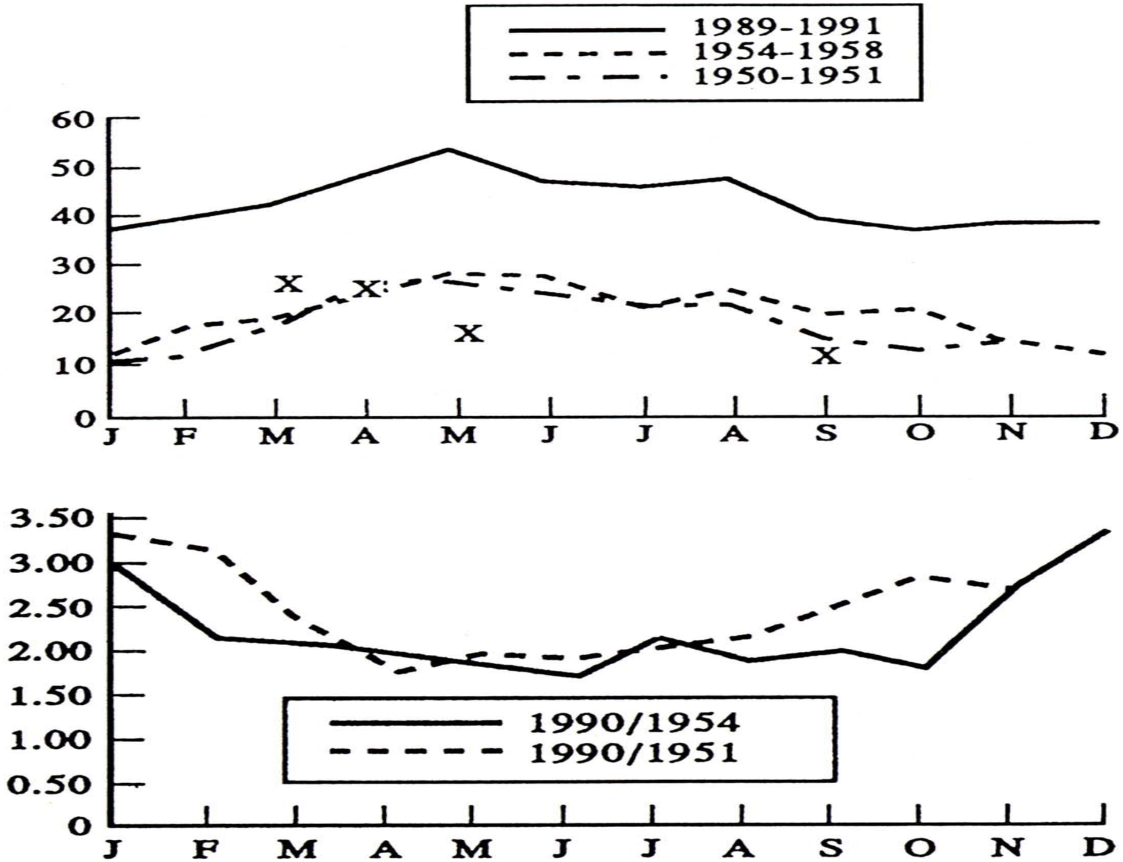


FIGURE 7 Comparison of averaged seasonal variation of surface ozone (monthly mean values at Arosa (Switzerland) during different time periods. (a) Concentrations in ppb, x: averaged concentrations calculated from the single measurements made in the 1930s during clear nights. (b) seasonal differences of the ratios from the recent measurements and the measurements of the 1950s (From Staehelin *et al.* (1994). *Atmospheric Environment* **28,** 75–87.)

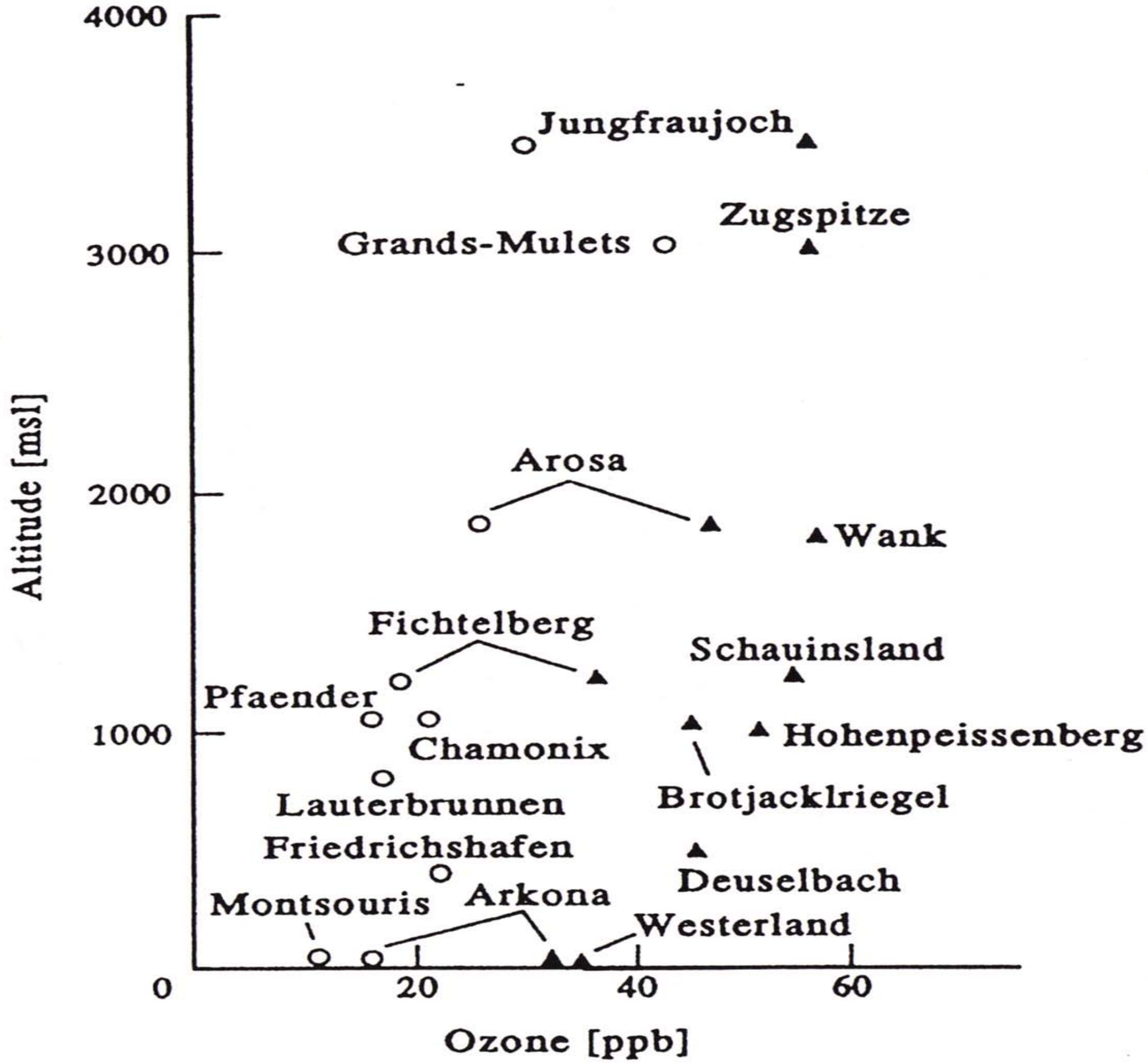
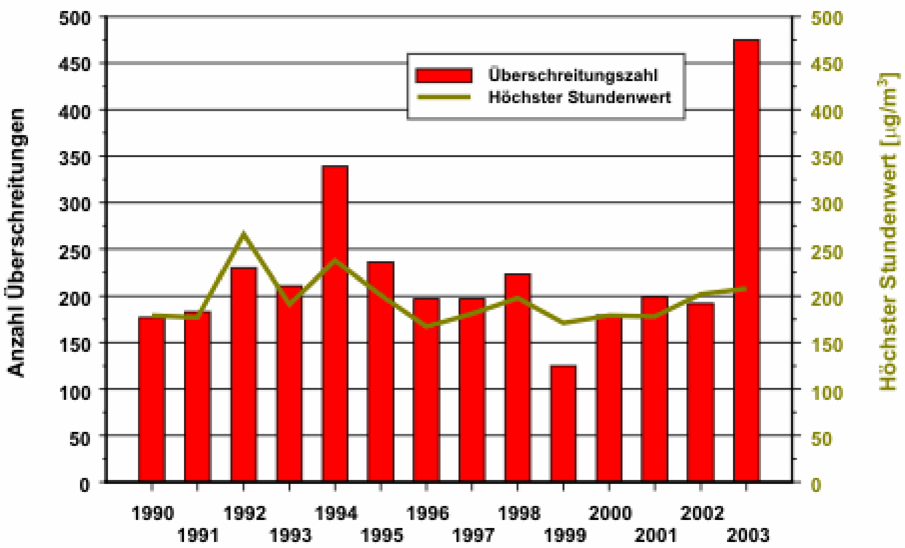


FIGURE 8 Historical (circles) and recent (triangles) surface ozone concentrations of August/September from different locations in Europe as a function of altitude. The historical measurements from the different sites also include measurements collected over short periods, whereas the recent data of 1988–1991 are based on continuous monitoring measurements. (For data sources, see Staehelin *et al.* (1994). *Atmospheric Enviroment* **28,** 75–87.)

Ozone trends in the Swiss plateau:

left: Ozone concentrations at Zürich Stampfenbachstrasse
right: multiple regerssion model to account for meterological variability (Ordonez et al., 2005)



O_3 (daily ozone max. 1992-2002) =
a1A1 + a2A2 + .. + b11 + b12 +…+ b21 + b22 + …. + c + ε

where*:*

-*A1, A2, … :* continuous variables

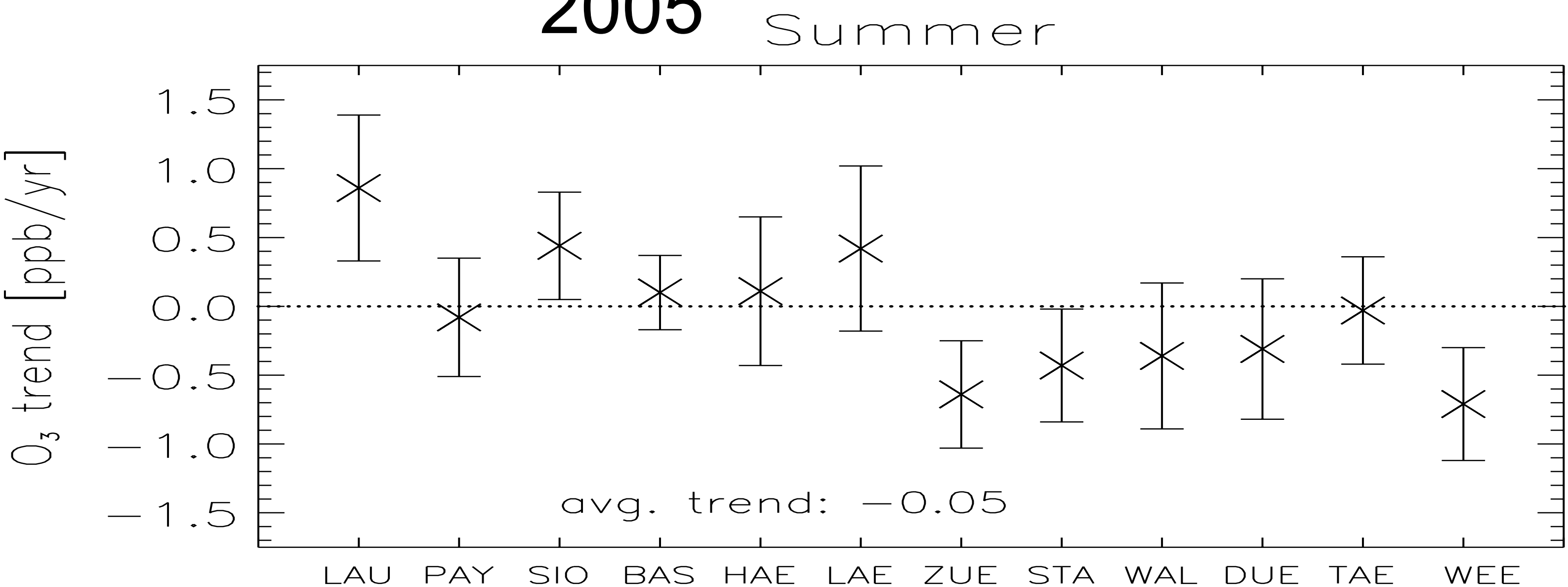
-*a1, a2, …:* coefficients of continuous variables

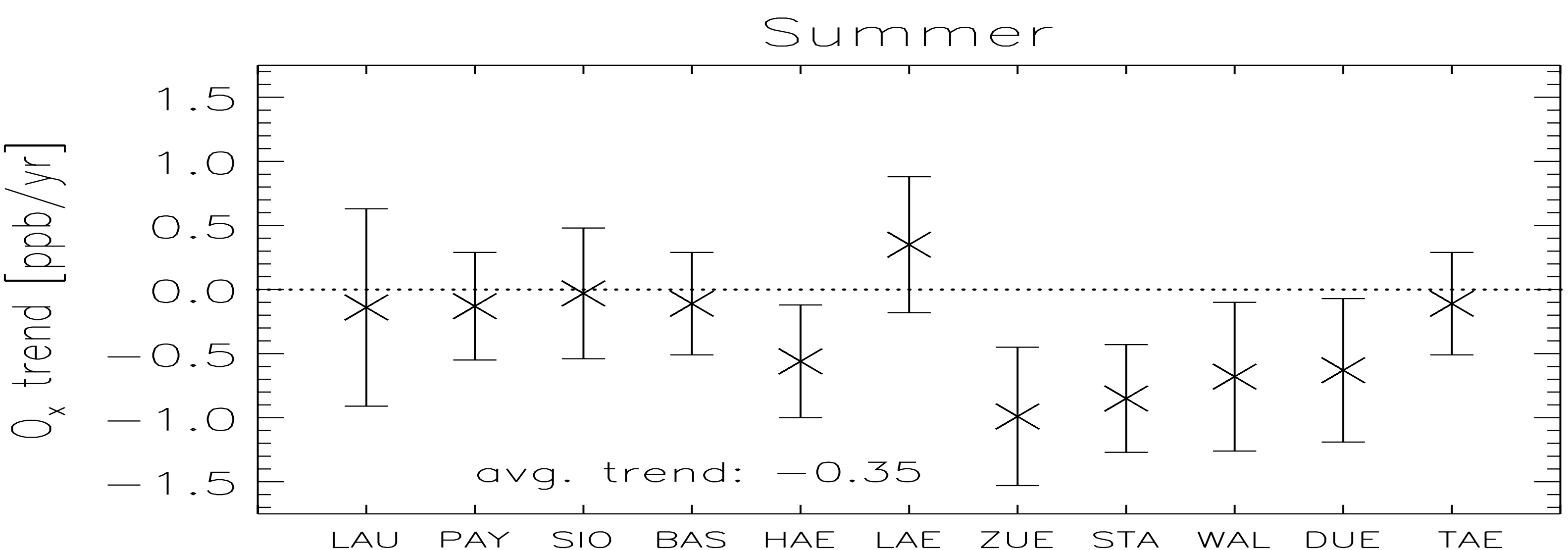
-*b11,b12,… b21, b22:*
coefficients or "treatment effects" of discrete variables B1, B2, ..
(e.g. day of the week)

- *c:* intercept

- *ε:* random error

Summer daily maxima (90th percentile) trends in CH north of Alps, Ordonez et al., 2005





Increase in background ozone over Europe in the 1990s. ***High mountain sites*** (since 1990)

Jungfraujoch (CH) **in ppb y^{-1}**(from C. Ordonez, PSI):
1990-2003: 04.00-06.00, winter: 0.68; summer: 0.64
Mace Head (Ireland) 1987-2003 (Simmonds et al., 2004):
winter: 0.63; summer: 0.39