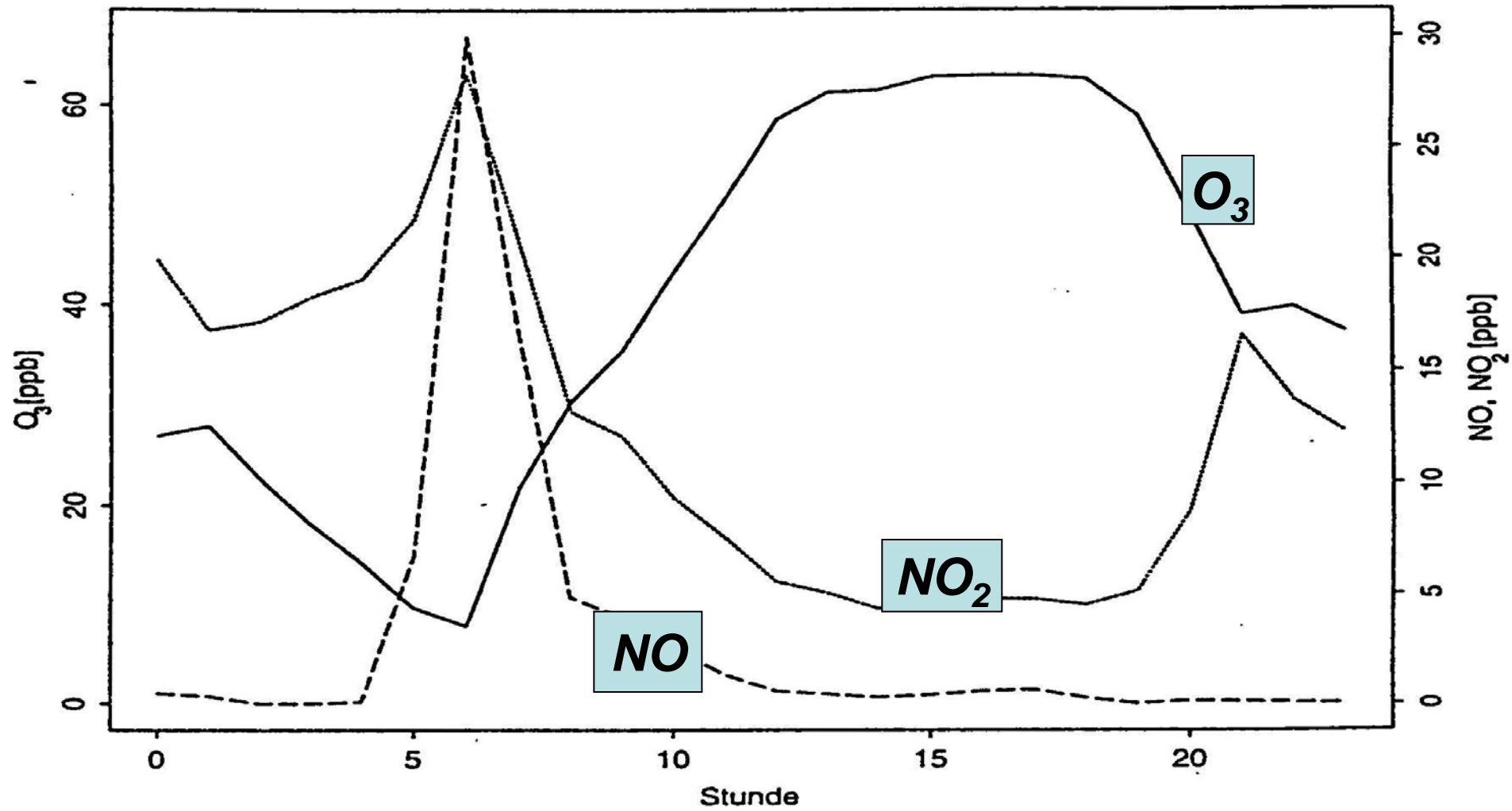


5. Trace gas concentrations in ambient air

Figure 18: Diurnal variation of NO_x and O_3

---: NO ;: NO_2 ; —: O_3



Notes to Fig.18: Diurnal variation at an urban site close to traffic emissions (NABEL station Dübendorf, mean of hourly mean values 18.-12. July, 1996)

- Pollutant concentrations in ambient air are strongly determined by meteorology.
- Fig. 16 shows the diurnal variation typical for polluted sites during high pressure summer condition
- During night an inversion layer develops which inhibits vertical mixing, and the primary air pollutants are emitted from ground into the small layer below the inversion
- Ozone concentrations decrease during night because of the titration reaction of NO and O₃ and surface destruction (compare „Sulfur Dioxide and Oxidations in Atmospheric Droplets and Deposition, chapter 2 on dry deposition). At the site of Fig. 18 NO is steadily released from a close traffic source.
- NO reacts with O₃ yielding an increase in NO₂ concentration starting after midnight (note that traffic emits NO_x dominantly in the form of NO).
- In early morning the close traffic emissions lead to a NO_x maximum and NO increases as well (when O₃ concentrations are very small).
- Later in the morning NO_x decreases while O₃ increases, which is (mainly) caused by the break up of the inversion layer, leading to the dilution of primary pollutants and the mixing down of O₃ from the layer lying above. Thus, chemical transformations are less important compared to mixing in the late morning.
- Around 20h the inversion layer is formed again and O₃ destruction by NO starts again.
- The layer above the nocturnal inversion layer is called **reservoir layer**
- The reservoir layer (also being part of the planetary boundary layer) is decoupled from the inversion. O₃ is not decomposed in the residual layer because NO emitted from surface is trapped below the inversion and no dry deposition occurs.
- Ozone (and other photooxidants) can be transported in the residual layer over large distance during night in summer smog episodes.
- Vertical mixing between the planetary boundary layer efficiently occurs during advective weather conditions such as passages of fronts and during convective conditions in summer.

Figure 19: meteorological condition for winter smog or London Smog (CH)



<http://home.intergga.ch/Hannes/i/Nebelmeer%20Burgstock%20rechts%20%20Pilatus.jpg>

Notes to Figure 19: „Winter smog“

- During high pressure situations in the cold season (winter or fall) meteorological conditions leading to temperature inversions can extend in time over several days. During such condition often high altitude inversions form which can lead to fog formation extending over the entire Swiss plateau.
- During such conditions primary pollutants emitted from the surface can accumulate because of lack of efficient vertical mixing.
- Primary pollutants which can accumulate during winter smog episodes are: SO_2 , NO_x (NO_2), particulates (PM10)
- Winter smog episodes terminate by changes in weather condition, such as a frontal passage, by which the accumulated primary pollutants are diluted into the free troposphere
- The severity of winter smog air pollution episode depends on the strength of the emissions and the duration of the high pressure condition.

Figure 20: Particulate concentrations during the first part of 2006 measured in Zurich and Basel (Switzerland) from NABEL

Stadt, Park: Zürich Feinstaub (PM10)

Stundenmittelwerte vom 01.01.2006 bis 30.03.2006



Agglomeration: Basel-Binningen Feinstaub (PM10)

Stundenmittelwerte vom 01.01.2006 bis 30.03.2006



Notes to Figure 20

- In winter 2006 very high primary air pollutant concentrations were measured in the Swiss plateau.
- Particulate concentrations exceeded by as much as a factor 4 the limiting value of the Swiss legislation (see Fig. 21).
- The exceptionally high concentrations occurred because of the long durations of the high pressure condition in early 2006.
- However, particulate concentrations larger than the limiting values occur every winter

4.6. Air quality thresholds

Figure 21: Wichtige Grenzwerte der Schweizerischen Luftreinhalteverordnung (in $\mu\text{g}/\text{m}^3$)

Air pollutant	PM ₁₀ ¹⁾	SO ₂	NO ₂	O ₃	(CO)
Jahresmittelwert	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

Fig. 22: Air quality guidelines of WHO

(World Health Organization) (WHO, 2006), in $\mu\text{g}/\text{m}^3$

$\text{PM}_{2.5}$, PM_{10} : particulate matter with aerodynamic diameter of less than 2.5.,
resp. 10 μm

Air pollutant	annual mean	24 h mean	8 hour mean	1 hour mean	10 min. mean
$\text{PM}_{2.5}$	10	25			
PM_{10}	20	50			
NO_2	40			200	
SO_2		20			500
O_3			100		

Notes to Fig. 21 and 22

- (National) air pollutant legislation define limit values for air quality.
- The Swiss standards are based on effects on human health and biota. Depending on the effects of the pollutants different criteria for the limit values are defined.
- In the Swiss legislation (Fig. 21) maximal values for annual means are defined for particulates (PM₁₀, meaning particulates with aerodynamical diameters of less than 10 μm), SO₂ and NO₂; values that are not allowed to exceed more than once a year (for most of the listed compounds), and maximal values for 95 percentiles (SO₂ and NO₂) and maximal values for 98 percentile (for O₃)
- The limit values are different for different countries
- WHO values are only concerning human health (Fig. 22) and they are „guidelines“ for national legislation

4.7. Anthropogenic emissions

Fig. 23: 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 (CLRTAP)

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

SO₂: - **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

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

The 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (1999) (see next page)

CORINAIR: COoRdination of INformation on AIR emissions

EMEP/CORINAIR Atmospheric Emission Inventory Guide book

Activity of CLRTAP: The Task Force on Hemispheric Transport of Air Pollution (TFHTAP; www.htap.org)

Fig. 24: The 1999 Gothenburg Protocol

http://www.unece.org/env/lrtap/multi_h1.htm

The Executive Body adopted the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone in Gothenburg (Sweden) on 30 November 1999. The Protocol sets emission ceilings for 2010 for four pollutants: sulphur, NO_x, VOCs and ammonia. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options. Parties whose emissions have a more severe environmental or health impact and whose emissions are relatively cheap to reduce will have to make the biggest cuts. Once the Protocol is fully implemented, Europe's sulphur emissions should be cut by at least 63%, its NO_x emissions by 41%, its VOC emissions by 40% and its ammonia emissions by 17% compared to 1990.

The Protocol also sets tight limit values for specific emission sources (e.g. combustion plant, electricity production, dry cleaning, cars and lorries) and requires best available techniques to be used to keep emissions down. VOC emissions from such products as paints or aerosols will also have to be cut. Finally, farmers will have to take specific measures to control ammonia emissions. Guidance documents adopted together with the Protocol provide a wide range of abatement techniques and economic instruments for the reduction of emissions in the relevant sectors, including transport.

It has been estimated that once the Protocol is implemented, the area in Europe with excessive levels of acidification will shrink from 93 million hectares in 1990 to 15 million hectares. That with excessive levels of eutrophication will fall from 165 million hectares in 1990 to 108 million hectares. The number of days with excessive ozone levels will be halved. Consequently, it is estimated that life-years lost as a result of the chronic effects of ozone exposure will be about 2,300,000 lower in 2010 than in 1990, and there will be approximately 47,500 fewer premature deaths resulting from ozone and particulate matter in the air. The exposure of vegetation to excessive ozone levels will be 44% down on 1990.

Notes to Fig. 23 and 24

- (International) discussions about air pollution started at the beginning of the 1970s. SO₂ pollution (see Section 3 in „Sulfur Dioxide and Oxidations in Atmospheric Droplets and Deposition) was the first subject of these discussions.
- For Europe a network of air pollution monitoring (EMEP) was established in 1976 which is still in operation focusing on air pollutants at rural sites in order to study the transport of air pollutants between different nations.
- In 1979 the Geneva convention on Long-Range Transboundary Air pollution was signed, which led to several protocols in which the countries agree to decrease emissions of some compounds within a defined period.
- In 1999 Gothenburg Protocoll was signed, aiming to abate Acidification, Eutrophication and Ground-level Ozone in a holistic way
- Protocols were signed by countries from Europe, USA, Canada and some others.
- CORINAIR provides guidelines for harmonized emission inventories prepared for the protocols to document emission changes.

Fig. 25: Anthropogenic emission inventories: w,w,w,w

Emission rate = EF x activity

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

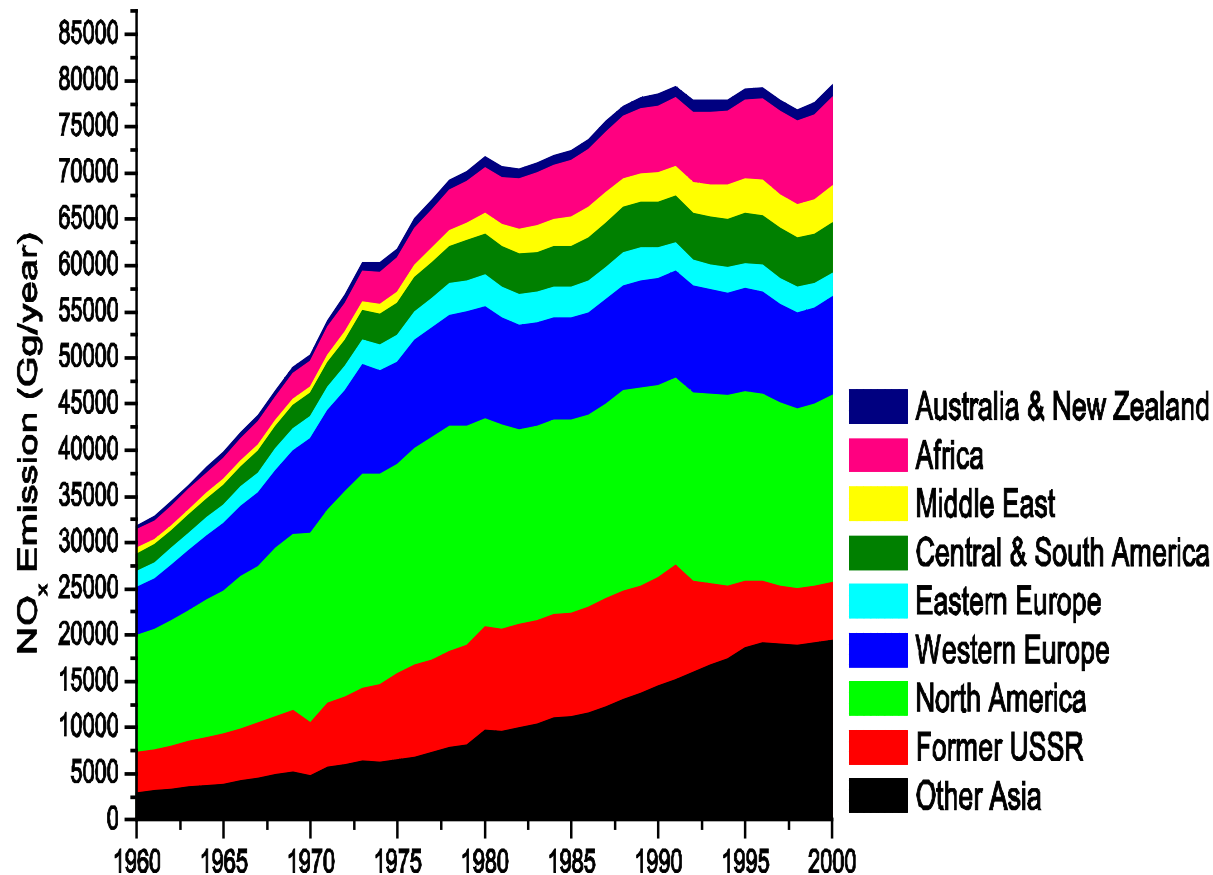
EF: e.g. emission of NO_x per driven kilometer

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

Notes to Fig. 25

- To study air pollution and to design air pollution abatement strategies the strengths of dominant emission sources need to be adequately known.
- Any chemical simulation requires the knowledge of the emission sources, (often also including biogenic source strengths).
- Anthropogenic emissions are usually quantified by separating the quantitative description of an **activity** leading to the emission of specific compound (e.g. road traffic) and the emission factor (**EF**).
- The EF can depend on many variables. For road traffic emissions they include: Engine type (gasoline vs. diesel), used technology (e.g. catalytic convertes in gasoline engines), engine size, driving condition (acceleration, etc.), road gradient, etc.
- For every emission inventory the information of the four w's needs to be specified.
- Emission inventories of different sophistication have been constructed, depending on the available information and the specific problem to be addressed.

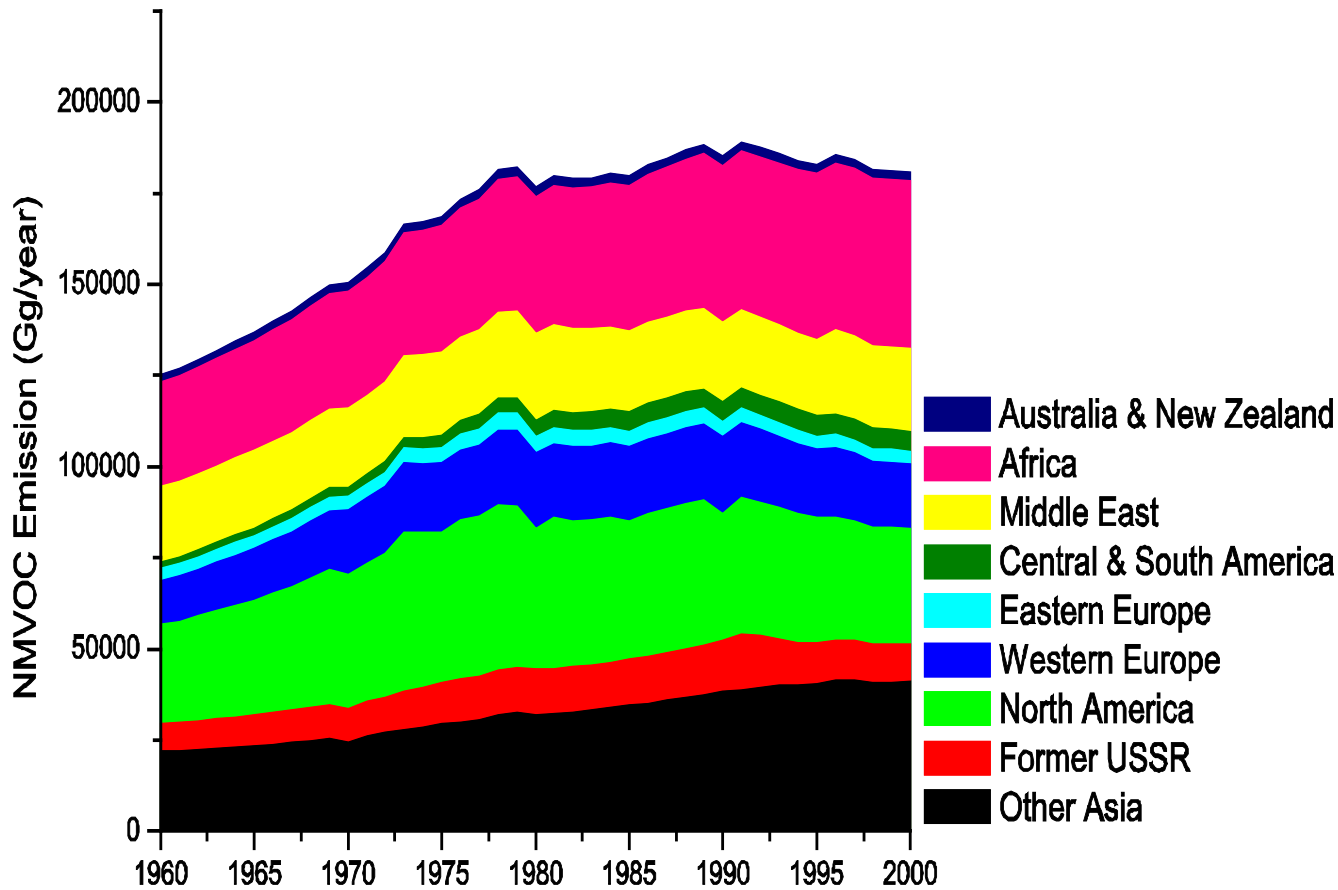
Fig. 26: Fossil fuel related groundbased NO_x emissions from continents



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

Em = Ac x Technology Penetration Factor x EF
(TPF: only one for OECD and non-OECD countries)

Fig. 27: Fossil fuel related ground-based VOC-emissions (from TEAM) from continents



Notes I to Fig. 26 and 27

- The team model is an emission model developed to calculate global emissions and their longterm changes.
- The fossil fuel related ground based emissions from continents are calculated from the use of fossil fuels reported to the International Energy Agency (IAEA). The EF's depend on the used technology (e.g. use of catalytic converters in road traffic). For road traffic different EFs were (only) used for OECD and other countries. The temporal introduction of this technology was modeled by a „technology penetration factor“.
- The long-term evolution of global fossil fuel related emissions from continents show a similar behaviour for NO_x and VOC emissions.
- In the decades following World War II the anthropogenic emissions strongly increased, mainly in the industrialized countries, because of the exceptional economic growth.

Notes II to Fig. 26 and 27

- Around the end of the 1970s anthropogenic emissions in the industrialized countries started to stabilize or to decrease because of the introduction of new technologies introduced to reduce air pollution.

Emissions during the 1990s:

- According to the team model NO_x and VOC fuel related continental emissions stabilized in the 1990s on global scale.
- During the 1990s the emissions decreased in the industrialized countries because of air pollution legislation.
- During the 1990s the emissions decreased because of economic recession in Russia and the countries which belonged to the USSR in the earlier time.
- Large increases were reported from developing countries, particularly in Asia such as China, compensating the decrease of emission in other parts of the world.
- Note, that the determination and evaluation of reliable emission inventories is a challenging task.

4.8. Long-term changes in tropospheric ozone

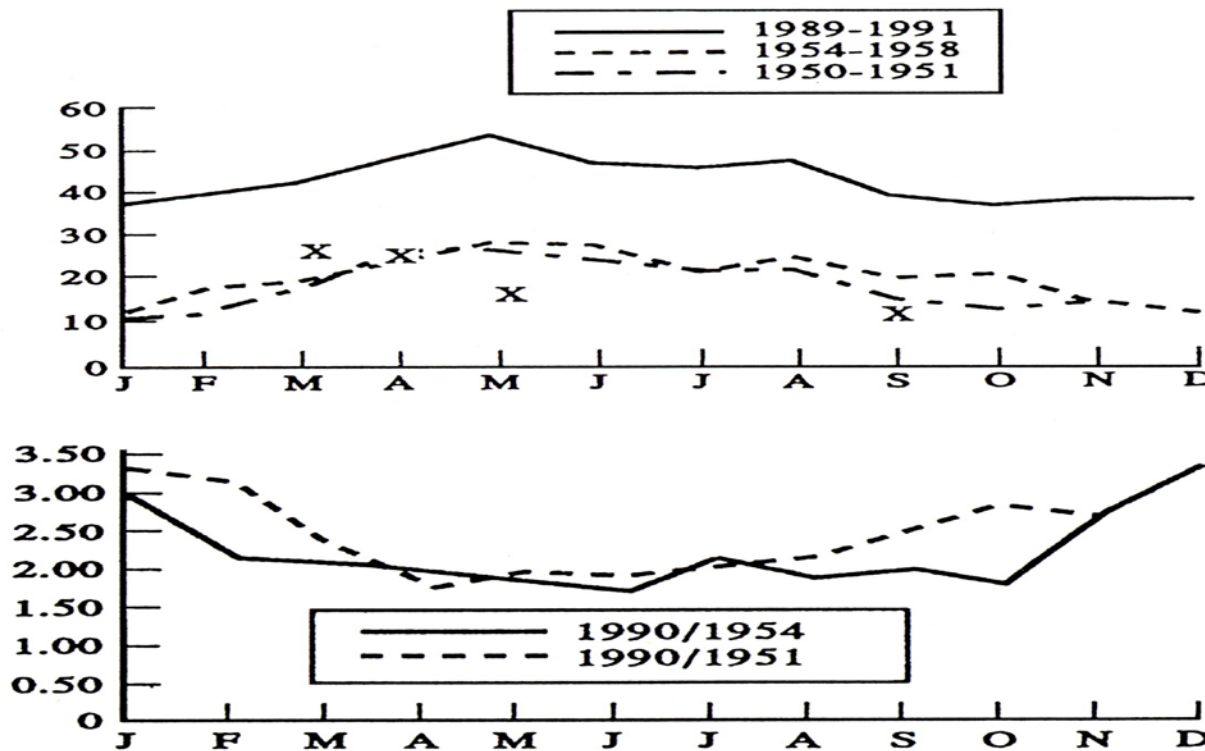


Fig. 28:
(Surface)
ozone
concentrations
from Arosa
(Staehelin et al.,
1994)

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.)

**Fig.
29**

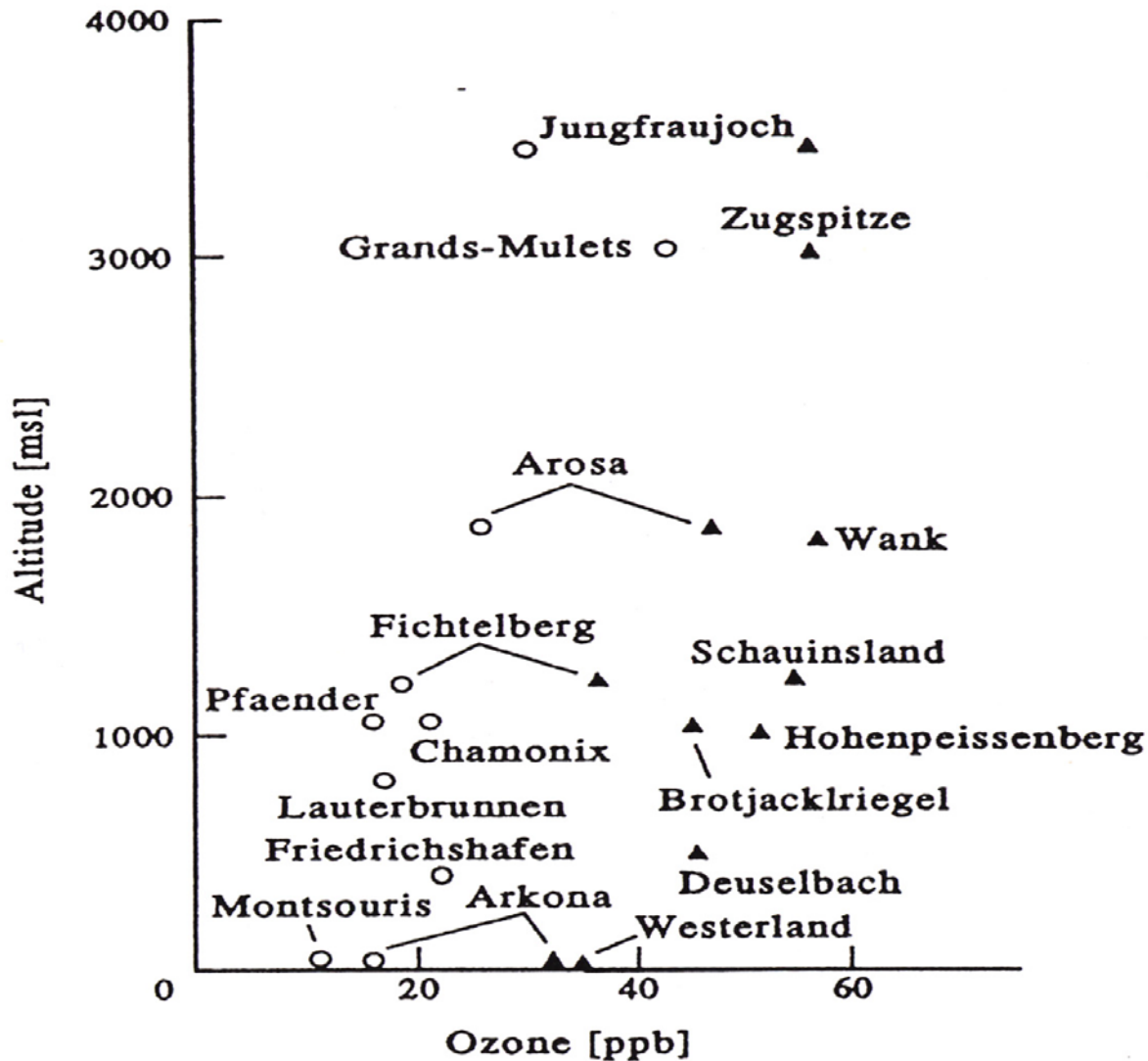
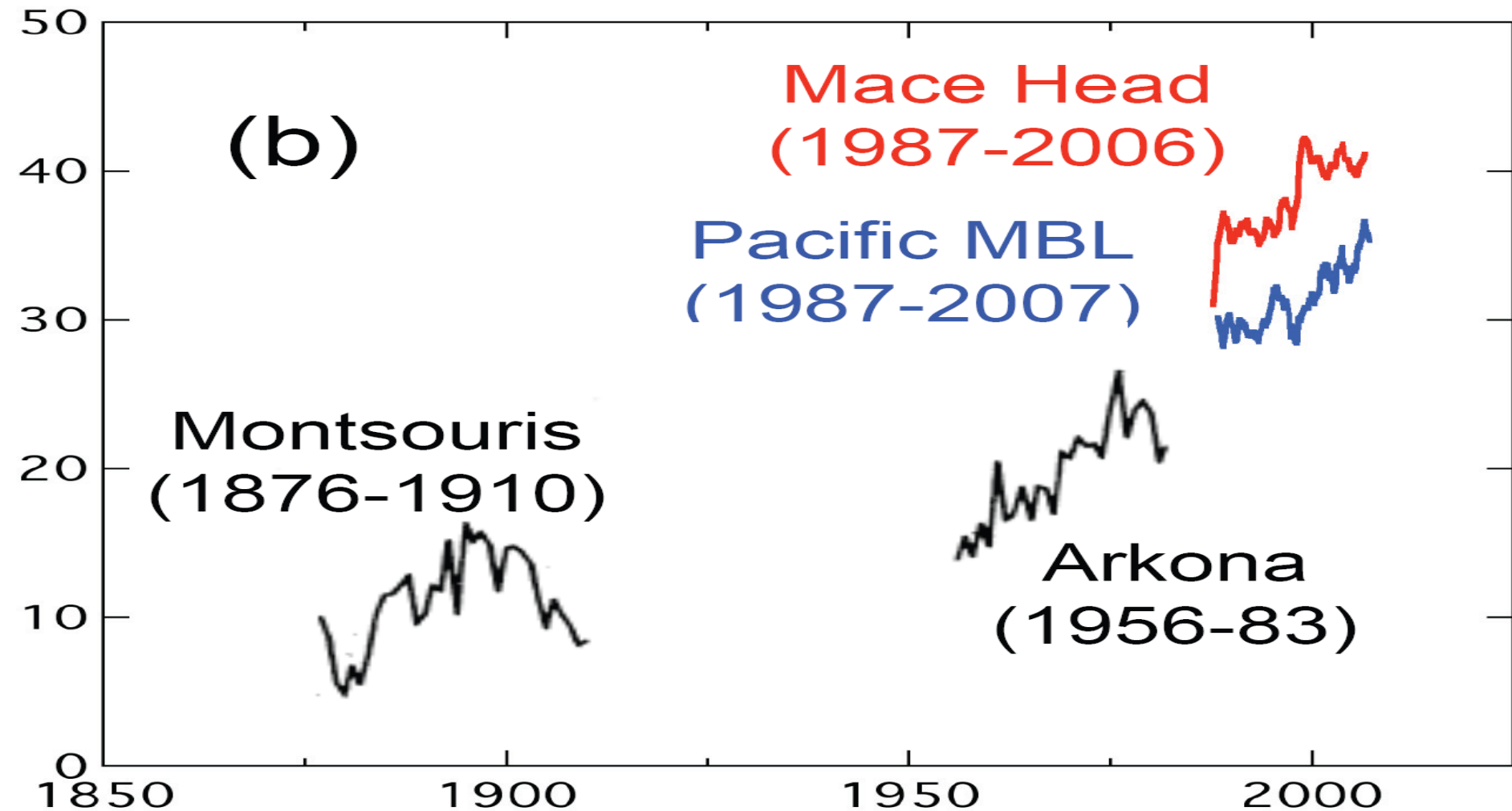


FIGURE 8 Historical (circles) and recent (triangles) surface ozone concentrations of August/September from different locations in Europe as a function of altitude. The historical measurements from the different sites also include measurements collected over short periods, whereas the recent data of 1988–1991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

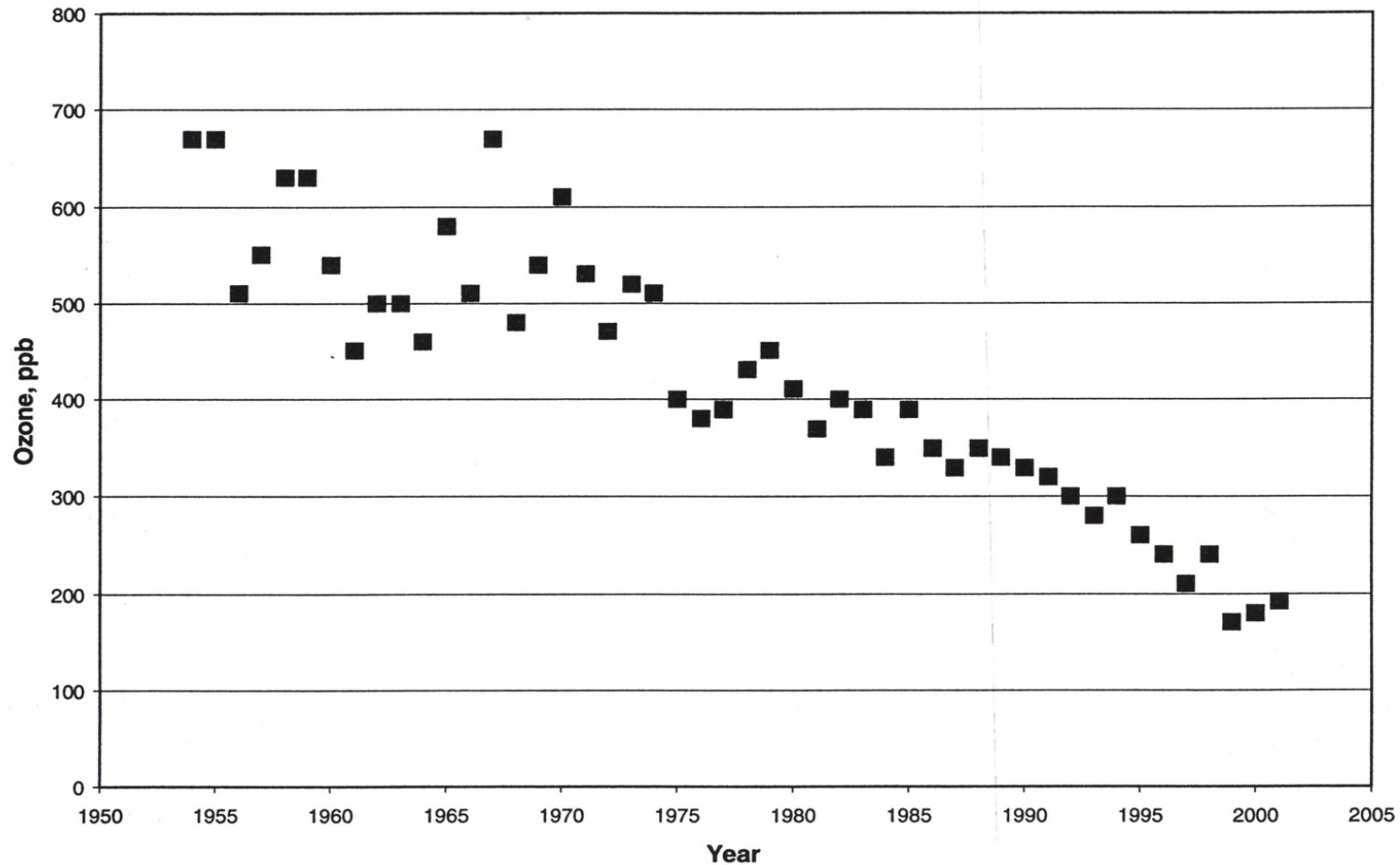
Fig. 30: Long-term ozone changes in the (marine) boundary layer (Parrish et al., 2009)



Notes to Fig. 28 and 30

- Only few reliable ozone measurements from the time before around 1960 exist.
- Schönbein, the discoverer of ozone, developed a method which enabled him to show (already in 1842), that O_3 is present in ambient air. However, this type of method is (quantitatively) not reliable and therefore measurements with „Schönbein“ papers should be ignored for trend analysis.
- Many O_3 measurements with a reliable chemical method were made at the Alpine resort village Arosa in the 1950s. Single measurements of O_3 close to Earth's surface were performed by (open path) spectroscopy in the 1930s. At the same site O_3 measurements were repeated in 1989-1991 showing an increase by more than a factor 2 (see Fig. 28).
- Ozone was measured in the time before the end of the 1950s in selected campaigns in Europe north of the Alps. They are plotted in Fig. 29 as function of elevation confirming that ozone increased by more than a factor of 2 all over Europe.
- The large increase in background ozone between the late 1950s and the early 1990s is most probably caused by the very large increase in ozone precursor emissions (see Fig. 26 and 27) in the decades following World War II.
- Ozone changes in the marine boundary layer in the West coast of North America and Mace Head (West coast of Ireland) show a similar increase during the 1990s (Fig. 30) and a very large increase compared to measurements performed 1867-1910 at Montsouris, which is close to Paris (Volz and Kley, 1988), .
- The very low values of the Montsouris series are not confirmed by other (reliable) methods. SO_2 is an interference of the chemical method used at Montsouris and SO_2 concentrations were most likely large in Paris during this period (comp. „Sulfur Dioxide and Oxidations in Atmospheric Droplets and Deposition“). Volz, A. and Kley, (1988), tried to remove such air masses by making use of local wind direction measurements of the observatory, but it is difficult to judge whether all SO_2 polluted air could be removed completely by this procedure.

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



**Fig.
31**

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).

Notes to Fig. 31

- In the Los Angeles area surface ozone concentrations were extremely high in the 1950s and 1960s (exceeding the limiting values of the Swiss legislation by more than a factor of 10).
- In this area the ozone precursor emissions very strongly decreased in the last decades.
- Ozone maxima decreased by more than a factor of 3 in the decades after the early 1970s.
- Nevertheless, ozone maxima (with 200 ppb) are still very high.

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