



Air Pollution Control and Air Chemistry: The atmospheric oxidation capacity

(6th lecture)

Detlev Möller

Chair for Atmospheric Chemistry and Air Pollution Control

Faculty of Environmental Sciences and Process Engineering

Brandenburg Technical University Cottbus, Germany

Objectives:

To describe the atmospheric chemical O_xH_y system being an redox cycle with the tendency to oxidize reduced trace substances such as sulphur, nitrogen and carbon.

- oxidants and O_xH_y redox cycle,
- ozone chemistry and radical formation,
- oxidative stress
- summer smog, ozone dynamic

What does mean oxidation (*or oxidising*) capacity *or* potential?

It is the ability of the atmosphere to oxidize trace substances.

Most trace substances (emission) are entering the atmosphere in reduced form:

Sulphur(-II)	H ₂ S, DMS	→ Sulphur(IV)	SO ₂
Sulphur (IV)	SO ₂	→ Sulphur(VI)	SO ₄ ²⁻
Nitrogen(-III)	NH ₃	→ Nitrogen(II)	NO
Nitrogen(I)	N ₂ O	→ Nitrogen(II)	NO
Nitrogen(II)	NO	→ Nitrogen(V)	HNO ₃
Carbon(-IV)	CH ₄ , NMVOC (RCH ₃)	→ Carbon(II)	CO
Carbon(II)	CO	→ Carbon(IV)	CO ₂

oxidation process



Each **oxidation** step is combined with a **reduction** (redox process).

In the atmosphere, most important oxidants are O_xH_x species establishing the redox cycles between water (H_2O) and oxygen (O_2) via active intermediates (radicals and peroxides).

There is no general (mathematical) definition. Often it is identified with the OH radical concentration. We can not define it similar to the redox potential in aqueous solutions.

From kinetic point of view, $X_i^{\text{red}} + OX_j \rightarrow + \text{Products}$, we can

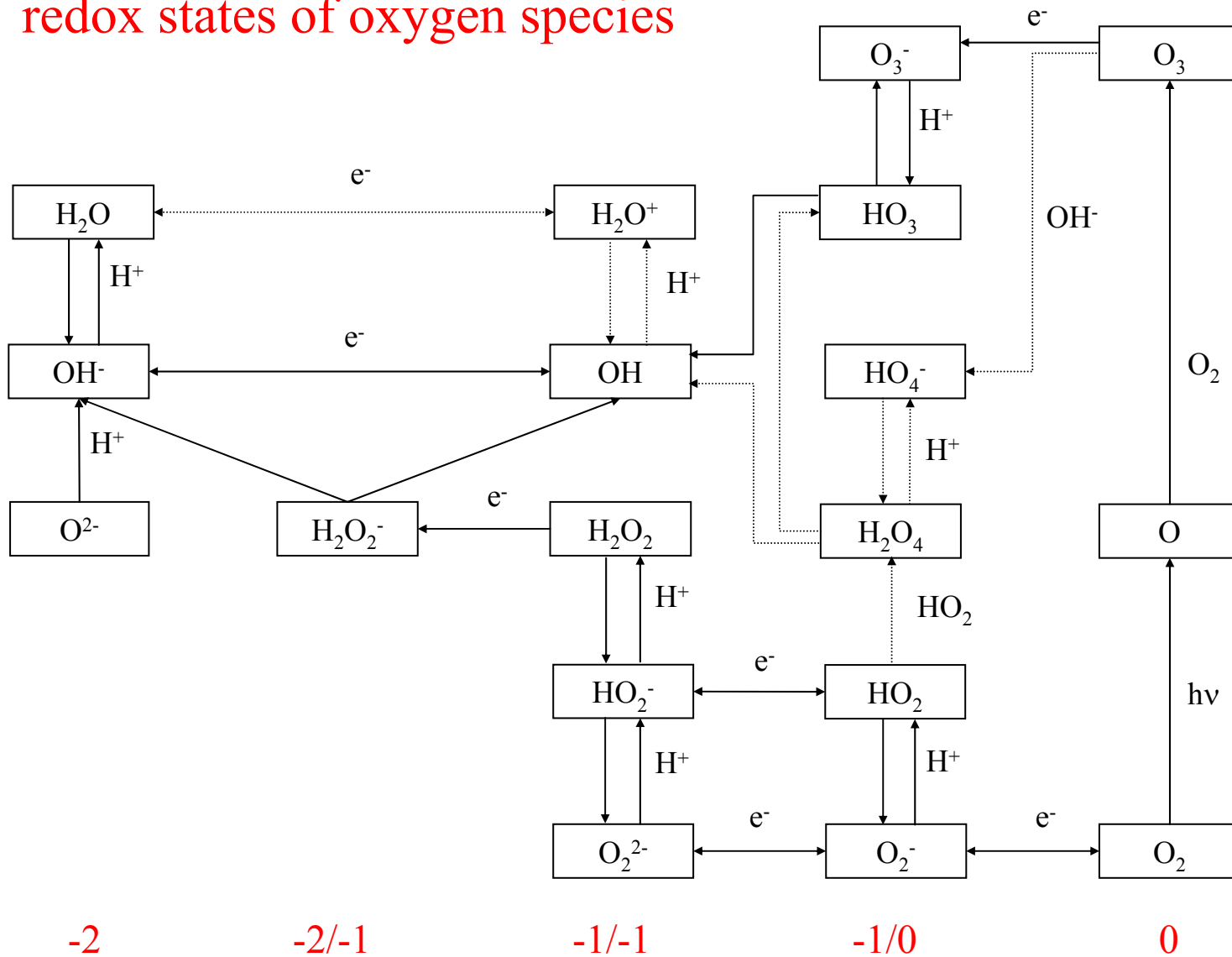
design it as the **free reaction energy (Gibb's potential)**: $P_{\text{therm}}^{\text{ox}} = \sum_j \Delta_R G_j$

and as the **specific oxidation potential (rate)**: $P_{\text{kin}}^{\text{ox}} = \sum_j k_j [OX_j]$

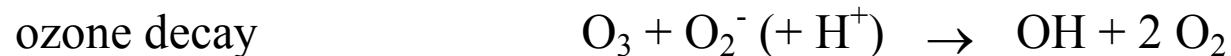
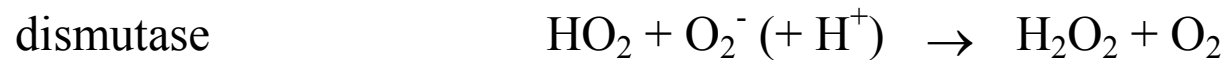
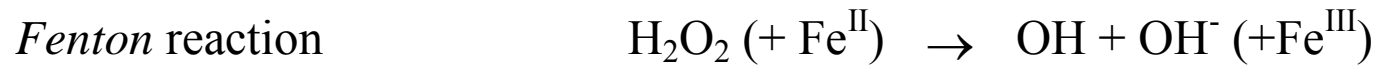
All important H_xO_y components

redox level	species	formation/destruction	name
-3	H ₂ O ⁻	H ₂ O + e ⁻	aquated electron
-2	H ₂ O	OH + H / OH ⁻ + H ⁺	water
	H ⁺ (H ₃ O ⁺) -		hydrogen ion (hydrogenium)
	OH ⁻	OH + e ⁻	hydroxyl ion
	[O ₂ ⁻]	O ₂ + e ⁻	oxide
-1	H ₂ O ⁺	H ₂ O - e ⁻ / OH + H ⁺	water anion
	OH	O + H / H ₂ O - H	hydroxyl radical
	HO ₂ ⁻	HO ₂ + e ⁻	hydroperoxide anion
	H ₂ O ₂	OH + OH	hydrogenperoxide
-1/±0	O ₂ ⁻	O ₂ + e ⁻	hyperoxide anion
	HO ₂	O ₂ + H / O + OH	hydroperoxoradical
	O ₃ ⁻	O ₃ + e ⁻	ozonide anion
	HO ₃	OH + O ₂	ozonide
	HO ₄ ⁻	O ₃ + OH ⁻	ozone acid anion (hypothetical)
	H ₂ O ₄	HO ₂ + HO ₂ / 2 OH + O ₂	ozone acid (hypothetical)
±0	H	-	hydrogen
	O	-	oxygen, atomar
	O ₂	O + O	oxygen, molecular
	O ₃	O + O ₂	ozone

redox states of oxygen species



basic H_xO_y reactions in aqueous phase

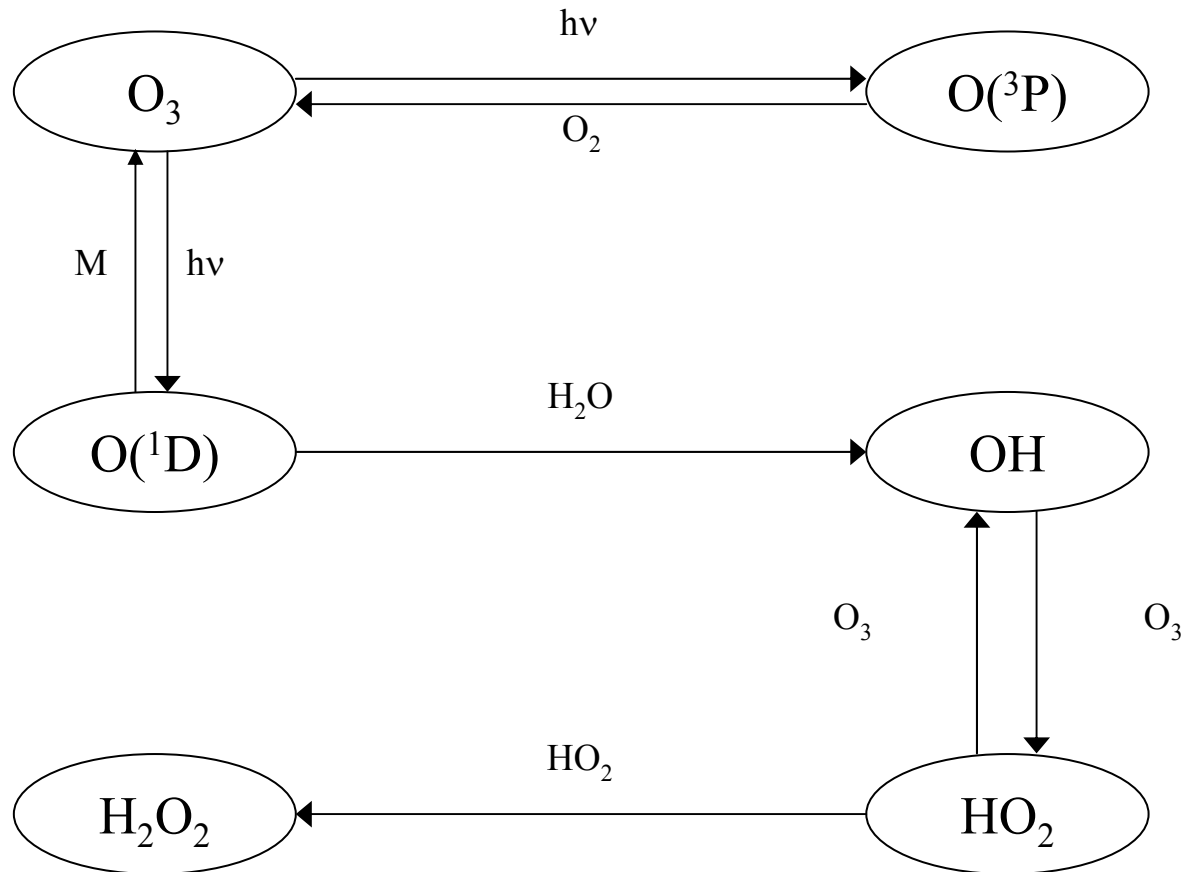


Atmospheric chemistry

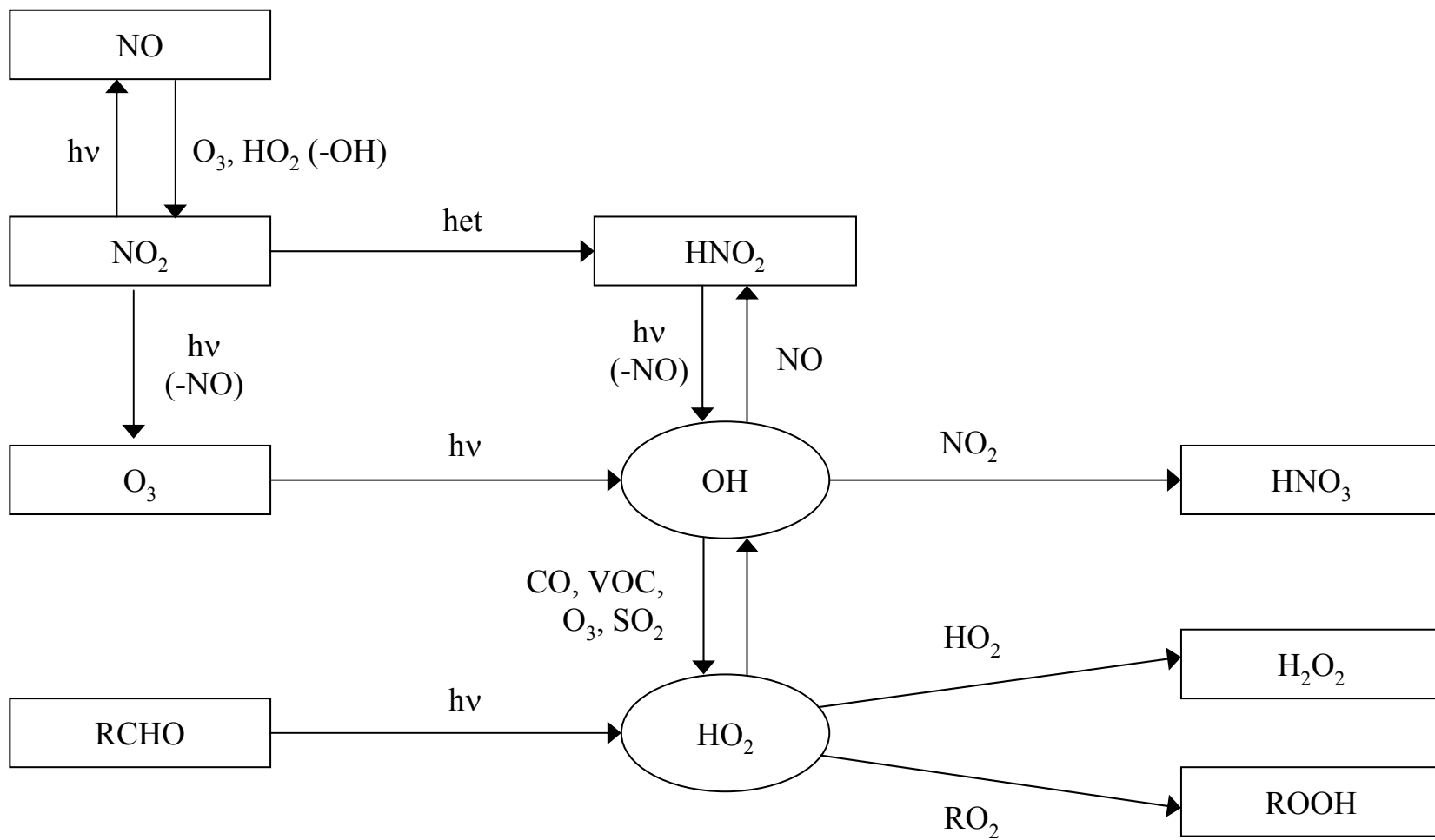
Ozone formation within the troposphere

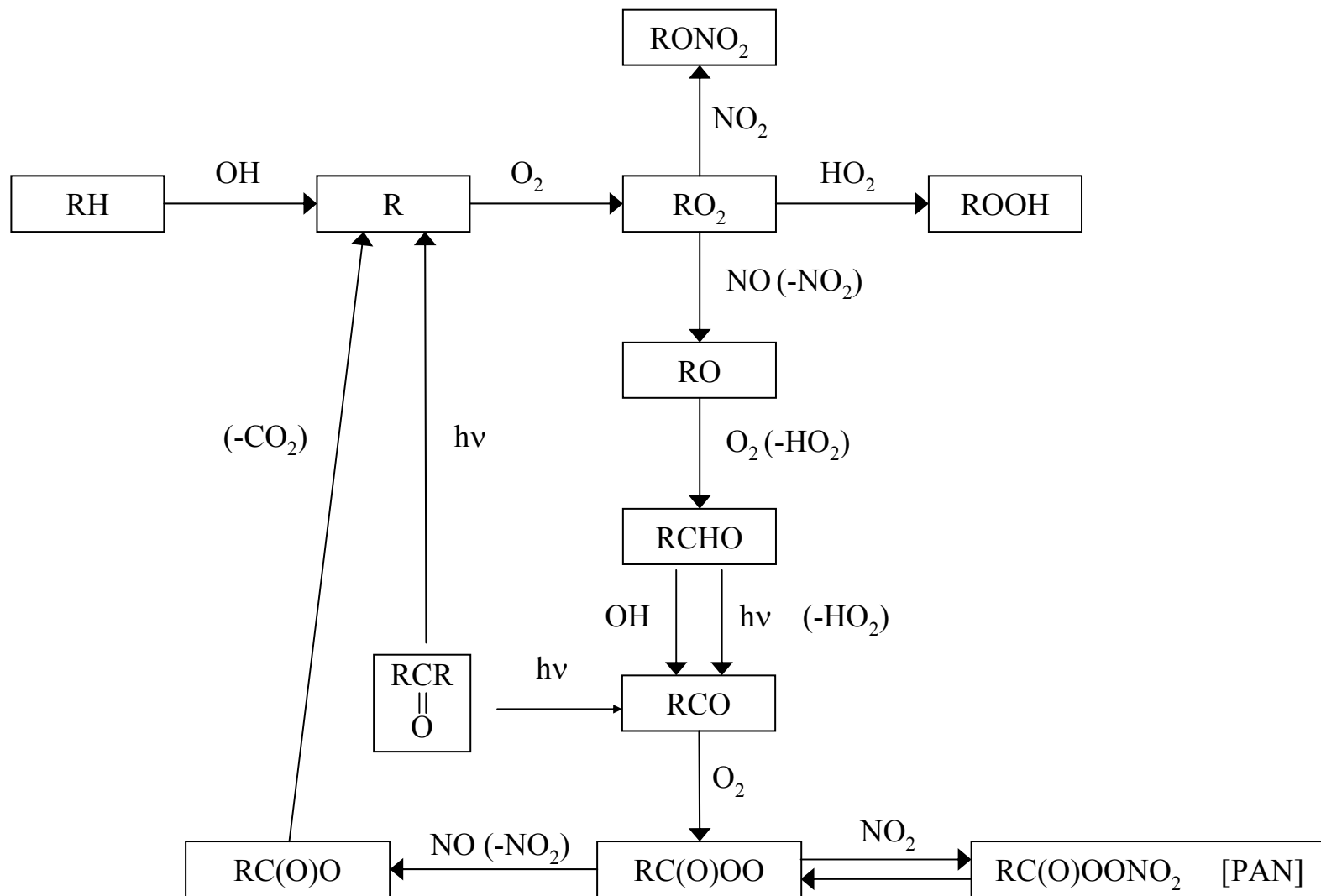


OH chemistry of the clean atmosphere



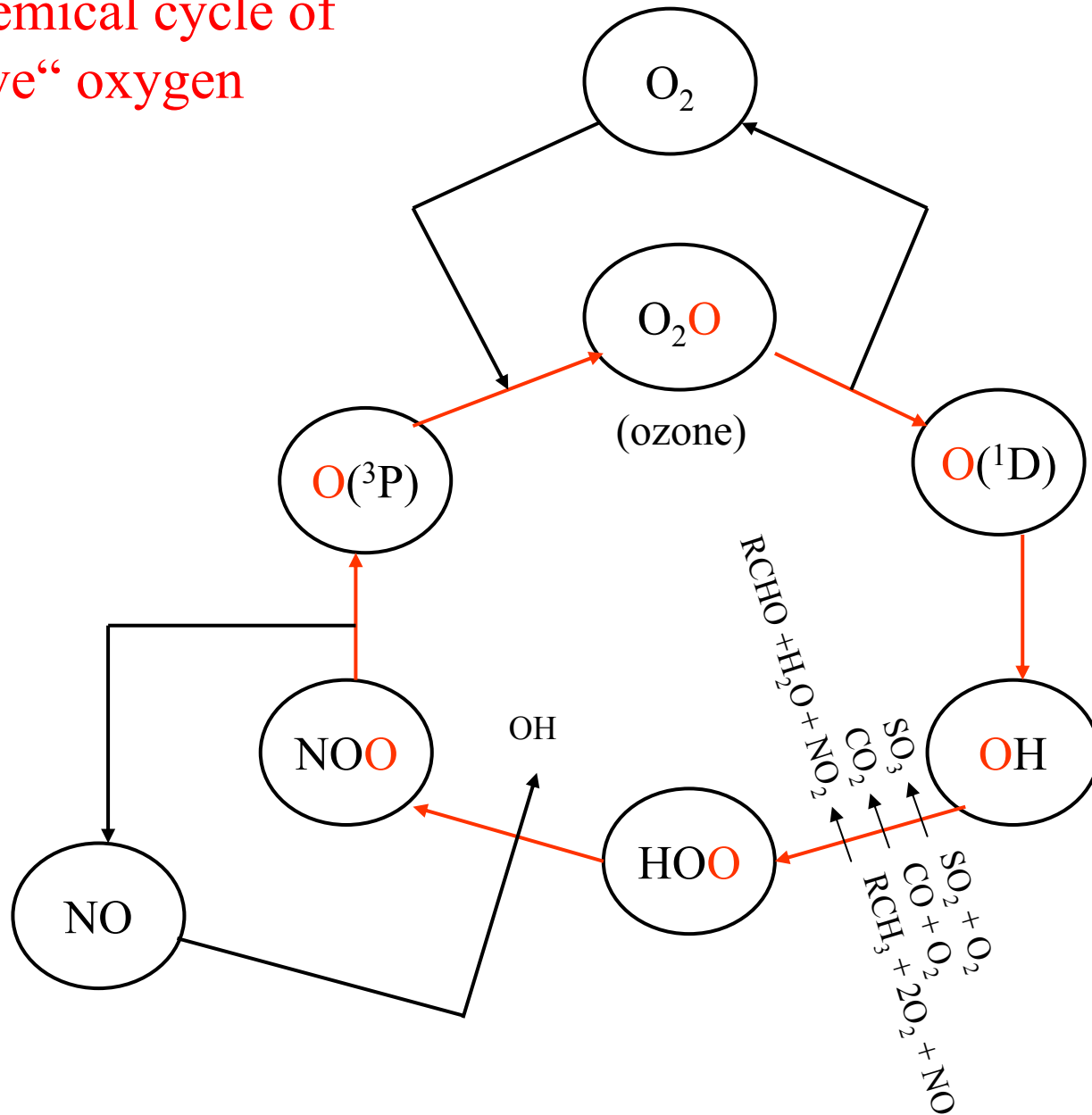
OH chemistry of the polluted atmosphere





organic radical chemistry

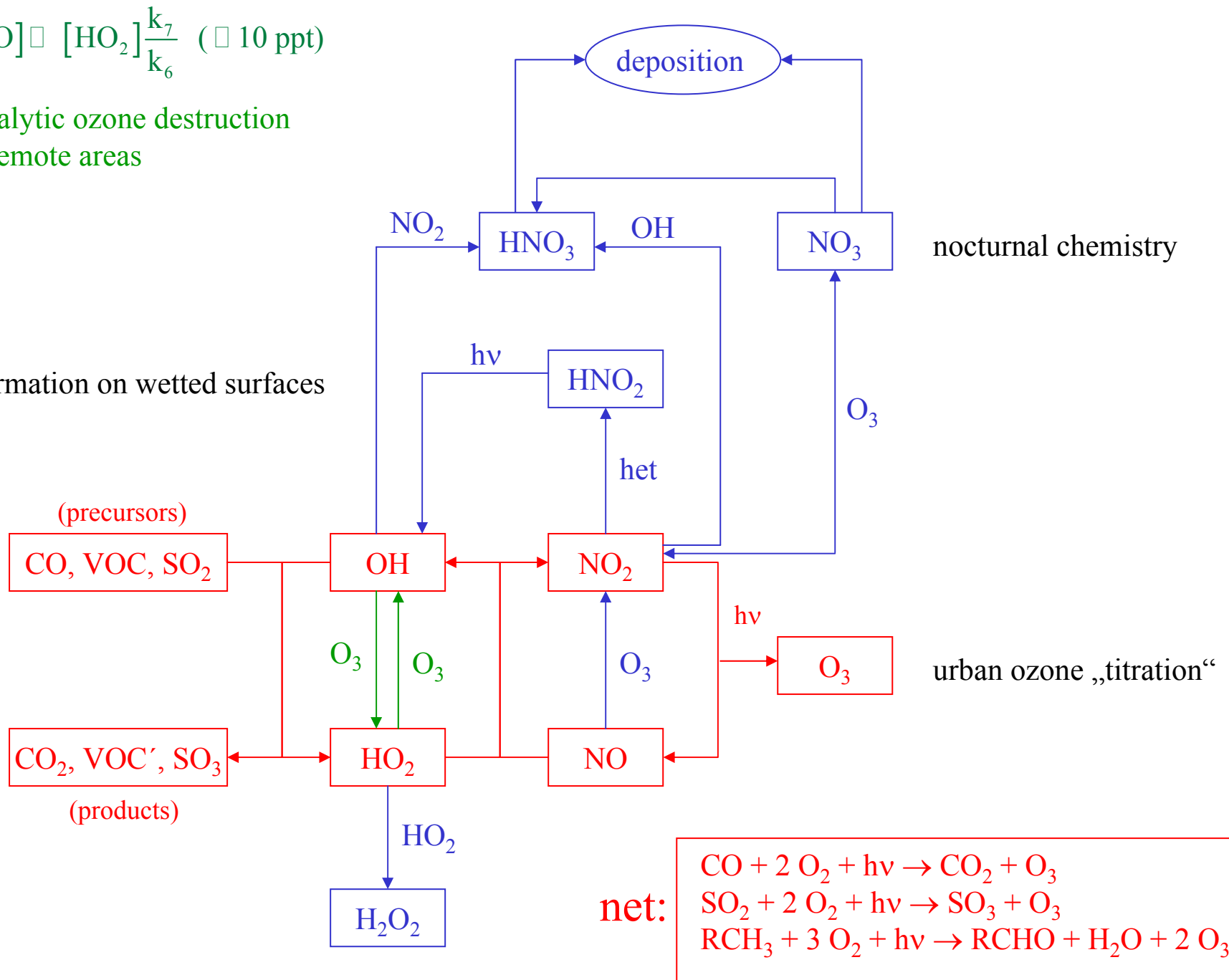
The chemical cycle of „reactive“ oxygen



$$[\text{NO}] \ll [\text{HO}_2] \frac{k_7}{k_6} \quad (\ll 10 \text{ ppt})$$

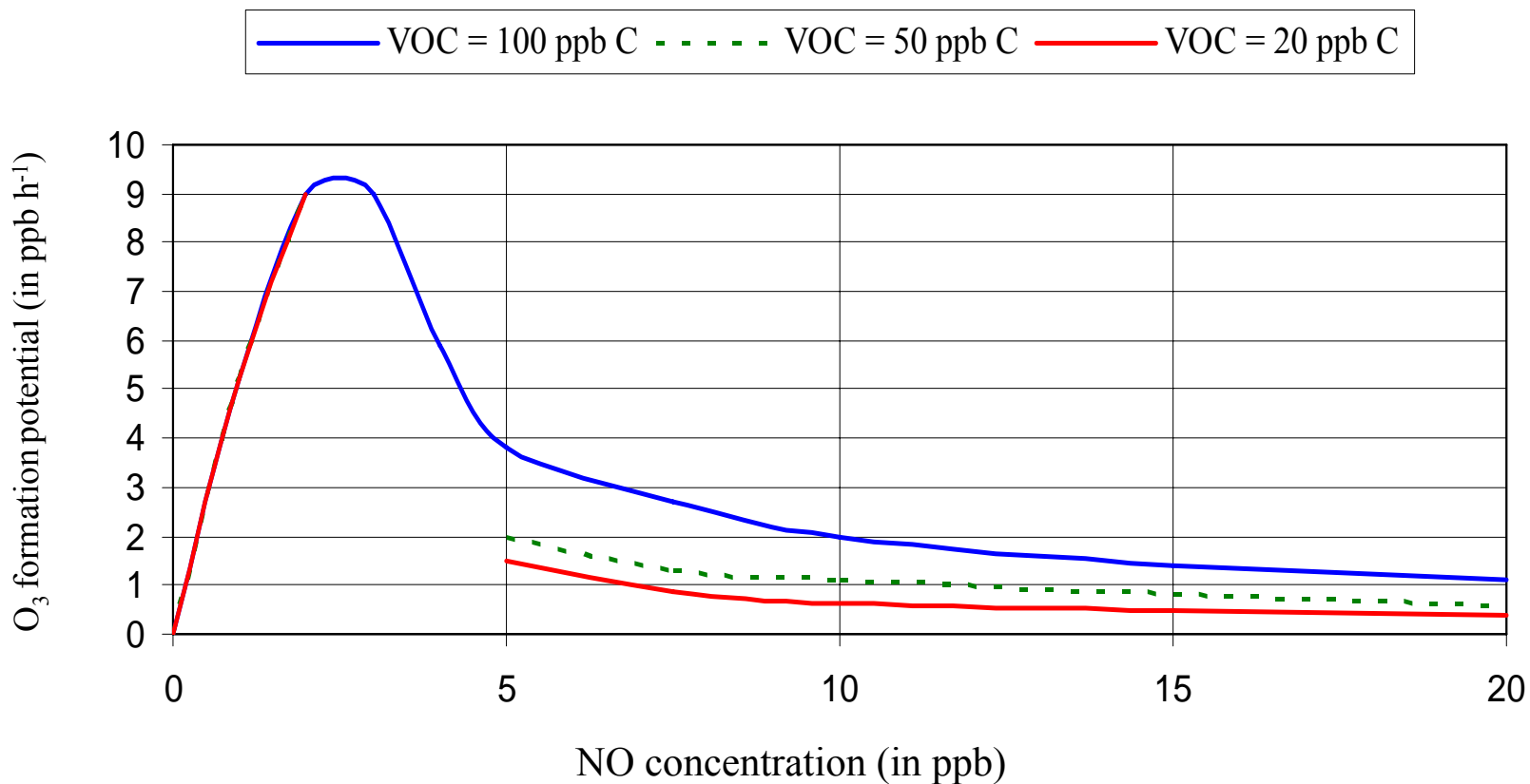
Catalytic ozone destruction
in remote areas

formation on wetted surfaces

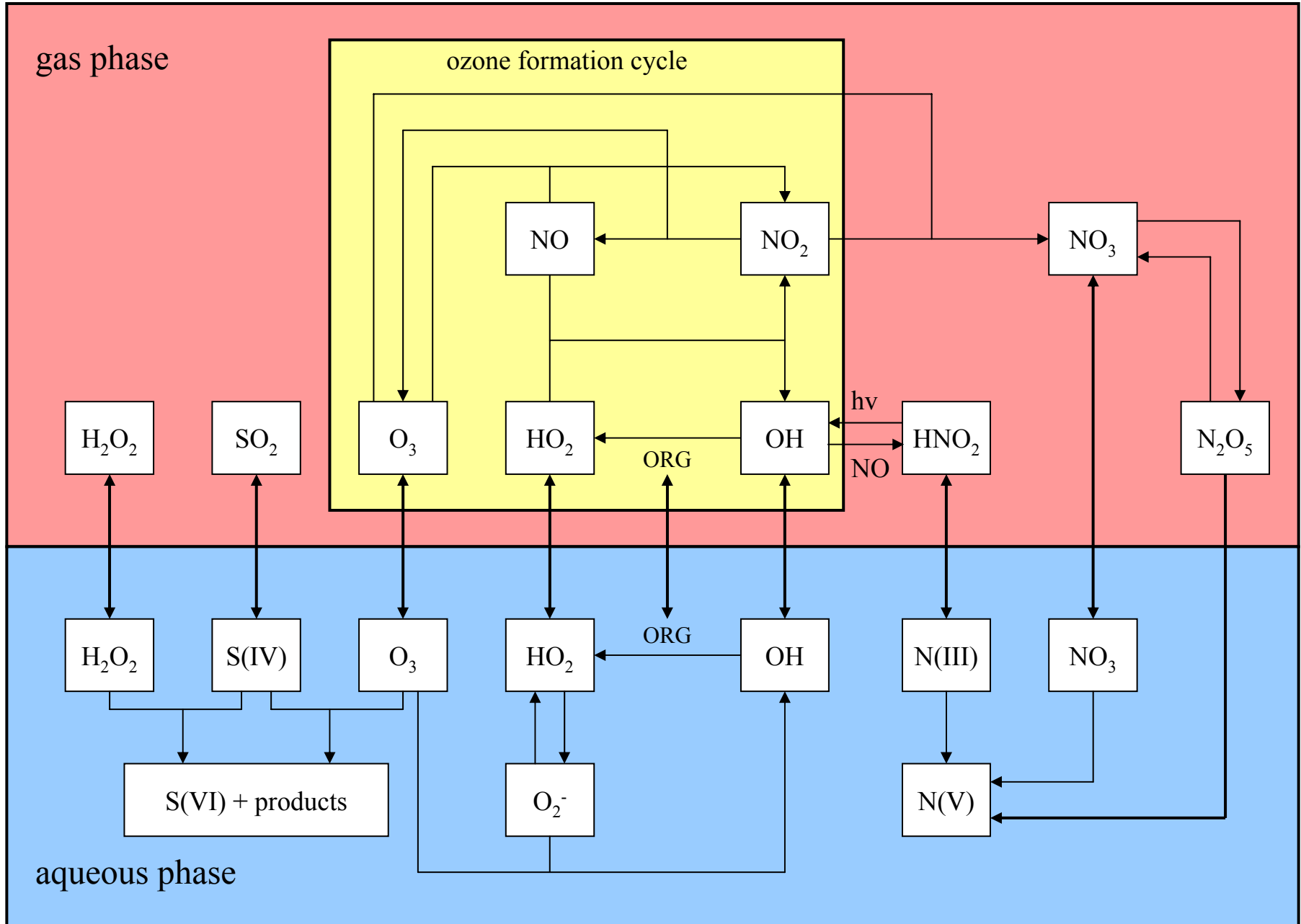


Dependence of ozone formation potential from NO and VOC concentration

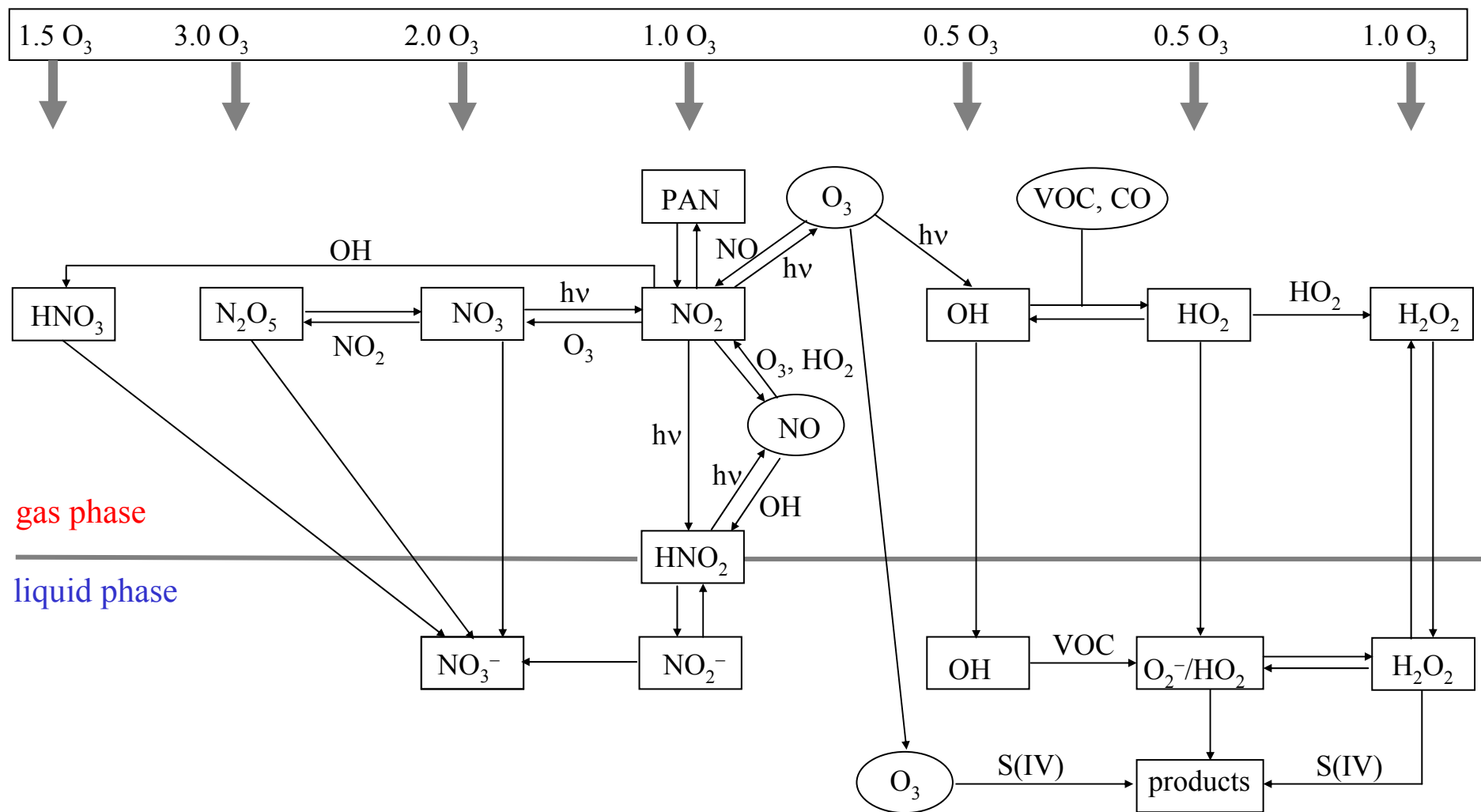
(Sillman diagramme)



Multiphase oxidant chemistry

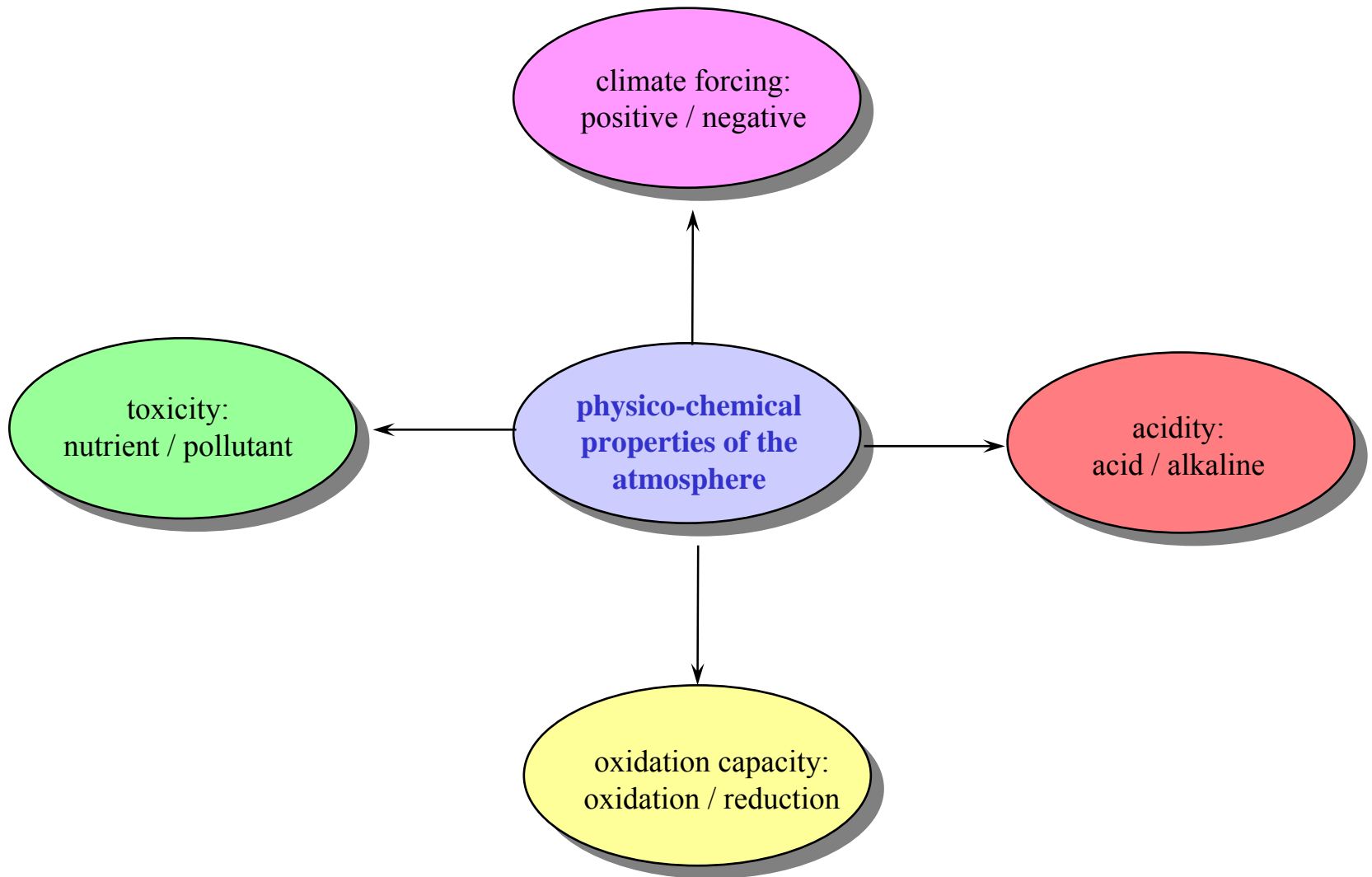


ozone stoichiometry in sink products



Oxidative stress

The scheme of atmospheric impact factors



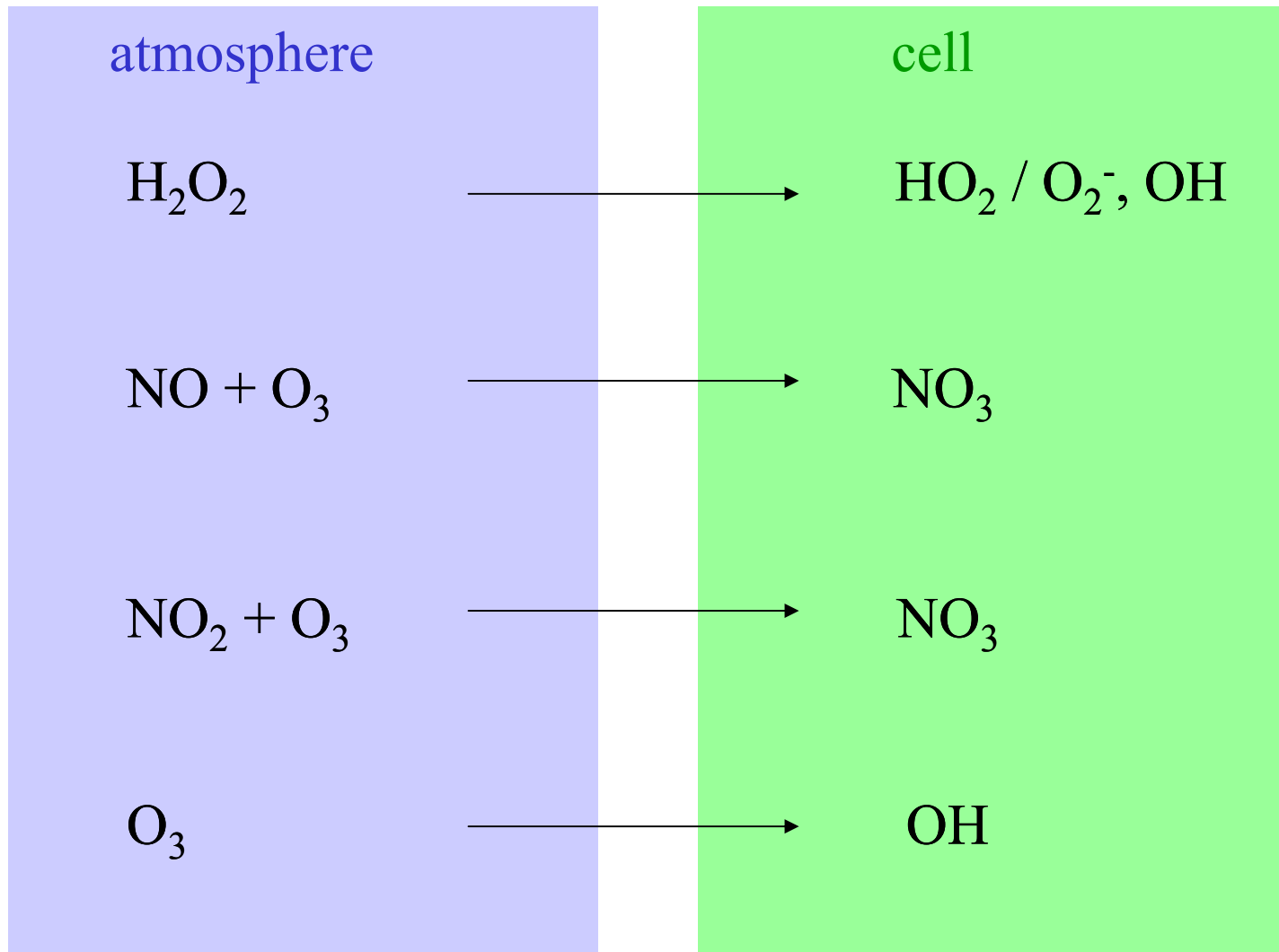
Oxidative Stress

Oxidative stress is imposed on cells as a result of one of three factors:

- 1) an increase in oxidant generation,
- 2) a decrease in antioxidant protection, or
- 3) a failure to repair oxidative damage.

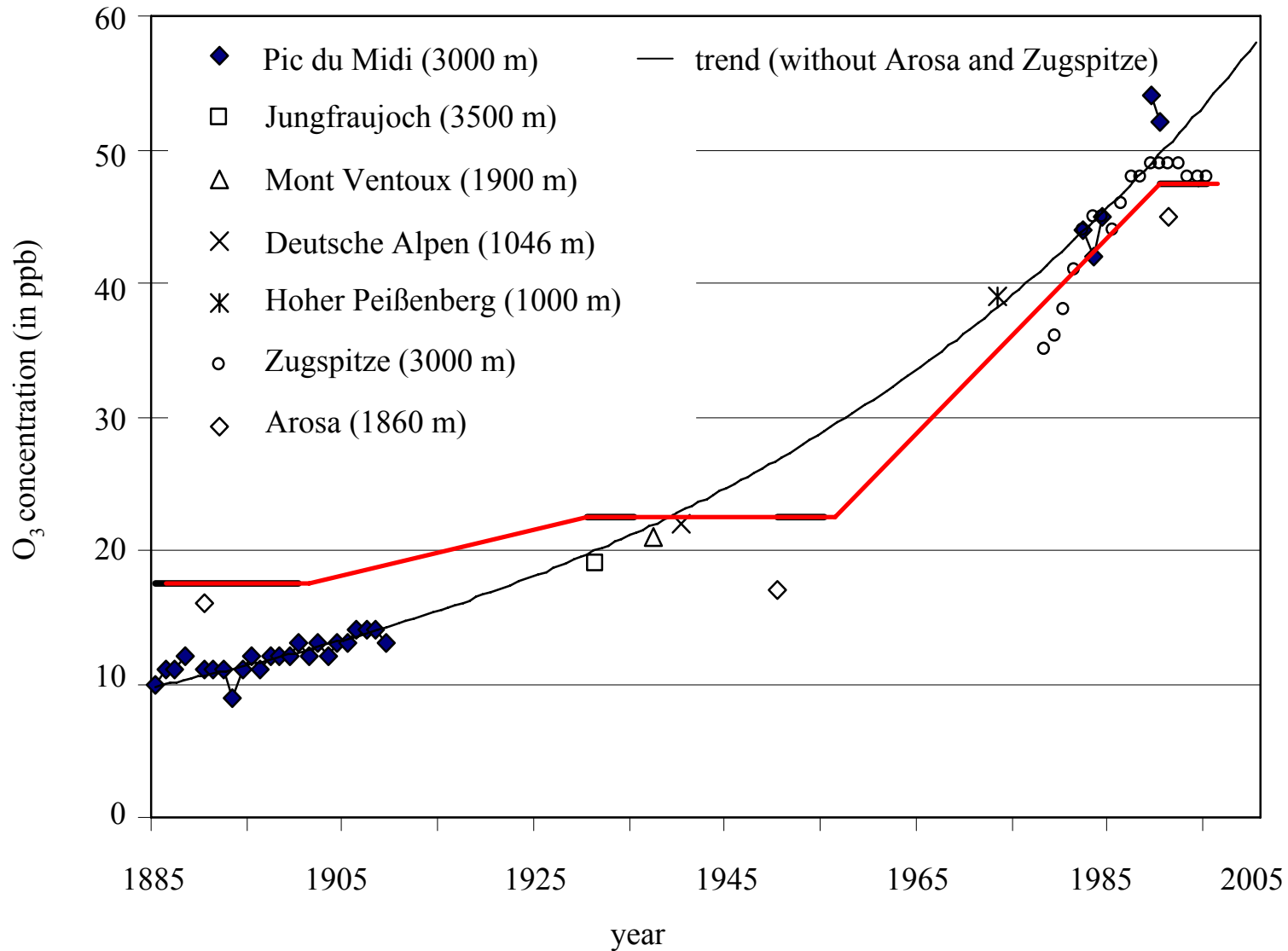
Cell damage is induced by reactive oxygen species (ROS). ROS are either free radicals, reactive anions containing oxygen atoms, or molecules containing oxygen atoms that can either produce free radicals or are chemically activated by them. Examples are hydroxyl radical, superoxide, hydrogen peroxide, and peroxynitrite. The main source of ROS *in vivo* is aerobic respiration, although ROS are also produced by peroxisomal β -oxidation of fatty acids, microsomal cytochrome P450 metabolism of xenobiotic compounds, stimulation of phagocytosis by pathogens or lipopolysaccharides, arginine metabolism, and tissue specific enzymes. Under normal conditions, ROS are cleared from the cell by the action of superoxide dismutase (SOD), catalase, or glutathione (GSH) peroxidase. The main damage to cells results from the ROS-induced alteration of macromolecules such as polyunsaturated fatty acids in membrane lipids, essential proteins, and DNA. Additionally, oxidative stress and ROS have been implicated in disease states, such as Alzheimer's disease, Parkinson's disease, cancer, and aging.

Atmospheric oxidative stress precursors



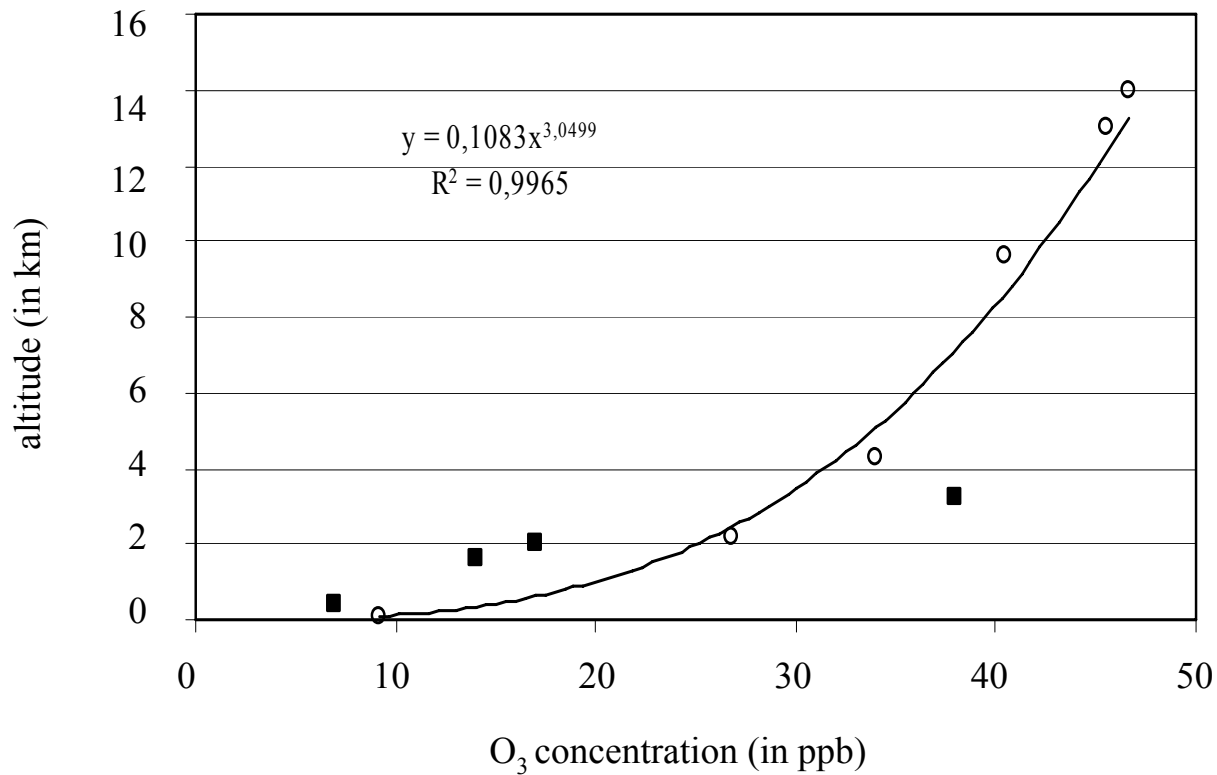
Ozone trend

European ozone trend



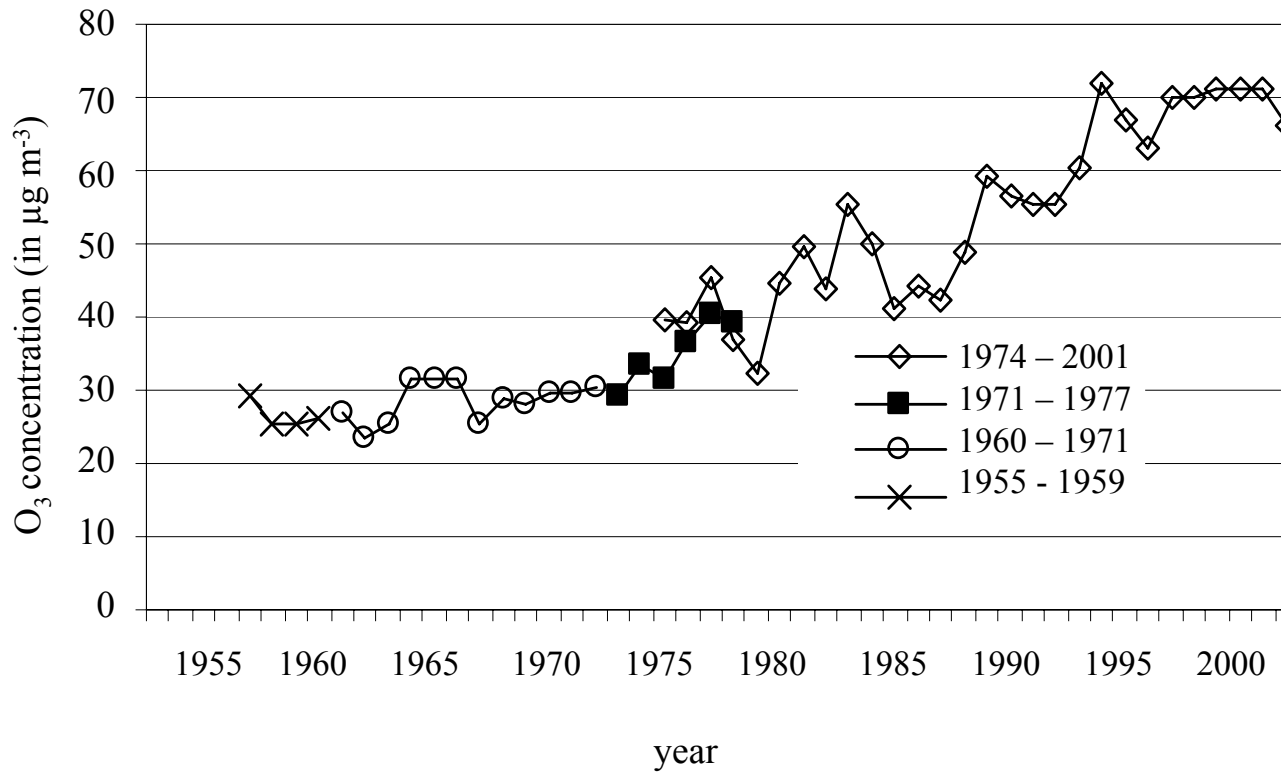
Ozone dependence from altitude

(after historic Soviet and Swiss data from the 1920s and 1930s)



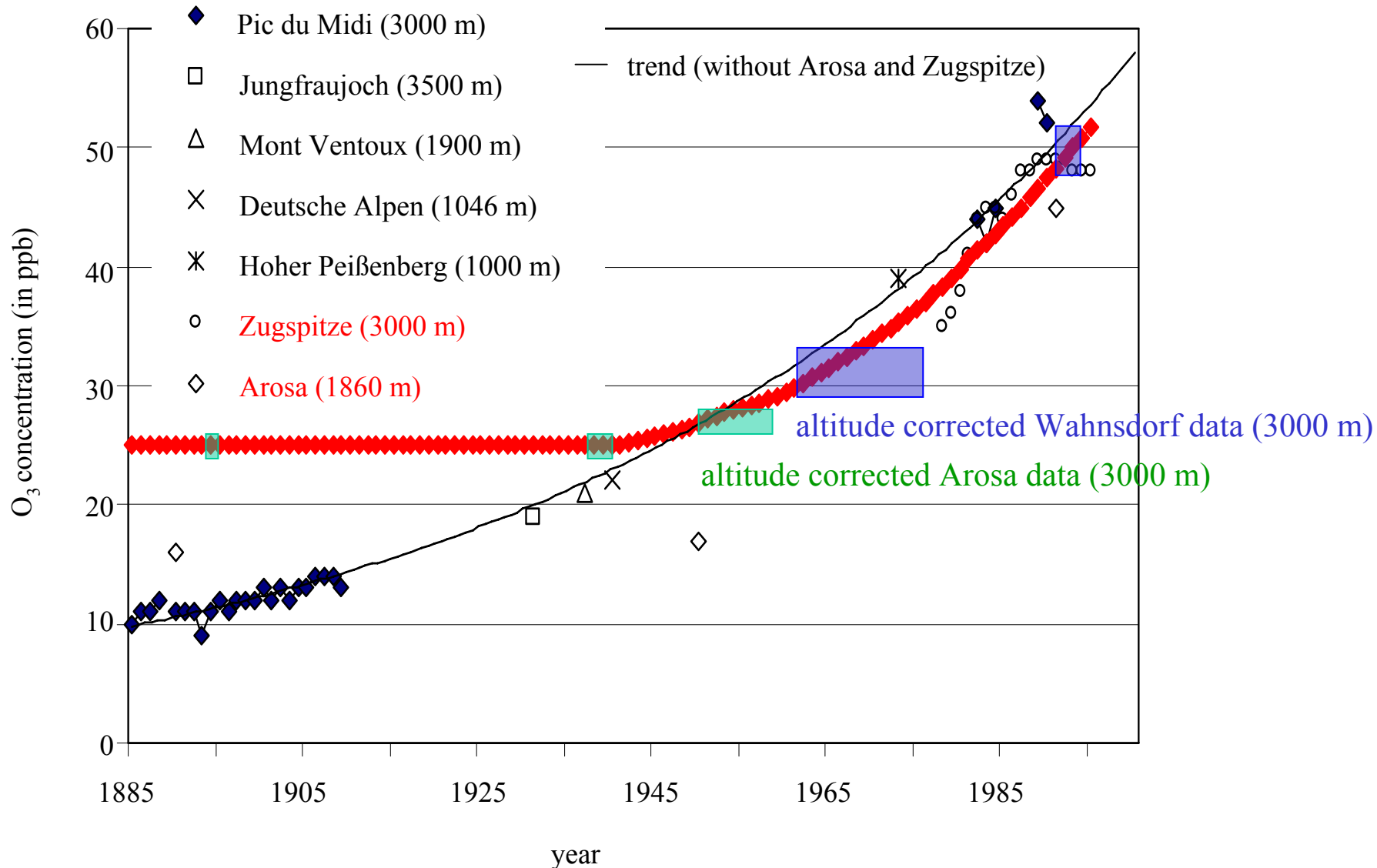
(note: in 2000-3000 m altitude about 15-20 ppb O₃ must be added to the ground level)

Ozone trend at the station Wahnsdorf (near Dresden)

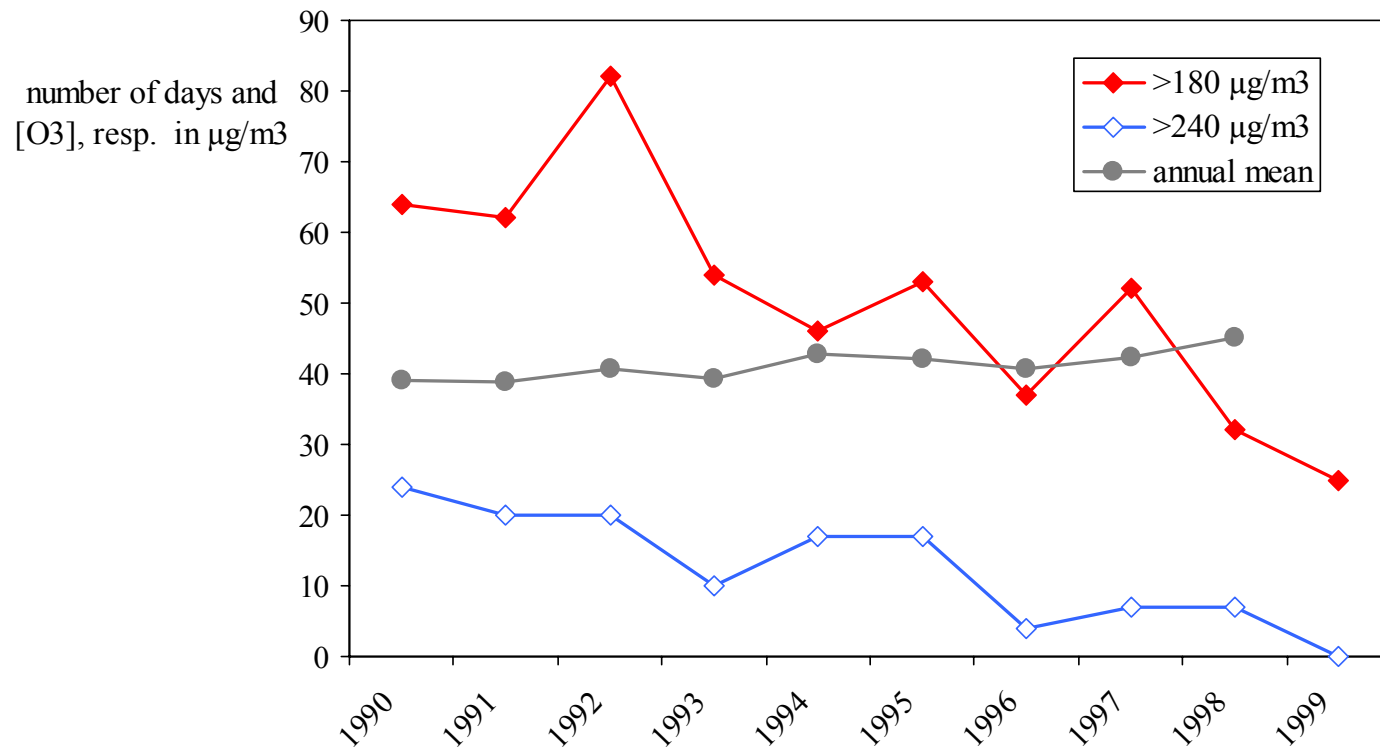


$$[O_3] = 35 + 1.4 \times (1974-2000), r^2 = 0.82$$

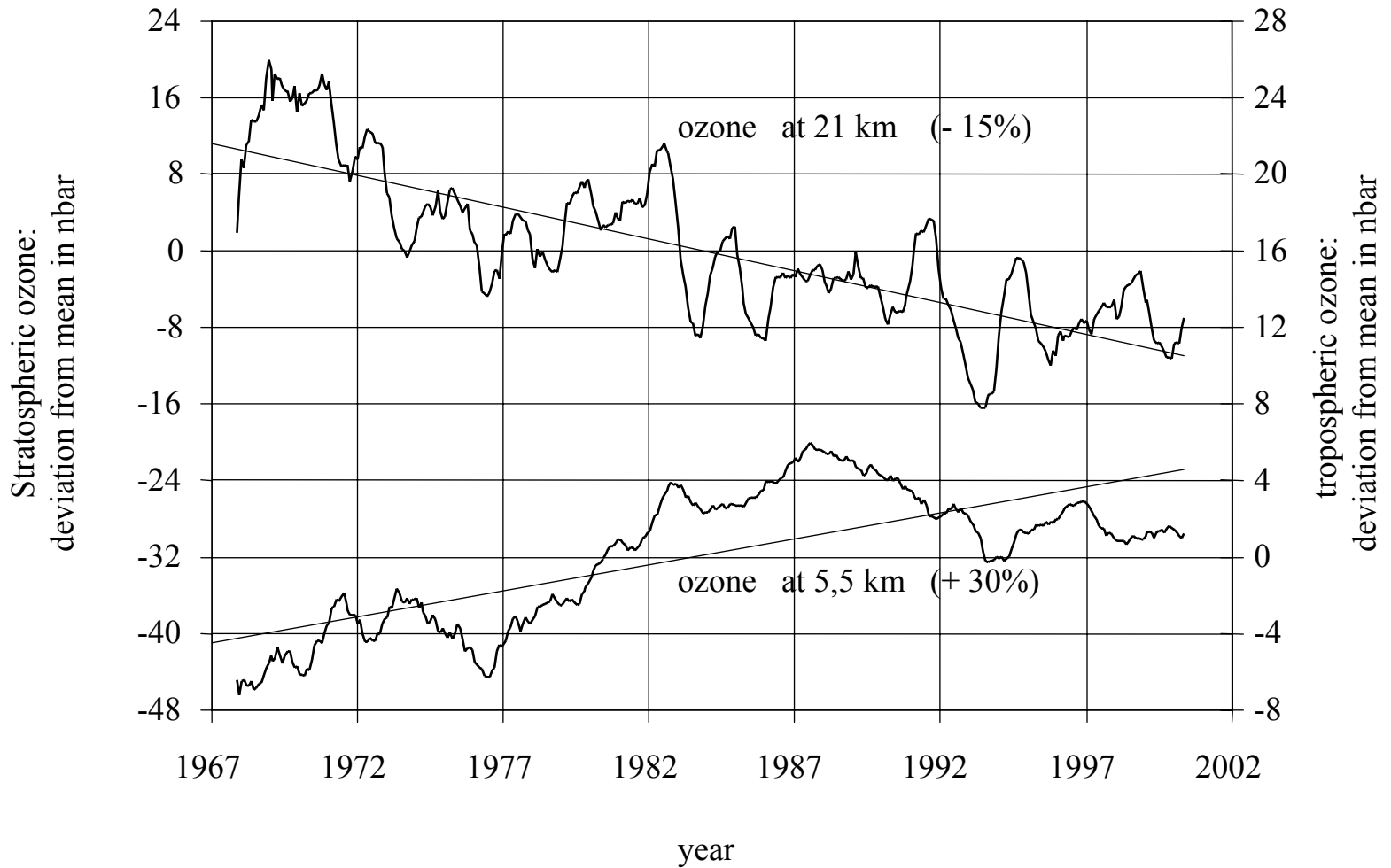
European ozone trend (Marengo curve)



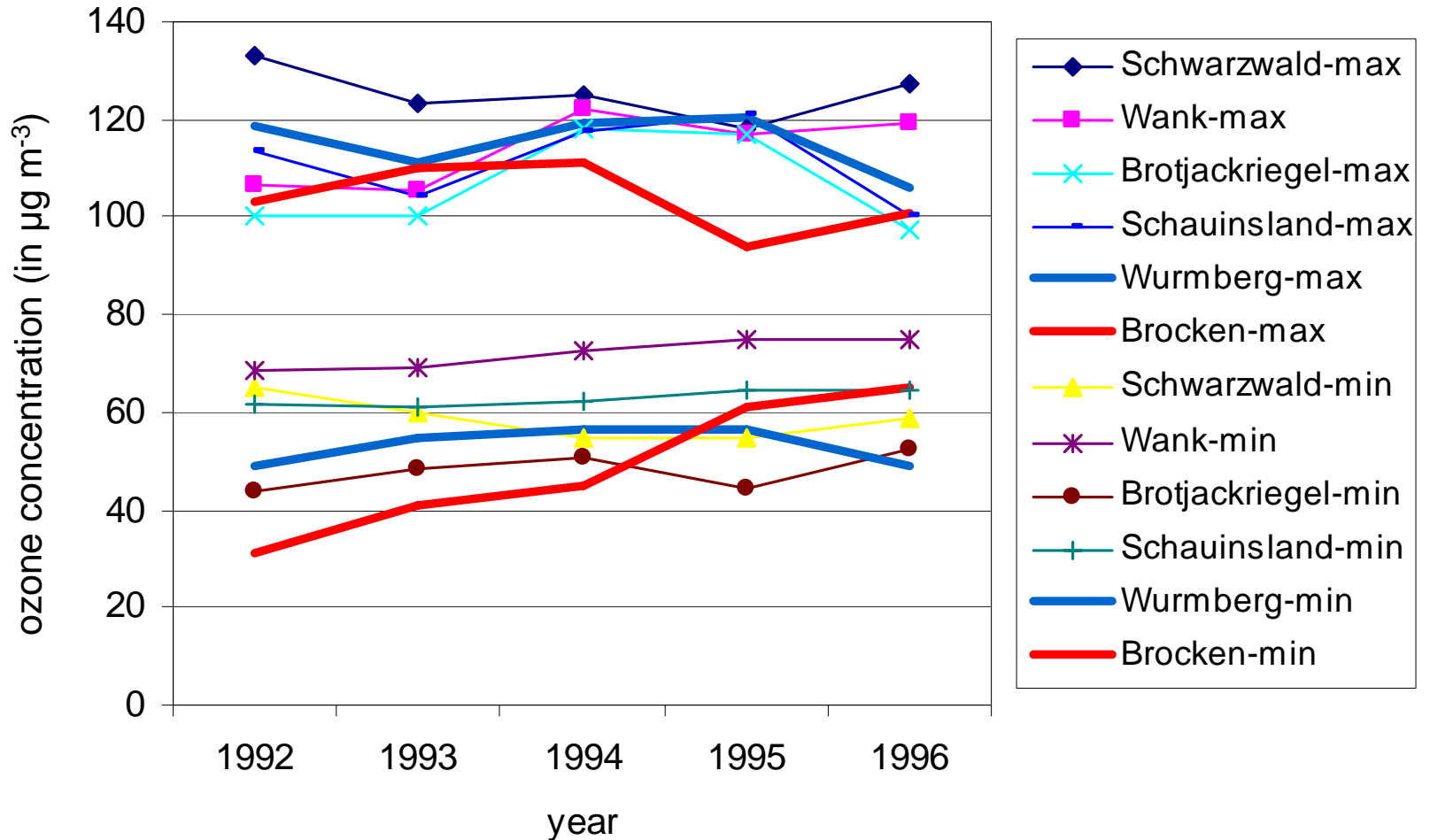
Number of days with exceedance found at least at one station and annual means from all stations in Germany (number of stations: 1990: 201 und 1999: 368); after Beilke 2000



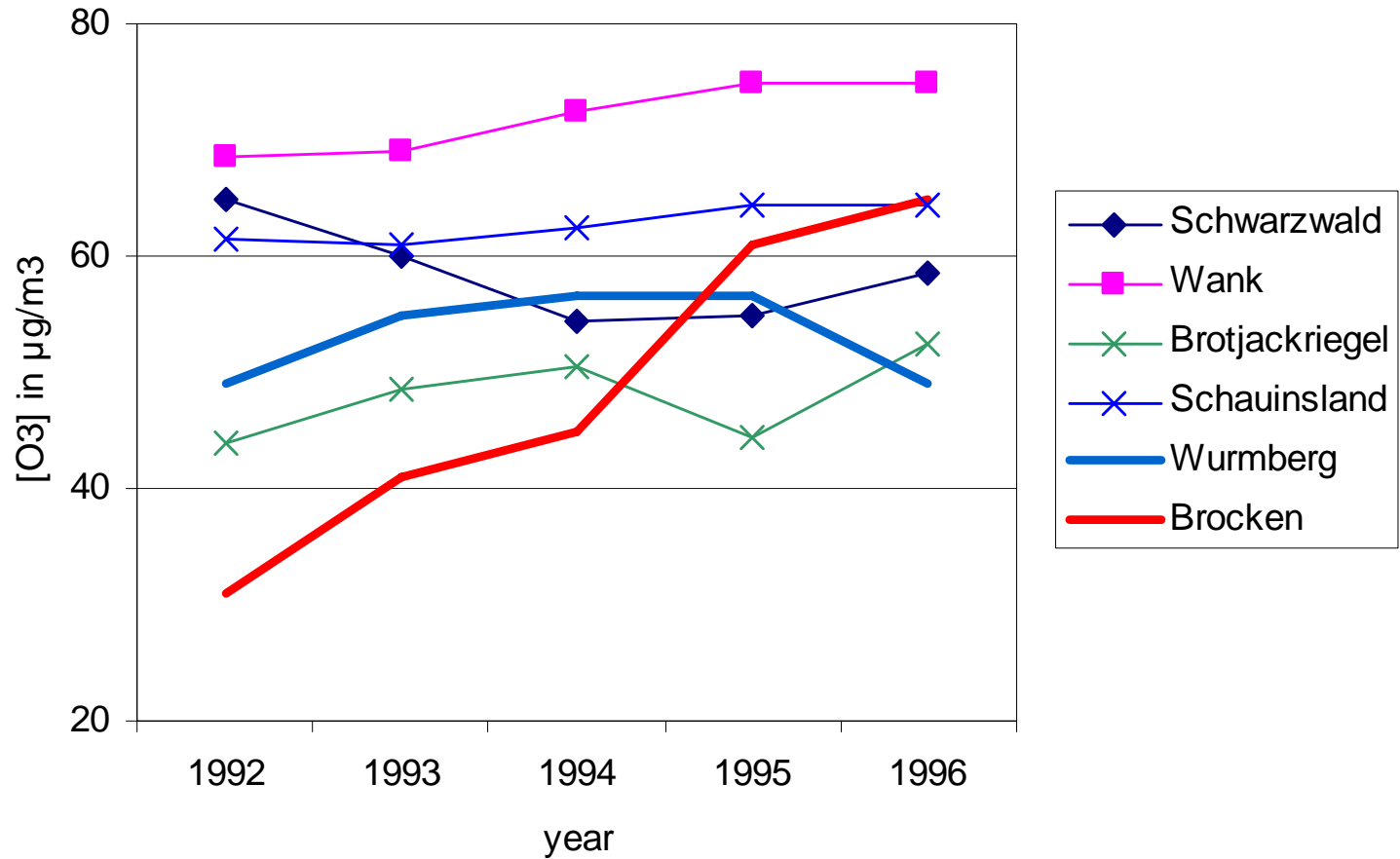
Ozone trend at station Hohenpeißenberg



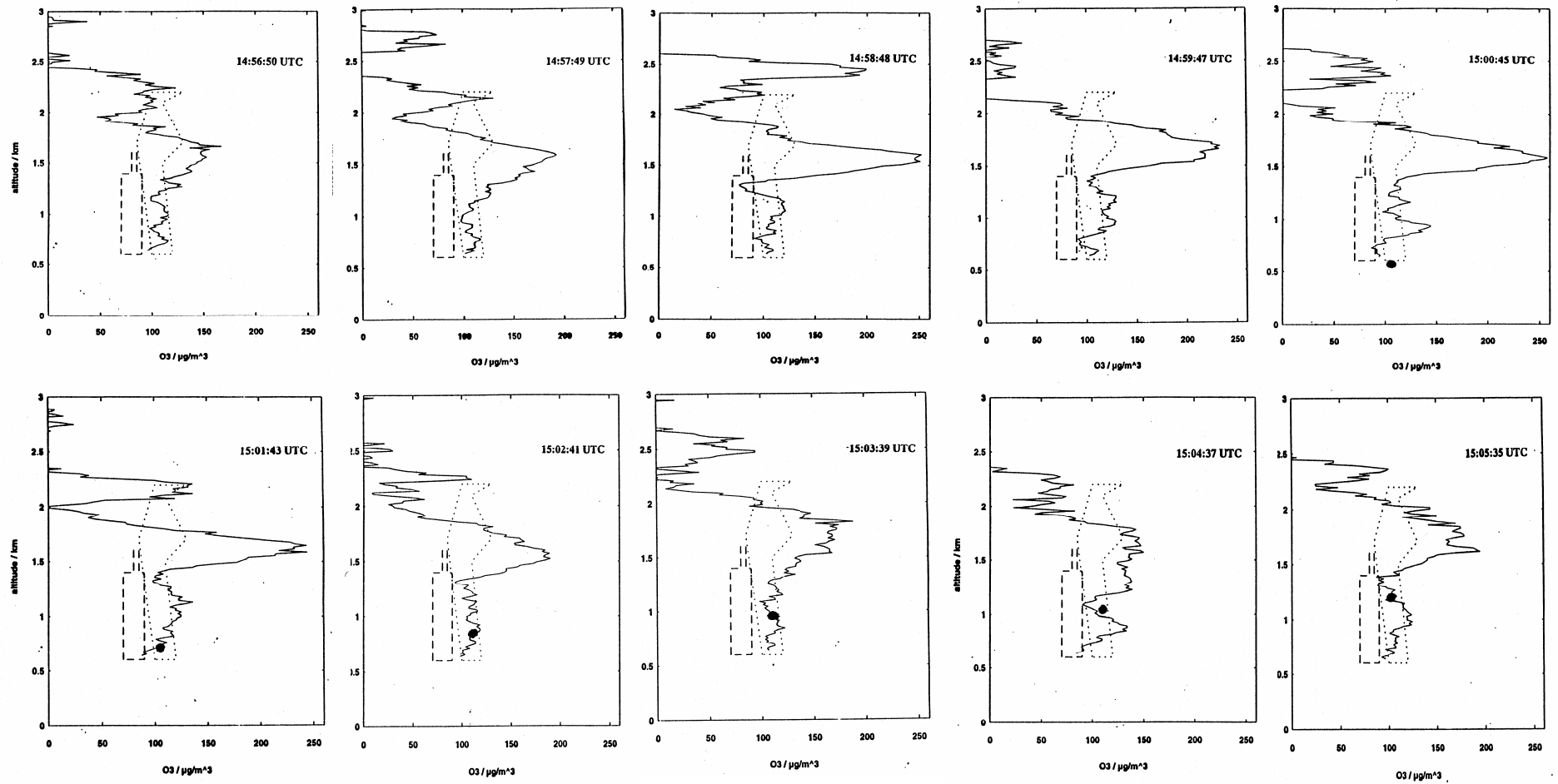
seasonal maximum (summer) and
minimum ozone (winter)



Trend ozone seasonal mean (winter)

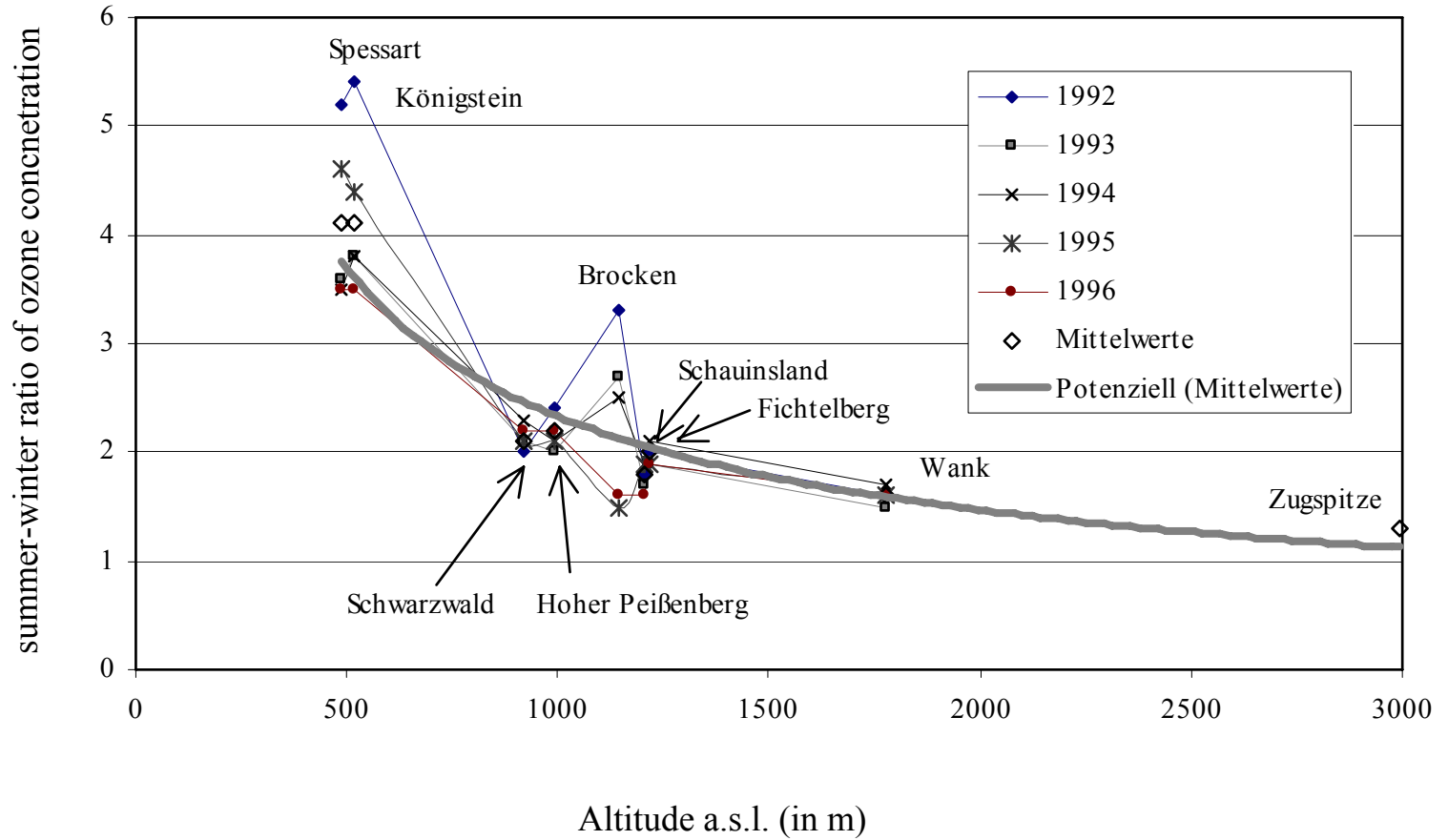


Ozone variation



Ozone profil measurements by BTU mobile lidar Elight M510 downtown Berlin (Alexanderplatz) during an intercomparison campaign with aircraft measurements In 1998 (BERLIOZ experiment)

Altitude and seasonal variation



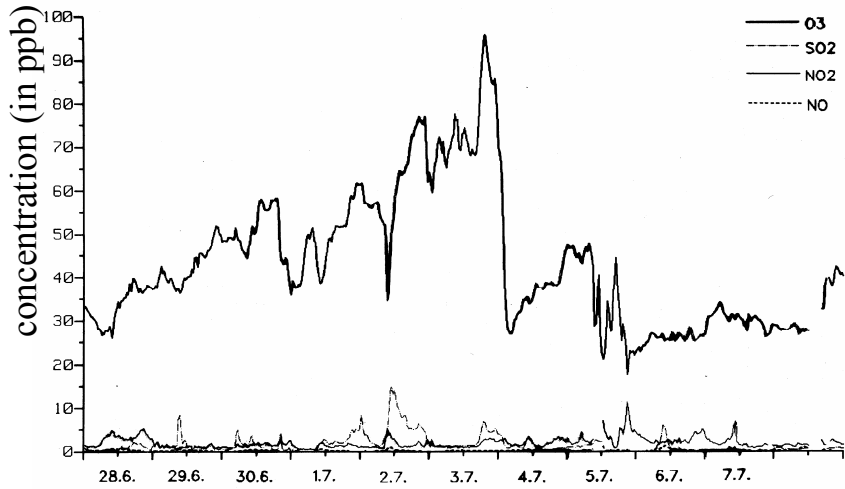
Summer smog

smog = **smoke** + **fog**

It is a meteorological situation when the formation of ozone is being an optimum: high pressure system in summer (sun shine and increased temperatures), low wind, no change of air masses over a few days

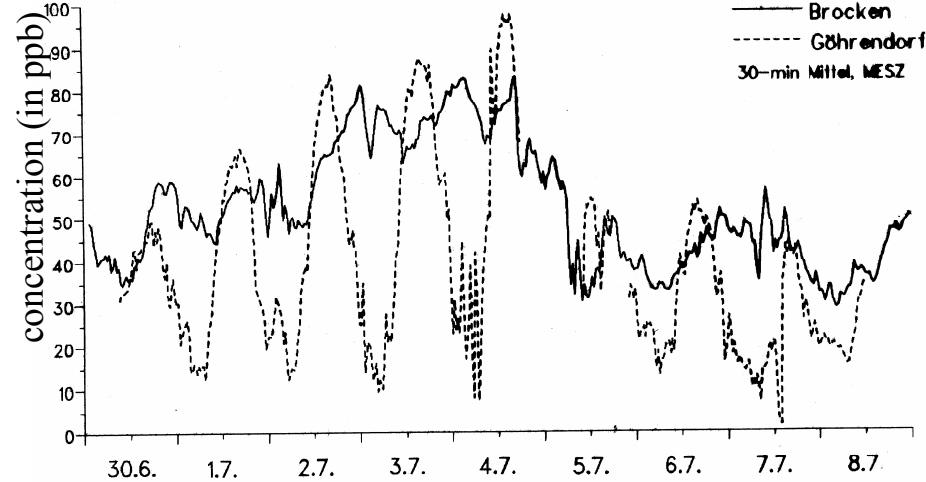
Note: the conditions are quite different from those for the winter smog

Summer smog measurement campaign at Mt. Brocken



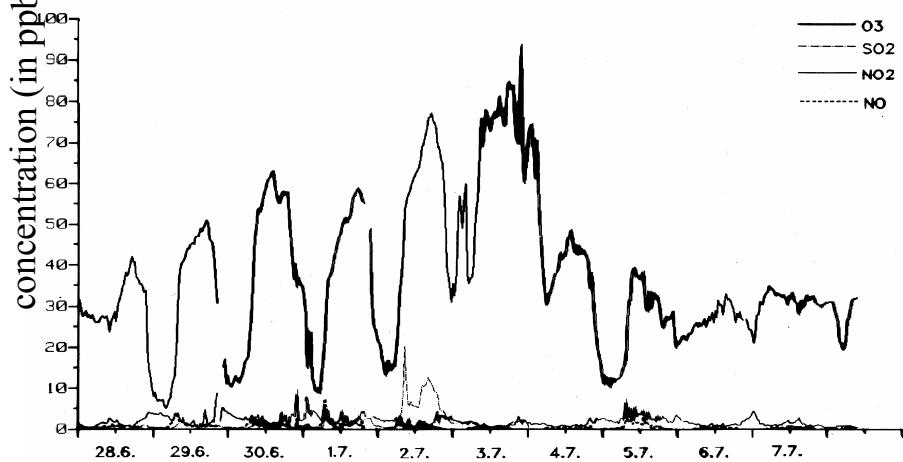
date (June 28 – July 8, 1993)

Summer smog measurement campaign 1994

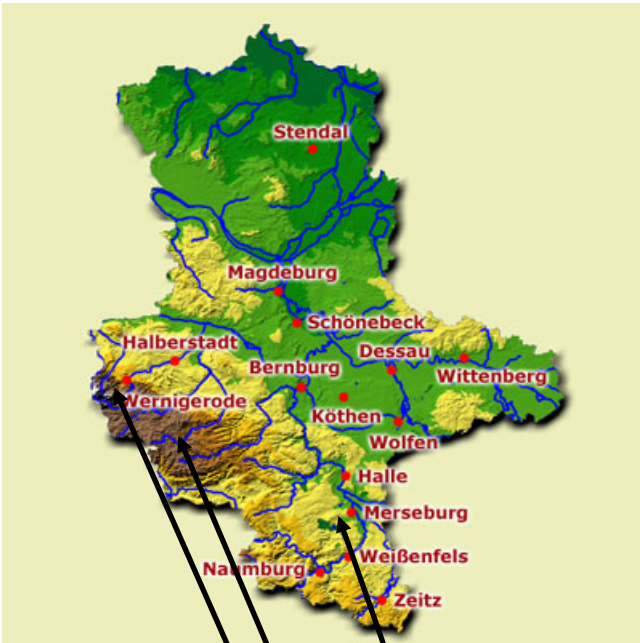


date (June 30 – July 8, 1994)

Summer smog measurement campaign at Harzgerode



date (June 28 – July 8, 1993)



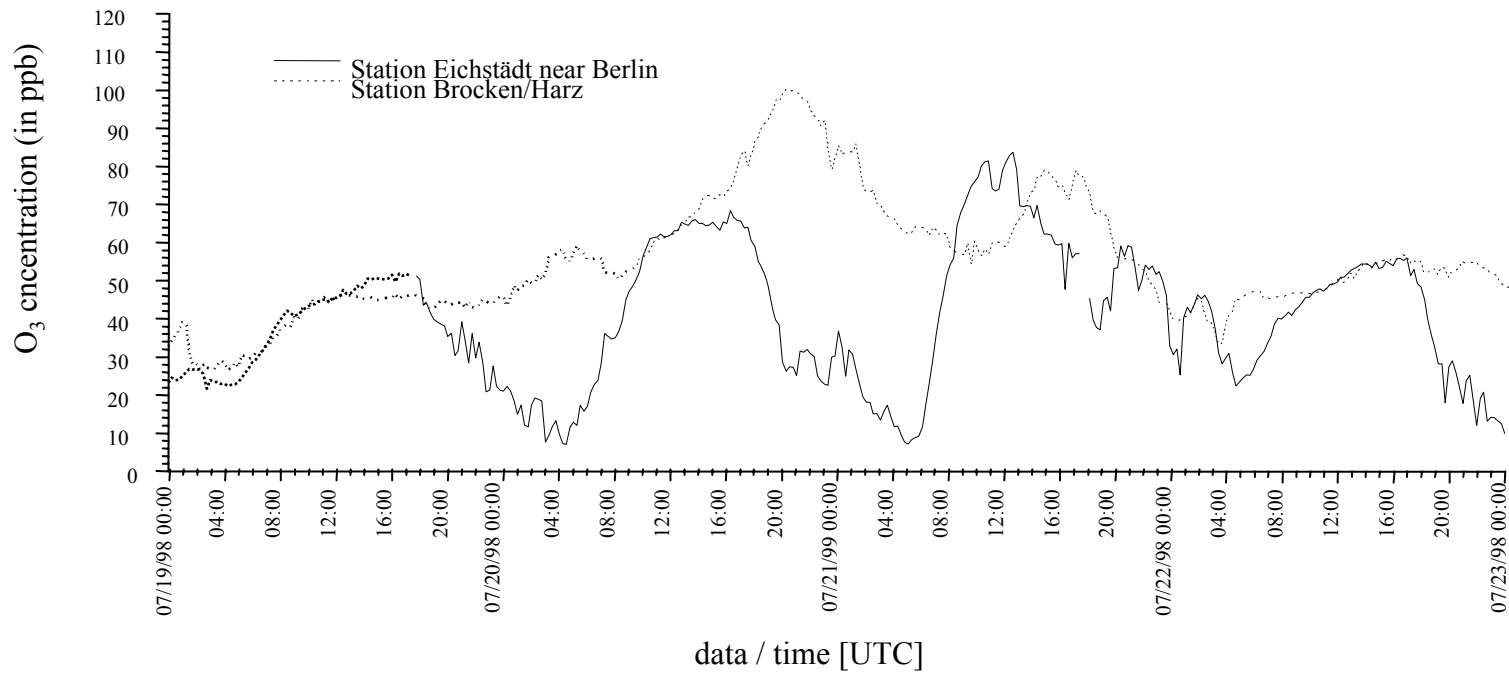
Mt. Brocken station

Harzgerode

Görendorf

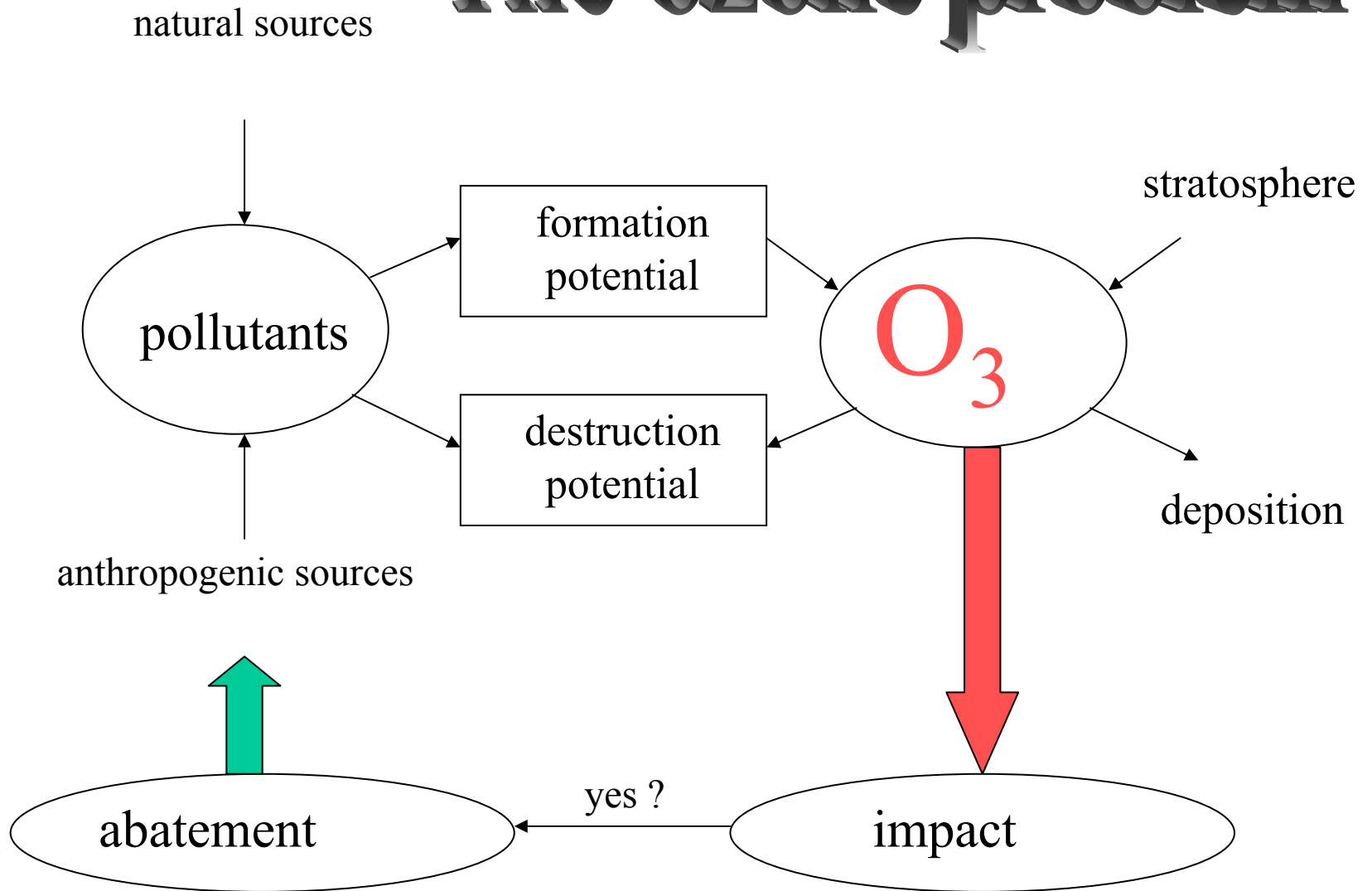


BERLIOZ measurement campaign 1998



The ozone problem

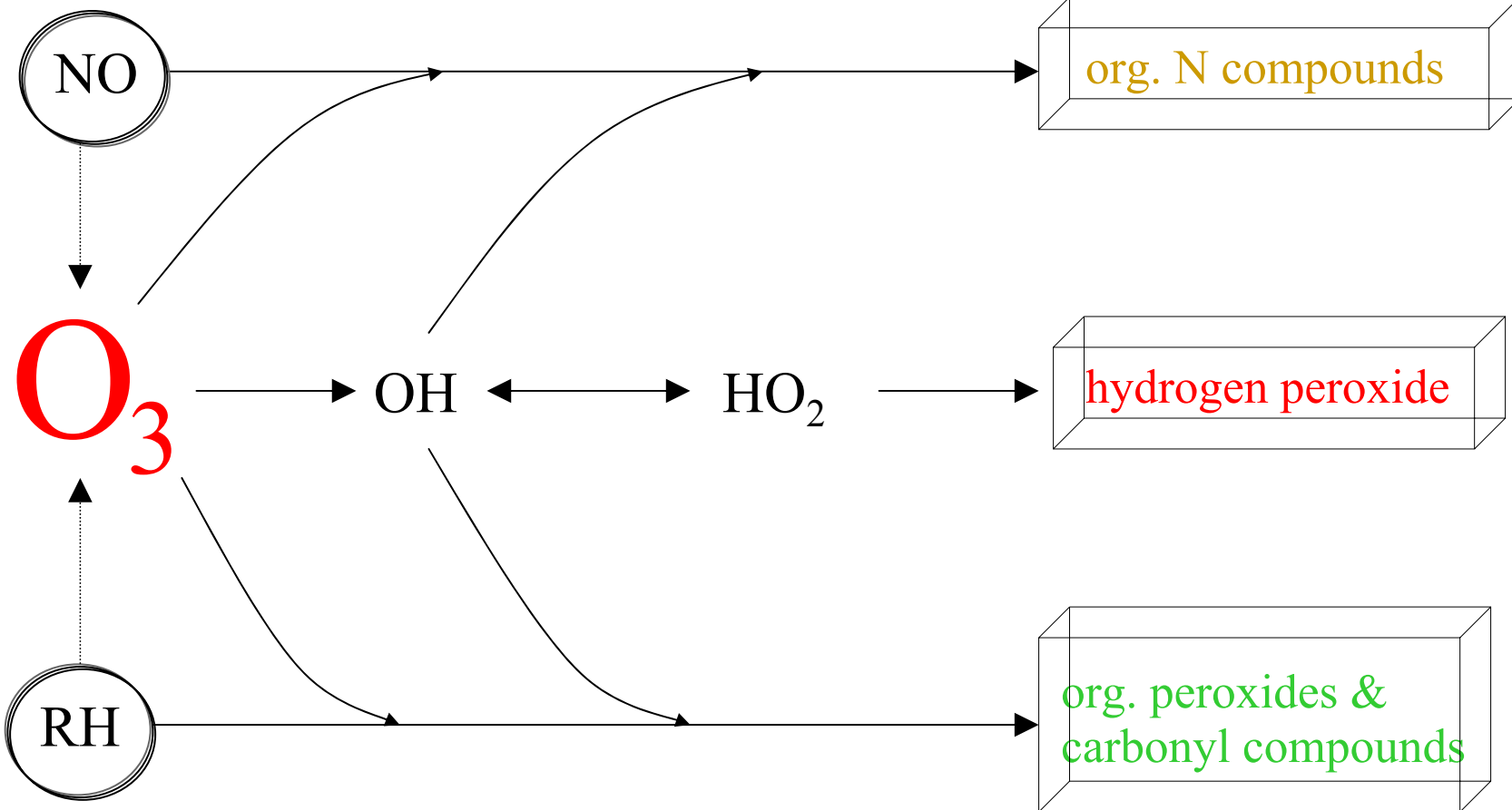
The ozone problem



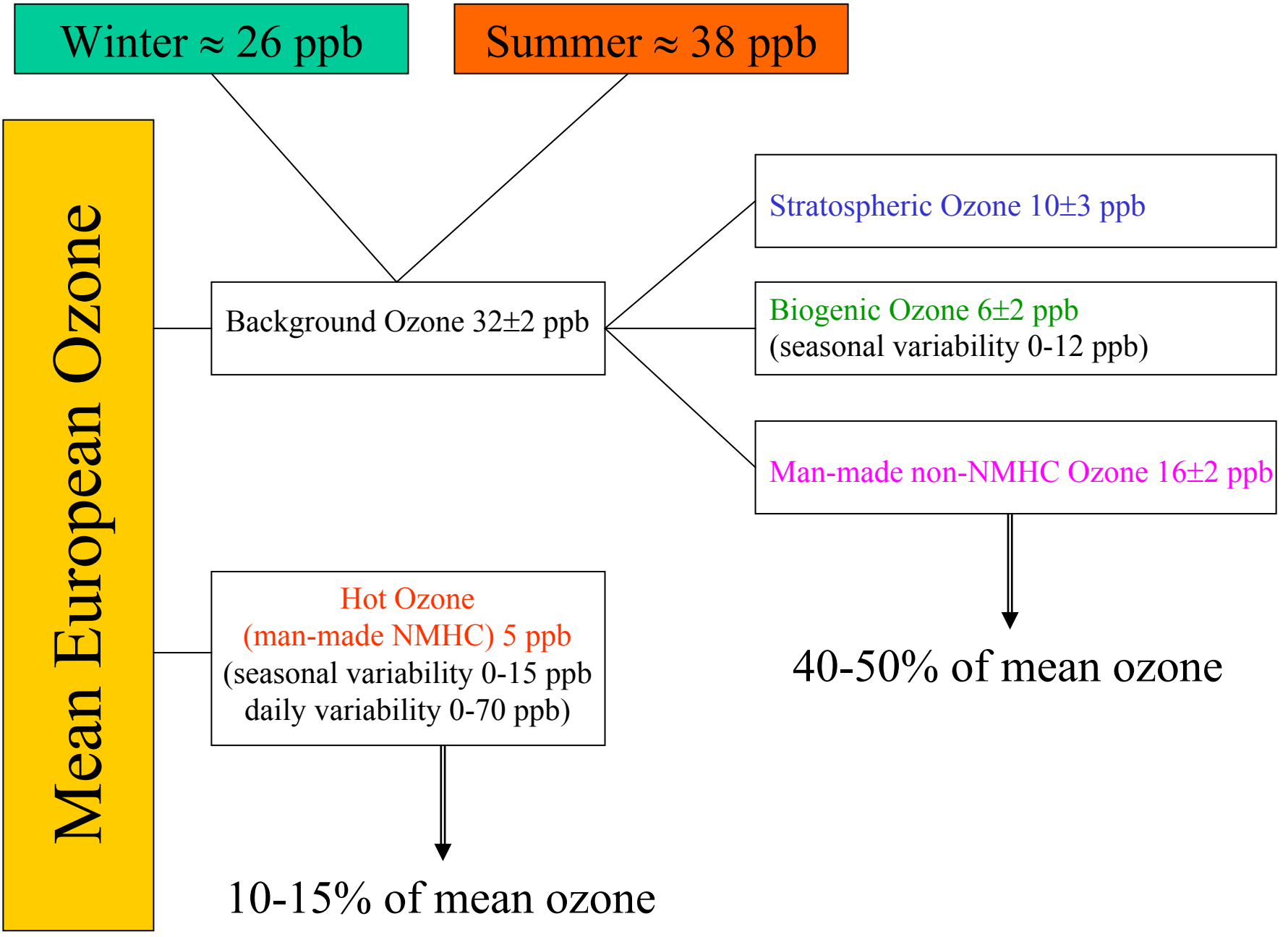
precursors

intermediates

harmful products



„photosmog“ – amplifying of toxicity



Contributions to the mean ozone concentration:



- 10 ppb natural background (photochem. and stratospheric)
- 20-25 photochemical from anthropogenic CH₄ and CO (regional man-made background)
- 30-35 ppb “basic contribution”
- the excess concentration > 30-35 ppb is given from NMVOC (“hot ozone”)



- concentrations > 60 ppb may be observed only during “summersmog“ situations
- since 1998 at no German station have been measured ozone with > 90 ppb
- the “basic concentration” of 30-35 ppb is globally increasing

ozone abatement

- Global models are showing that the ozone concentration will be reduced by only 15% when $[\text{NMVOC}] = 0$
- NMVOC are caused by 50-60% from traffic. 1/3 of the emission is originated during cold start, i.e., a catalytic converter with 100% efficiency may reduce only 2/3 of total NMVOC
- Introduction of catalytical converters among the car fleet did reduce significant the number of episodes with ozone exceedance (summersmog periodes)
- Essential is the reduction of NMHC with $\tau_{\text{OH}} < 3 \text{ d}$ (high ozone formation potential).
- The reduction of CO by using catalytic converters did not show any effect on the mean ozone concentration.
- “Key” for a reduction of the mean O_3 concentration seems the limitation of CH_4 emisisions
- Hence, the „mean ozone problem“ is linked with the “greenhouse problem” and the problem “food for an increasing world population”.



The problem of further increasing mean ozone concentrations can be solved only on global scale and not in a short-term approach.