Air Pollution Control and Air Chemistry:

Atmospheric Particulate Matter

7th lecture

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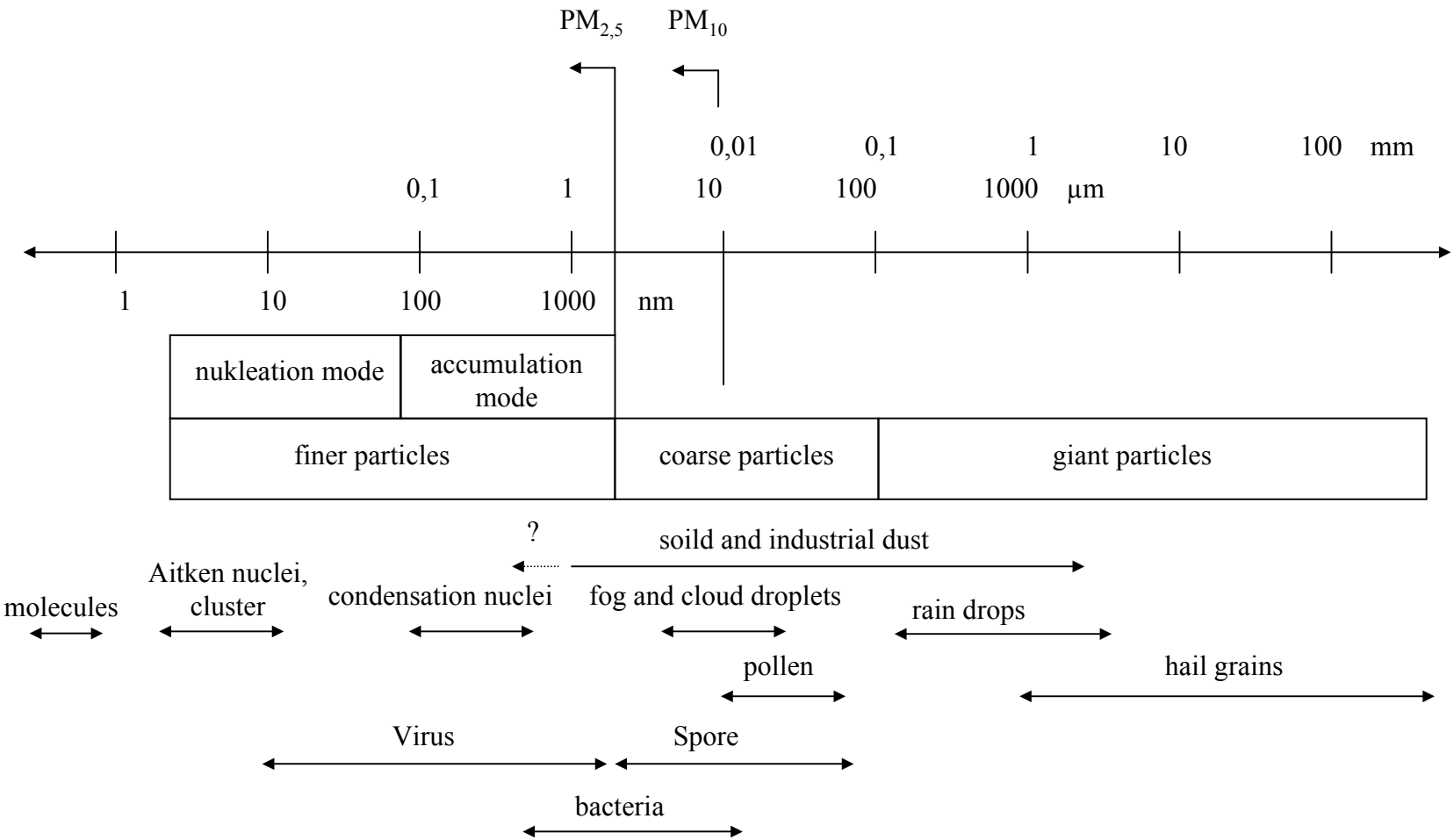
What PM is it? = Dust….

is a mixture of solid particles in the size range from 5 nm until 100 µm with different chemical (and biological) composition, different origin and fate, different structure (crystallography) and different life time. Each particle may be unique, however, one can classify different groups of PM.

Different meanings: particulate matter (PM)
suspended particulate matter (SPM)
dust

However, it is all the „same“: atmospheric aerosol

- Particle size range from few nm up to hundreds of µm.
- Very different chemical composition.
- Different forms and shapes.


PM2,5
PM10
0,01
0,1
1
10
100
mm
0,1
1
10
100
1000
µm
1
10
100
1000
nm
nukleation mode
accumulation mode
finer particles
coarse particles
giant particles
?
soild and industrial dust
molecules
Aitken nuclei, cluster
condensation nuclei
fog and cloud droplets
rain drops
pollen
hail grains
Virus
Spore
bacteria

Size Ranges and termination of atmospheric aerosol

radius range (in μm)	German meaning after Junge (1963)	english meaning after Whitby und Sverdrup (1973)	other (german) meanings
< 0,01	ultrafeine Partikeln	ultrafine mode	Cluster, Embryo
0,01-0,1	Aitkenkerne	nucleation mode	-
0,1-1	große Partikeln	accumulation mode	Feinststaub
>1	Riesenpartikeln	coarse mode	Staub
>5	-	-	Sedimentationsstaub

Why we are interested in PM studies?

1. Hygienic aspects (health, pollution)
2. Atmospheric physics (climate)
3. Atmospheric chemistry (multiphase chemistry)

What will we learn from PM studies?

1. Sources (primary species, processes)
2. Origin (local, long-range transport)
3. Relationships (chemical and physical)
4. Time variation (cycles, trends)

☛Design of abatement strategies

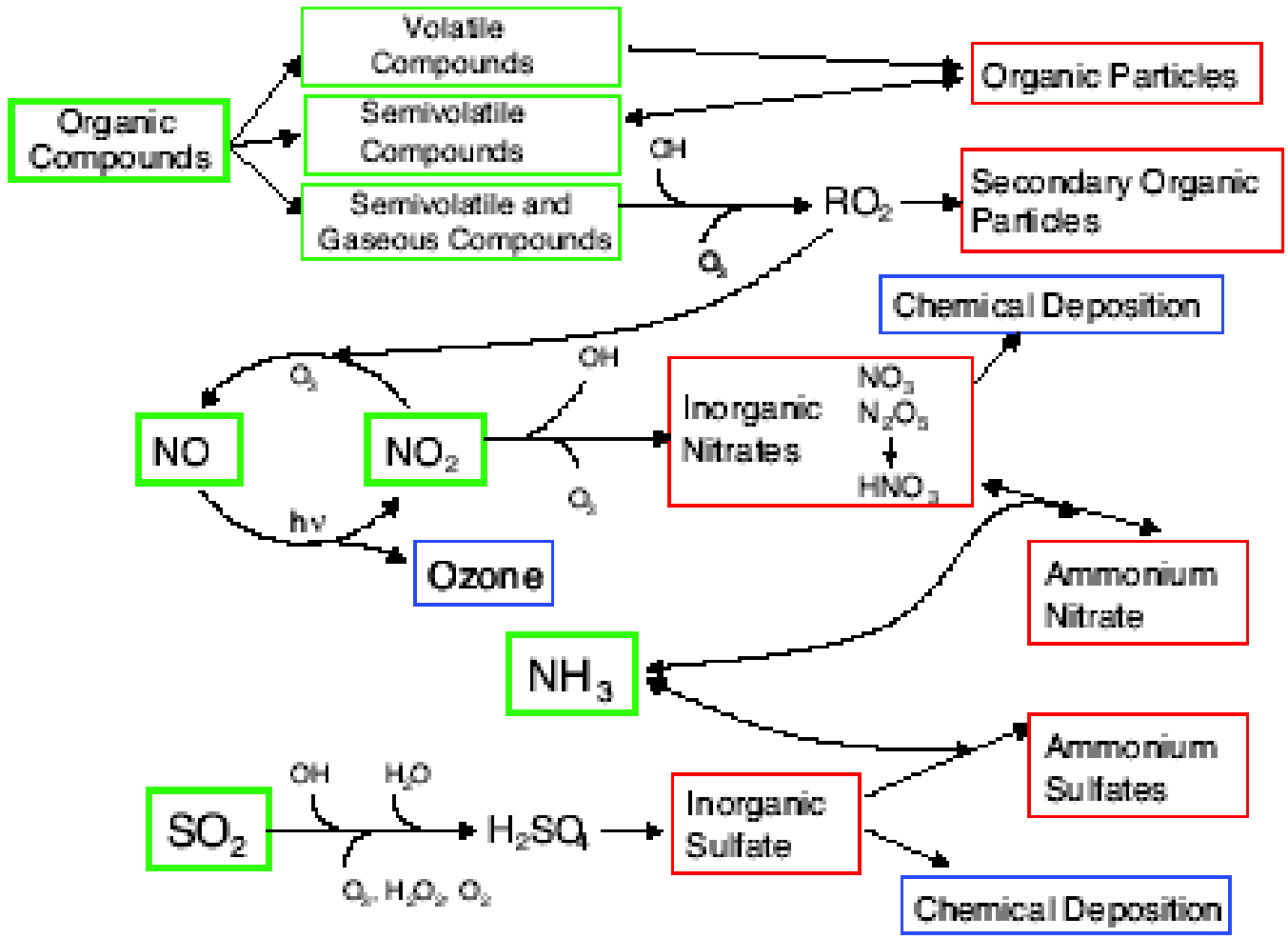
Analysis of PM data

1. Analysis of temporal variation
   - cycles (?): diurnal, seasonal
   - episodes (pollution events, air masses)
   - trends (pollution abatement, climate)
2. Size resolution frequencies (if available)
   - origin of species
3. Correlation between stations (if existing)
   - homogenity of concentration distribution (transport, transformation)
   - source characteristic: identity or difference
4. Correlation between chemical components (if analysed)
   - atmospheric chemical relations (e.g. ammonium sulphate)
   - origin (source region): identity or difference
5. Correlation with meteorological parameters (if measured)
   - characteristics of transport and (partly) transformation
6. Correlation with traffic data (if available)

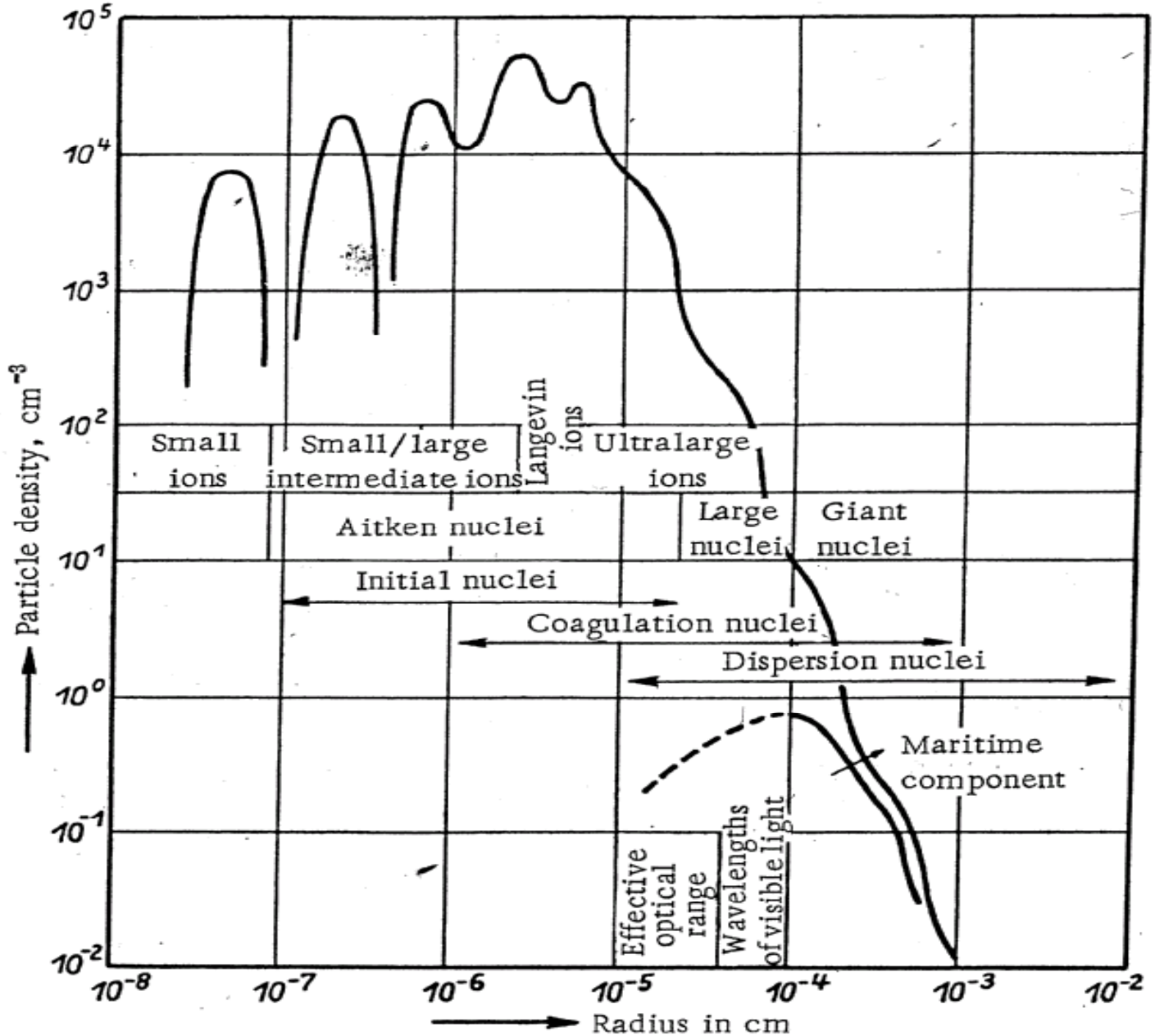
Origin of PM species

PM species	transfer	primary species	source
SO_4^{2-}	transport	seasalt SO_4^{2-}	ocean
	gas-phase oxidation ($\tau \approx 1$ d) aqueous-phase oxidation (cloud processing)	SO_2	combustion of fossil fuels
NH_4^+	fast gas-to-particle transformation	NH_3	fertilizing, livestocks, traffic (?), industry
NO_3^-	multi-step gas-phase oxidation ($\tau \approx 1$-2 d)	NO	fraffic, combustion, industrial high-temperature processes
Cl^-	transport	seasalt Cl^-	ocean
	fast gas-to-particle transformation	HCl	coal combustion, incineration
Na+ , Mg^{2+}	transport	seasalt Na^+	ocean
K^+ , Mg^{2+}	transport	K^+	soil
Ca^{2+}	transport	Ca^{2+}	flue ash, building activities, soils
EC	transport	EC (soot)	incomplete combustion
trace metals	transport	trace metals	different technical sources and processing, volcanoes,
OC (organics)	complex chemical transformation	NMHC	traffic, solvent use, biosphere
	transport and chemical degradation	biogenic OC	biosphere

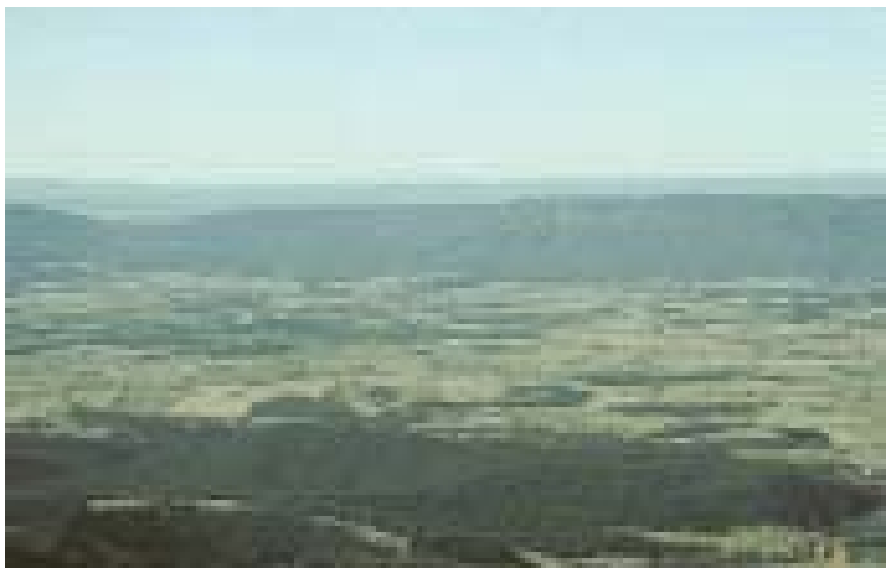
PM formation processes („Secondary Aerosol"): The major precursors are shown in green squares. The VOC can be gaseous (always in the gas phase), non-volatile (always in the condensed phase), and semivolatile (partitioned between the gas and condensed phases).



Size Distribution: Junge 1965



Regional Haze: Shenendoah and Yosemite Nat. Park



REGIONAL URBAN HAZE

Charles Darwin:
The Voyage of the Beagle (1839)
(*on "photochemical smog"*)

During this day I was particularly struck with a remark of Humboldt's, who often alludes to "the thin vapour which, without changing the transparency of the air, renders its tints more harmonious, and softens its effects." This is an appearance which I have never observed in the temperate zones. The atmosphere, seen through a short space of half or three quarters of a mile, was perfectly lucid, but at a greater distance all colours were blended into a most beautiful haze, of a pale French grey, mingled with a little blue. The condition of the atmosphere between the morning and about noon, when the effect was most evident, had undergone little change, excepting in its dryness. In the interval, the difference between the dew point and temperature had increased from 7^{o} to 17^{o} C.

Global natural emission of particulate ematter (in Tg a^{-1})

source	Peterson and Junge (1971)	Pueschel (1995)	Jonas et al. (1995)
primary emission			
sea salt	1000	300-2000	1300
soil dust	500	100-500	1500
volcanic ash	25	25-300	33
organic particulates (bioaerosol)	-	-	50
meteorites	10	0-10	-
secondary emissions			
sulfate from SO_2	244	105-420	12
sulfate from H_2S		16-32	90
sulfate from DMS		9	
nitrate from NO	75	74-700	22
ammonium from NH_3	-	269	-
organic condensates	75	15-200	55
total primary emission	1500	425-2800	2900
total secondary emission	400	480-1600	180
total	1900	900-4400	3080

Global man-made emission of particulate matter (in Tg a^{-1})

source	Peterson and Junge (1971)	Pueschel (1995)	Jonas et al. (1995)	Wolf and Hidy (1997)
primary emissions				
industry	56.4	56	100	74.5[b]
fossil fuel combustuion	43.4	43		132.7[c]
soot	-	24	20	-
traffic	2.2	2	-	-
forest fires[a]	-	3-150	80	105
agricultural burning	-	29-72	-	
others	31.2	18-31	-	32.5[d]
total primary emission	133	150-370	200	345
secondary emissions				
sulfate from SO_2	220	70-220	140	121
nitrate from NO	40	23-40	36	20
organic condensates	15	15-90	10	4
total secondary emission	275	110-250	186	145
total	408	260-620	390	490

[b] Pueschel named forest fires to natural sources; Jonas et al. to man-made sources.
[c] Cement production (52.6), copper (12.3), Zinc (6.0), paper production (3.6)
[d] coal (111) and oil (21,7)
[e] including 17.3 agricultural dust

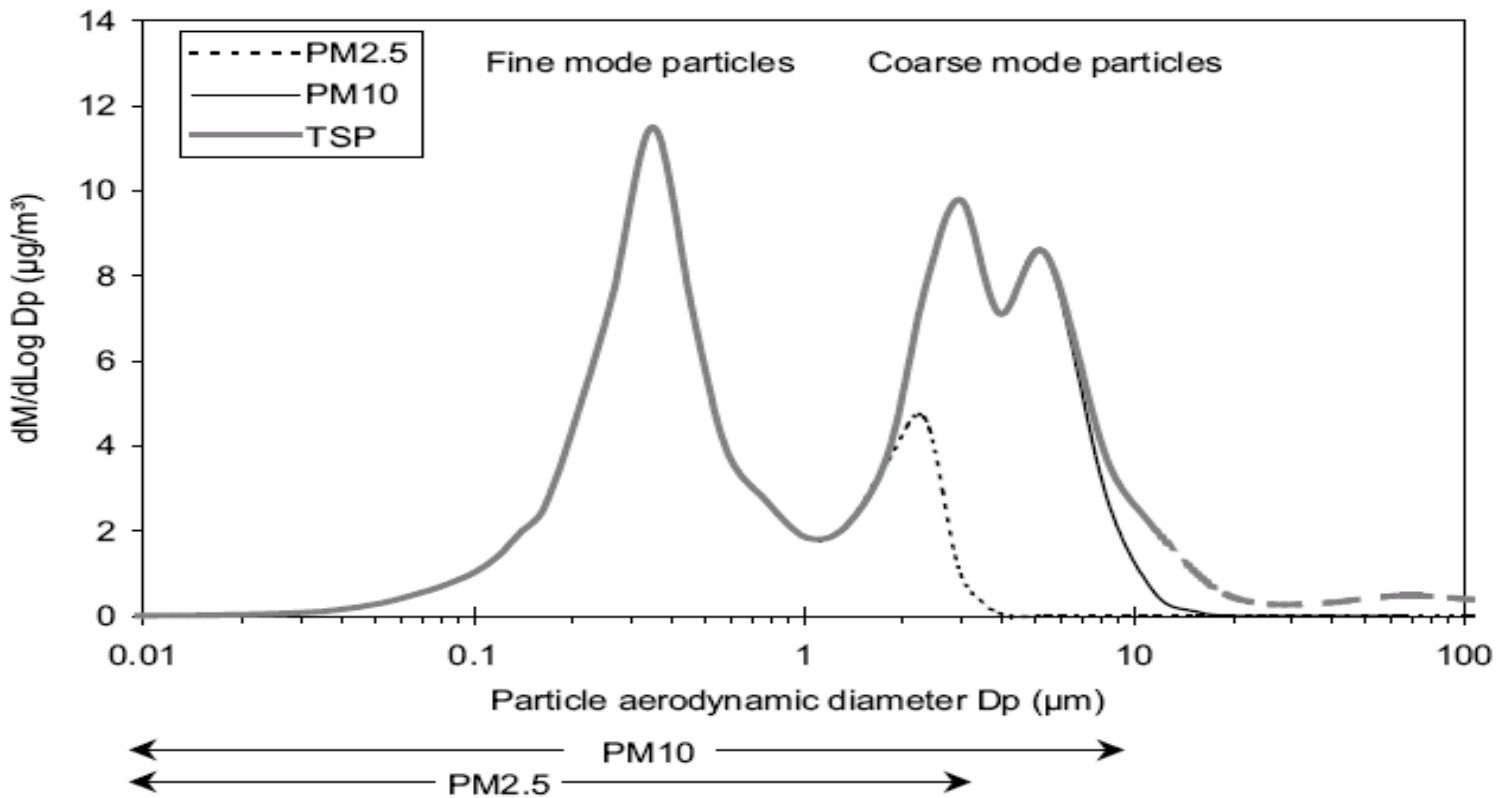
Deposition of soil dust above global ocean, after Duce et al. (1991)

sea	mean flux ($g\ m^{-2}\ a^{-1}$)	deposition ($Tg\ a^{-1}$)	iron deposition ($Tg\ a^{-1}$)
North Pacific	5.3	470	1.6
Sourh Pacific	0.35	39	0.14
Northen Atlantic	4.0	220	0.76
Southern Atlantic	0.47	24	0.08
North Indian Ocean	7.1	100	0.35
total	2.5	900	3.2

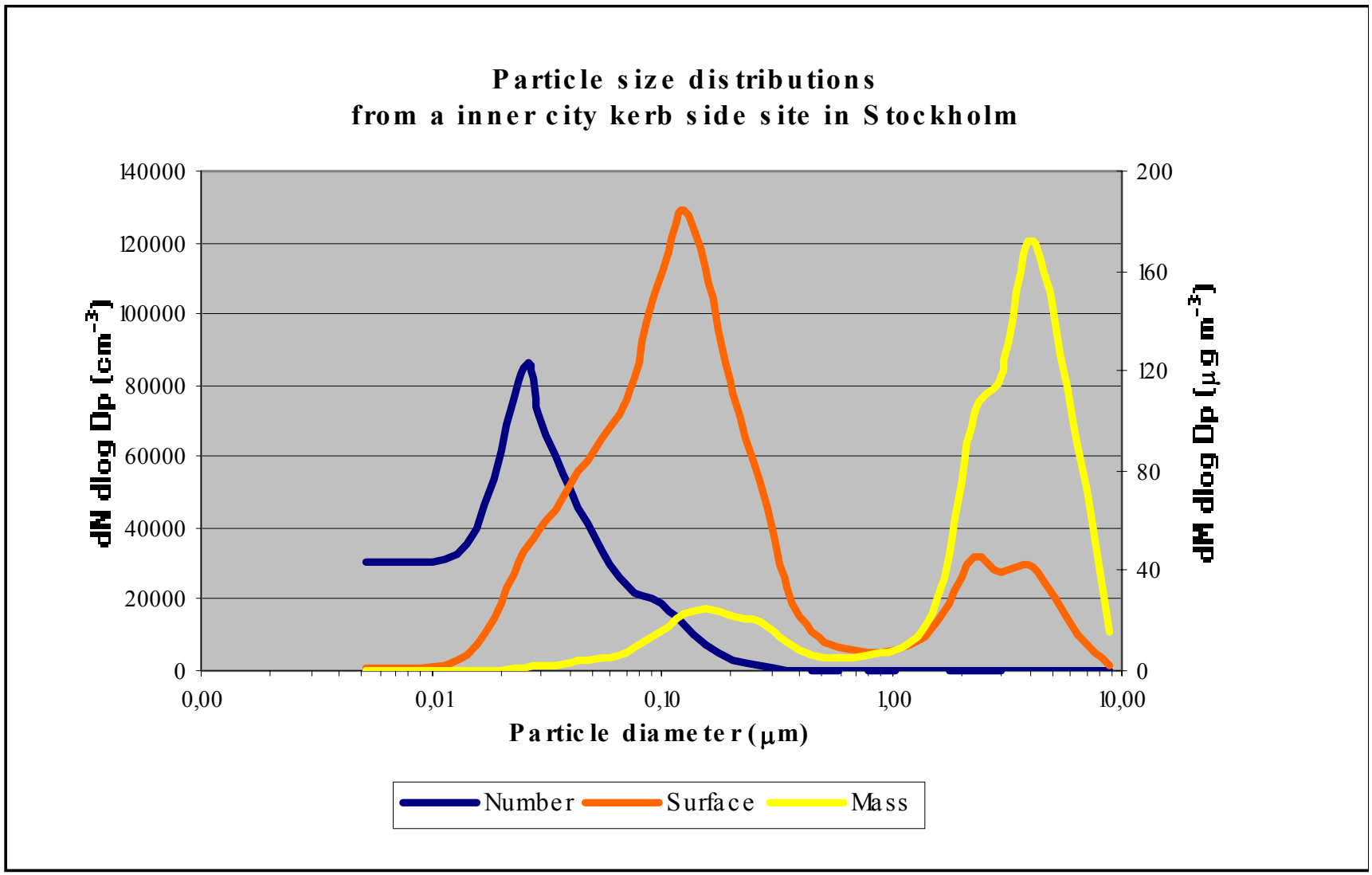
Specific emissions (in t km^{-2})
for the former Eastern and Western Germany in 1989,
after Friedrich (1999)

	west	east
SO_2	4.0	48.8
NO	7.1	4.4
dust	1.9	19.0
CO	33.2	33.5
CO_2	3103.0	2871.0

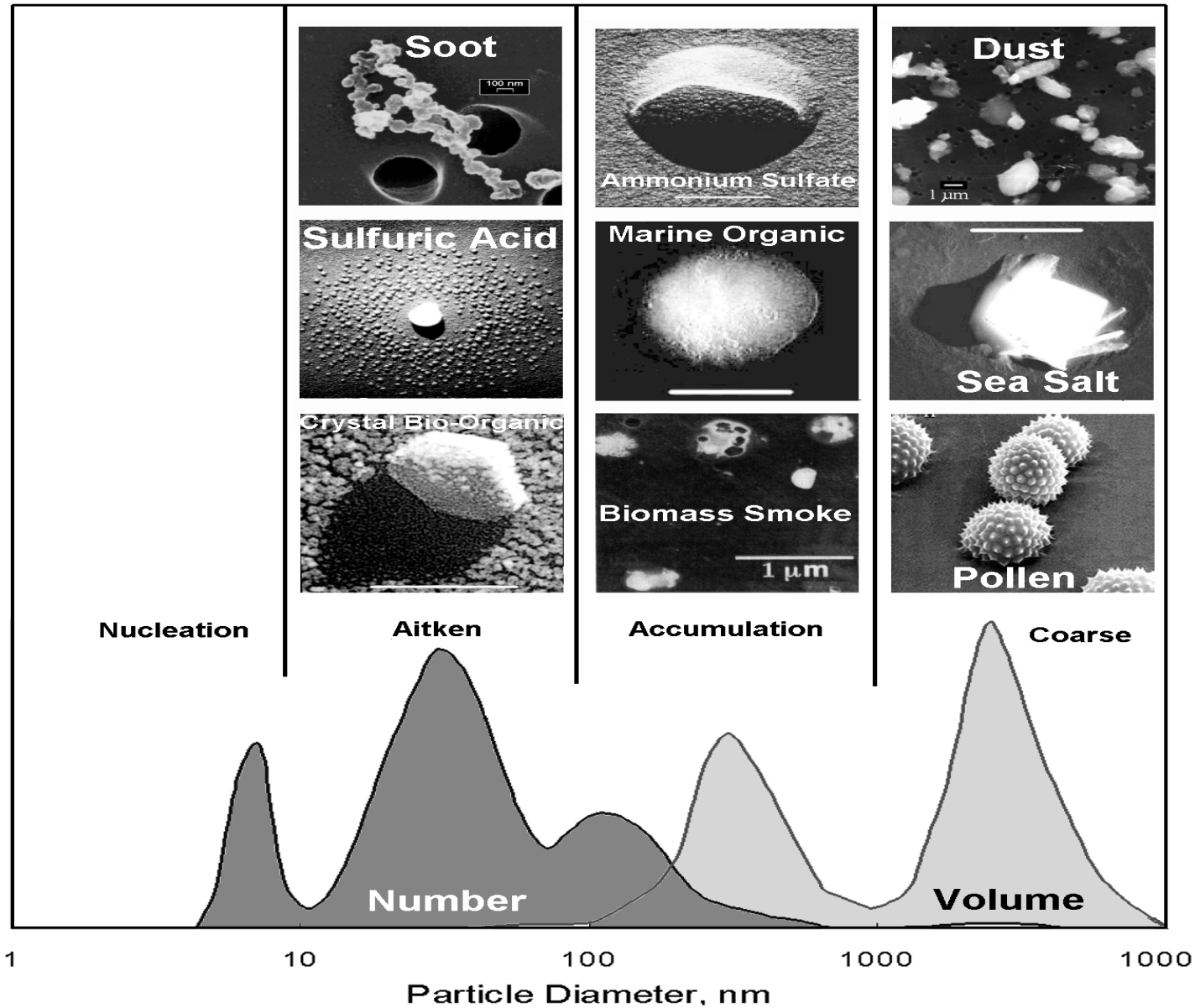
Fraction of the Total Suspended Particles (TSP) that are accounted for by PM2.5 and PM10



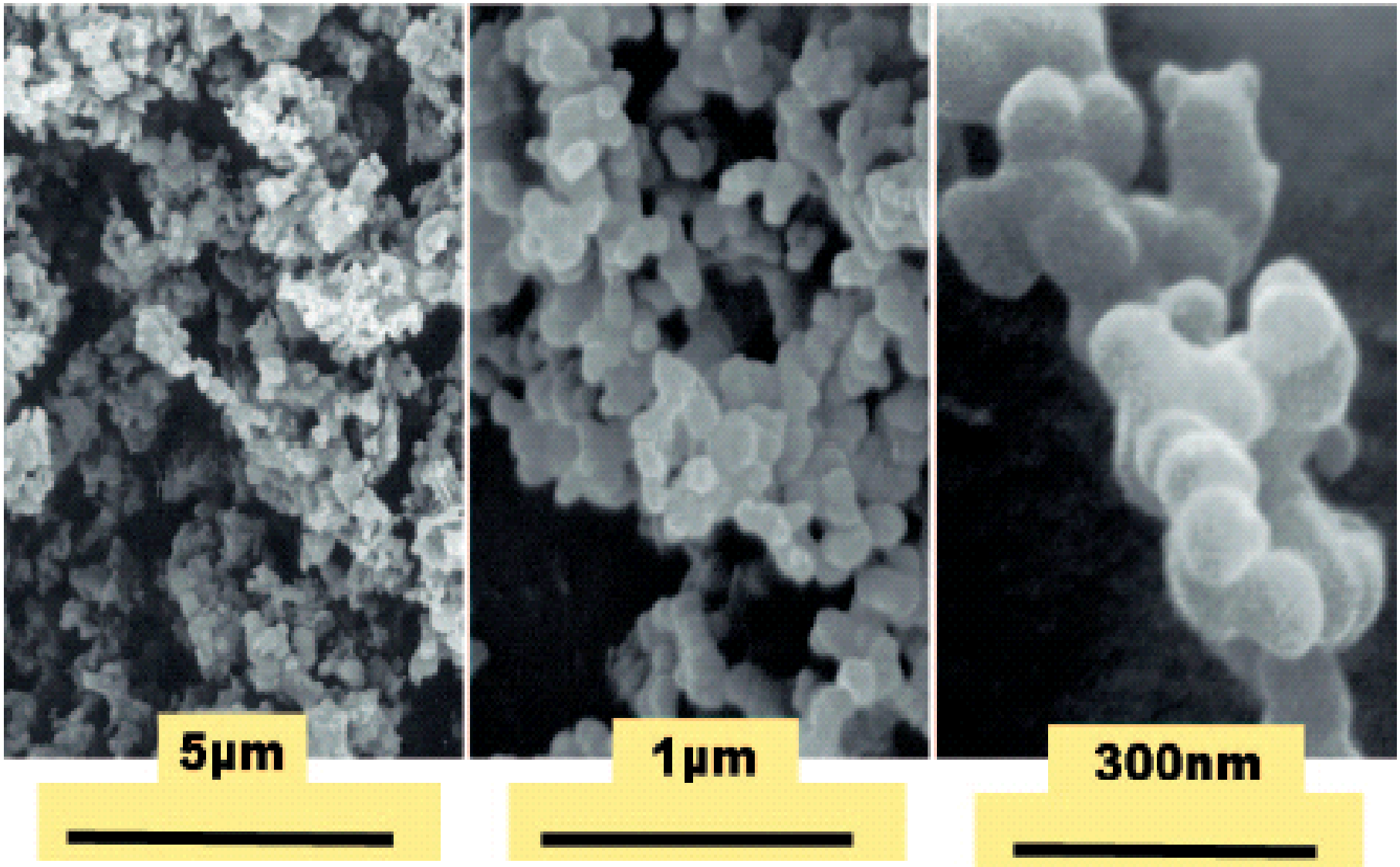
Number and Mass Size Distribution



Aerosol Size Distribution and Morphology



Soot nanoparticles viewed using Field Emission Scanning Electron Microscopy.



John Tyndall (1869):

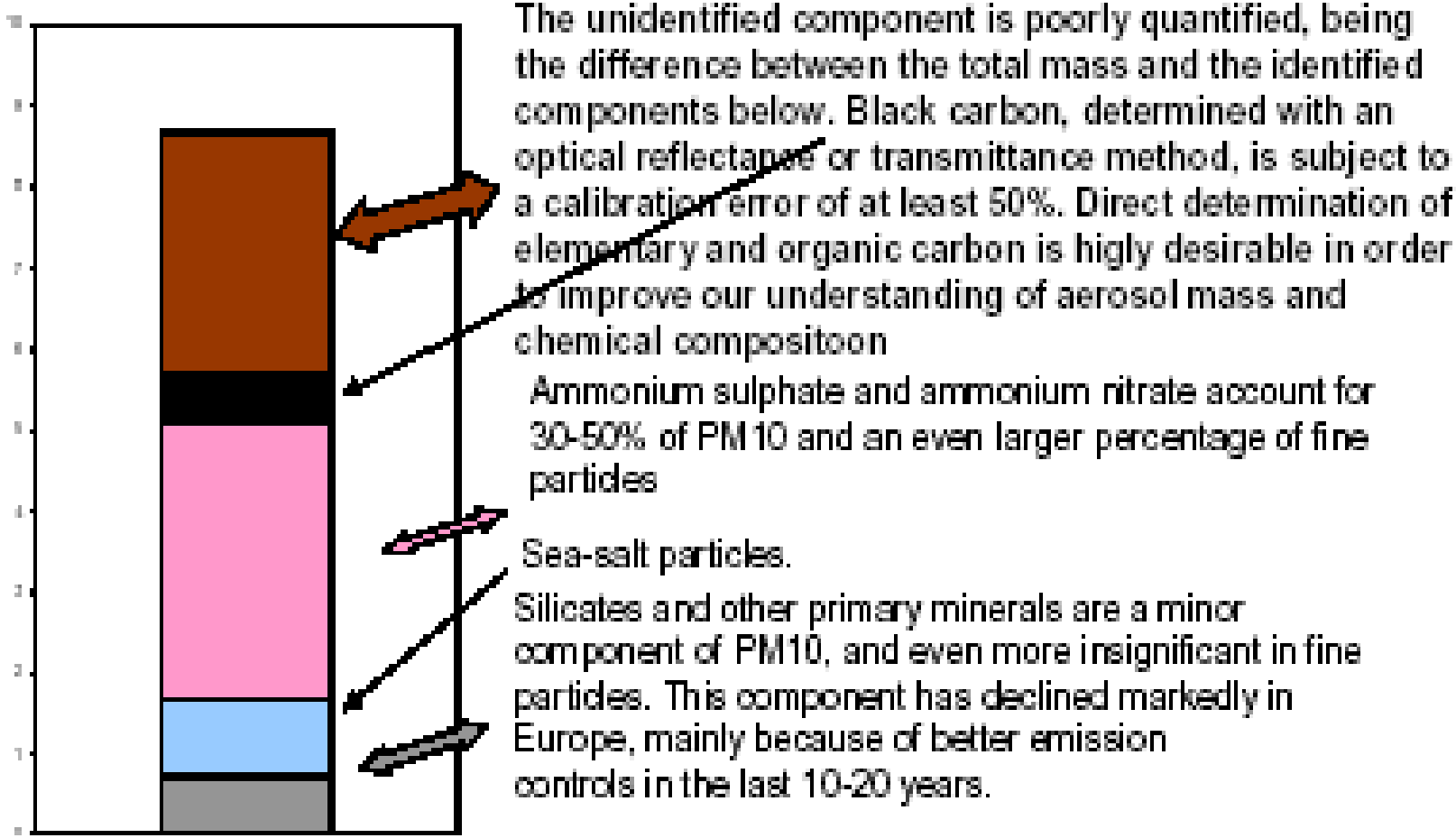
"On the Blue Color of the Sky, the Polarization of Skylight, and the Polarization of Light by Cloudy Matter General."

- **It has hitherto been my aim to render the chemical action of light upon vapour visible. For this purpose, substances have been chosen, one at least of whose products of decomposition under light shall have a boiling point so high that as soon as the substance is formed it shall be precipitated. By graduating the quantity of the vapor, this precipitation may be rendered of any degree of fineness, forming particles distinguishing by the naked eye, or particles which are probably far beyond the reach of our highest microscopic powers.**

- **I have no reason to doubt that particles may thus be obtained whose diameter constitutes a very small fraction of the length of wave of violet light. In all cases, when the vapours of the liquids employed are sufficiently attenuated, no matter what the liquid may be, the visible action commences with the formation of a blue cloud.**

Example: Chemical composition of PM10 (micrograms per m^3) at Birkenes in Southern Norway.

(Data from W. Maenhaut, Univ. of Gent, and NILU.)



Particulate Matter Standards

NO STANDARD EXISTS FOR NANOPARTICLES

PM & Health

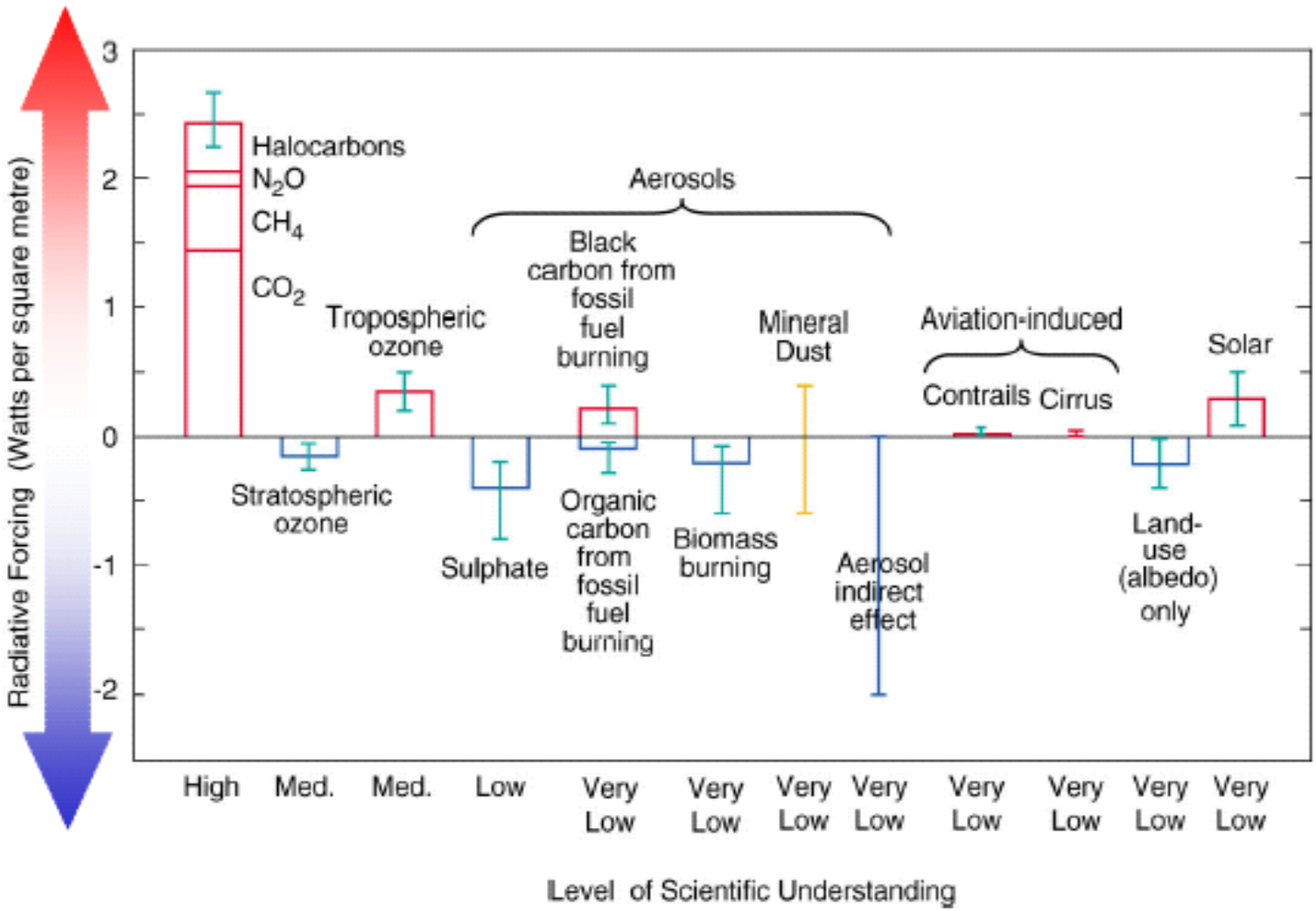
EU standards for Particulate Matter (PM10)

24-hour limit value	50 µg/m³ PM10 not to be exceeded > 35 times/year.	to be met 1 jan 2005
	50 µg/m³ PM10 not to be exceeded 7 times/year	to be met 1 jan 2010
annual standard	40 µg/m³ PM10	to be met 1 jan 2005
	20 µg/m³ PM10	to be met 1 jan 2010

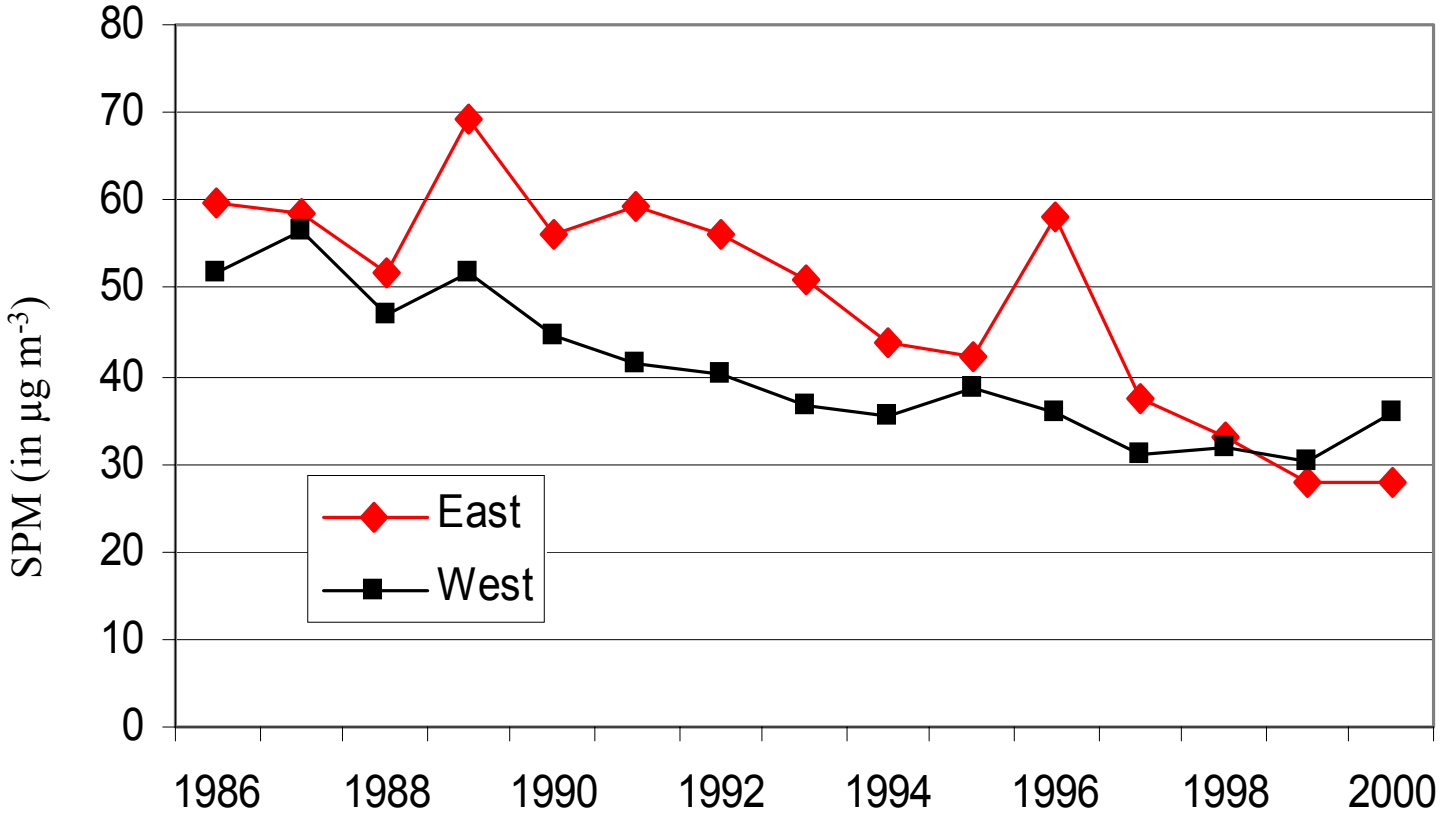
US-EPA PM standards for PM10 and PM2.5

24-hour limit value	65 µg/m³ PM2.5 3-year average of 98% percentile
annual standard	50 µg/m³ PM10 (3-yr average)
	15 µg/m³ PM2.5 (3-yr average)

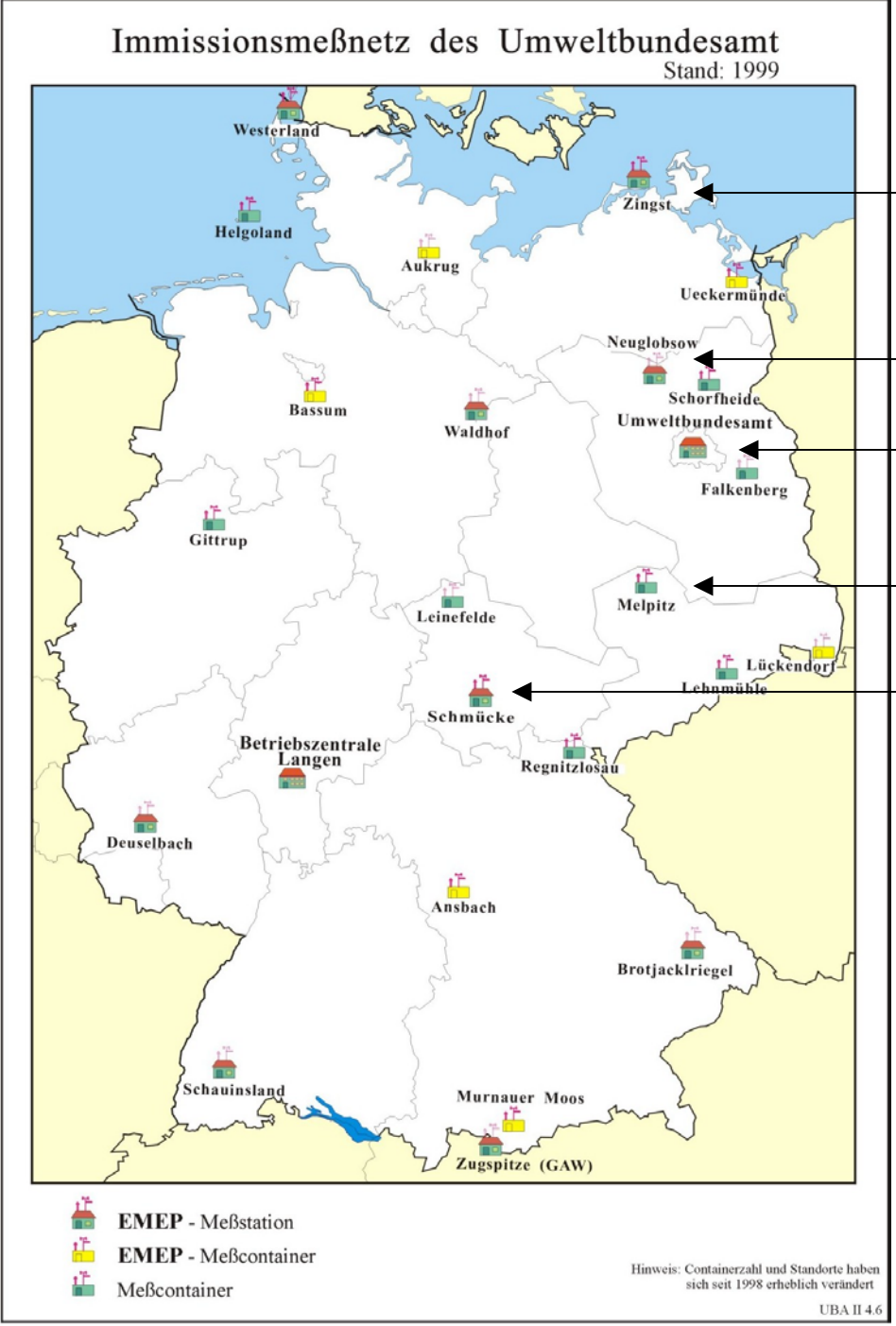
AEROSOL & CLIMATE



Mean of all stations (about 300 of UBA and State administrations) Eastern and Western Germany



Mean	1986-1990	1991-1996	1997-1999
East	59	52	32
West	50	38	32



(air pollution measurement sites of UBA)

Zingst

Neuglobsow

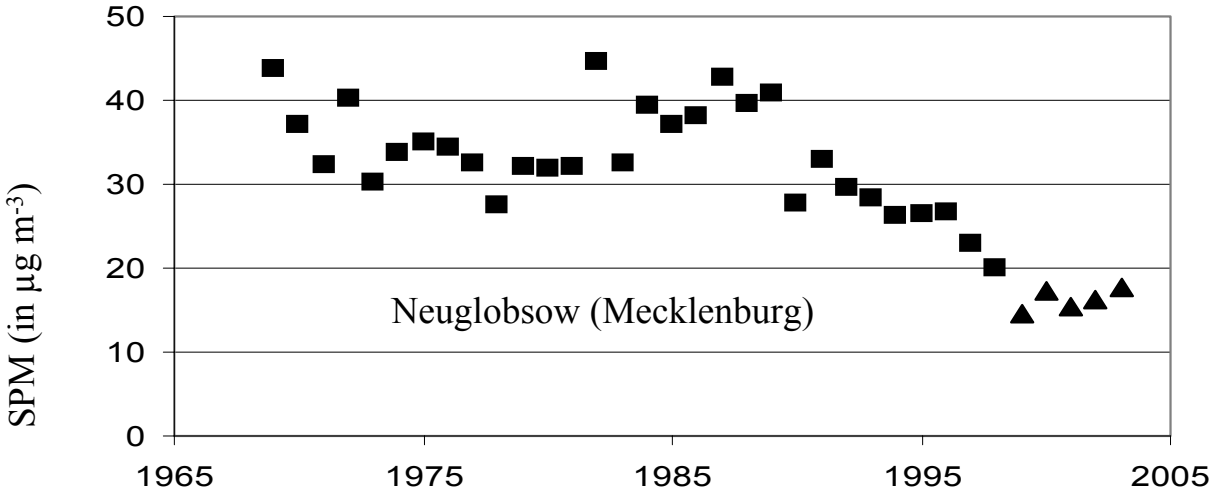
Berlin (Senatsverwaltung)

Melpitz

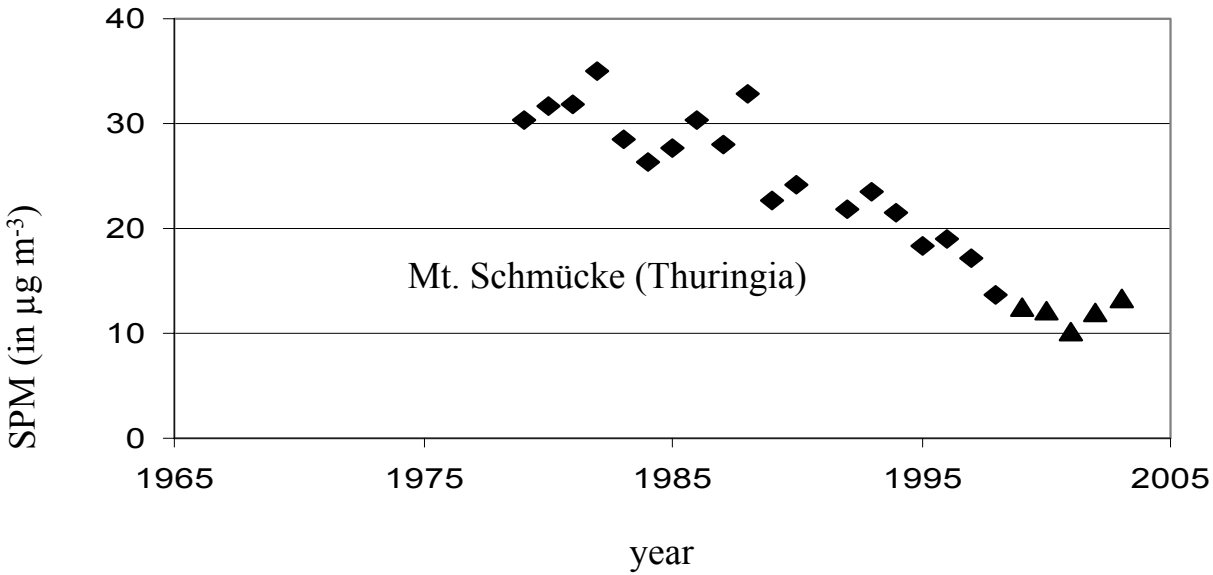
Schmücke

At Schmücke continuous measurements of some pollutants and SPM are carried out by the Institute for Tropospheric Reseach, IfT Leipzig.

In Berlin/Brandenburg area 2001-2002 measurements of PM10 at 7 sites were done by BTU Cottbus (projects from Berlin Senatsverwaltung, Federal Ministry BMBF and BTU funding)



mean 1969-1989 (TSP) 36.1±4.7
mean 1990-1998 (TSP) 26.8±3.7
mean 1999-2003 (PM10) 16.3±1.3

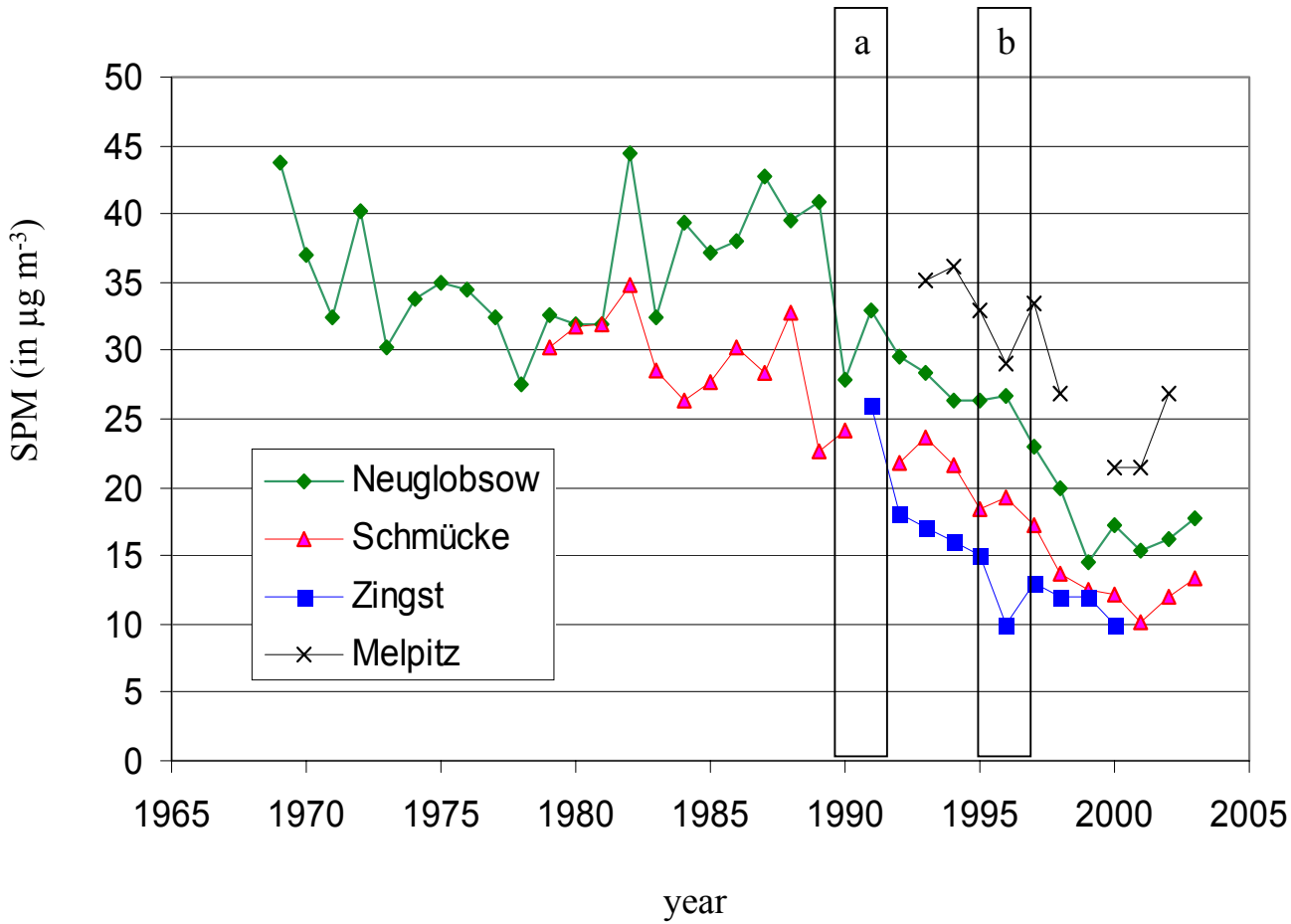


mean 1979-1988 (TSP) 30.3±2.7
mean 1989-1998 (TSP) 20.6±3.4
mean 1999-2003 (PM10) 12.0±1.2

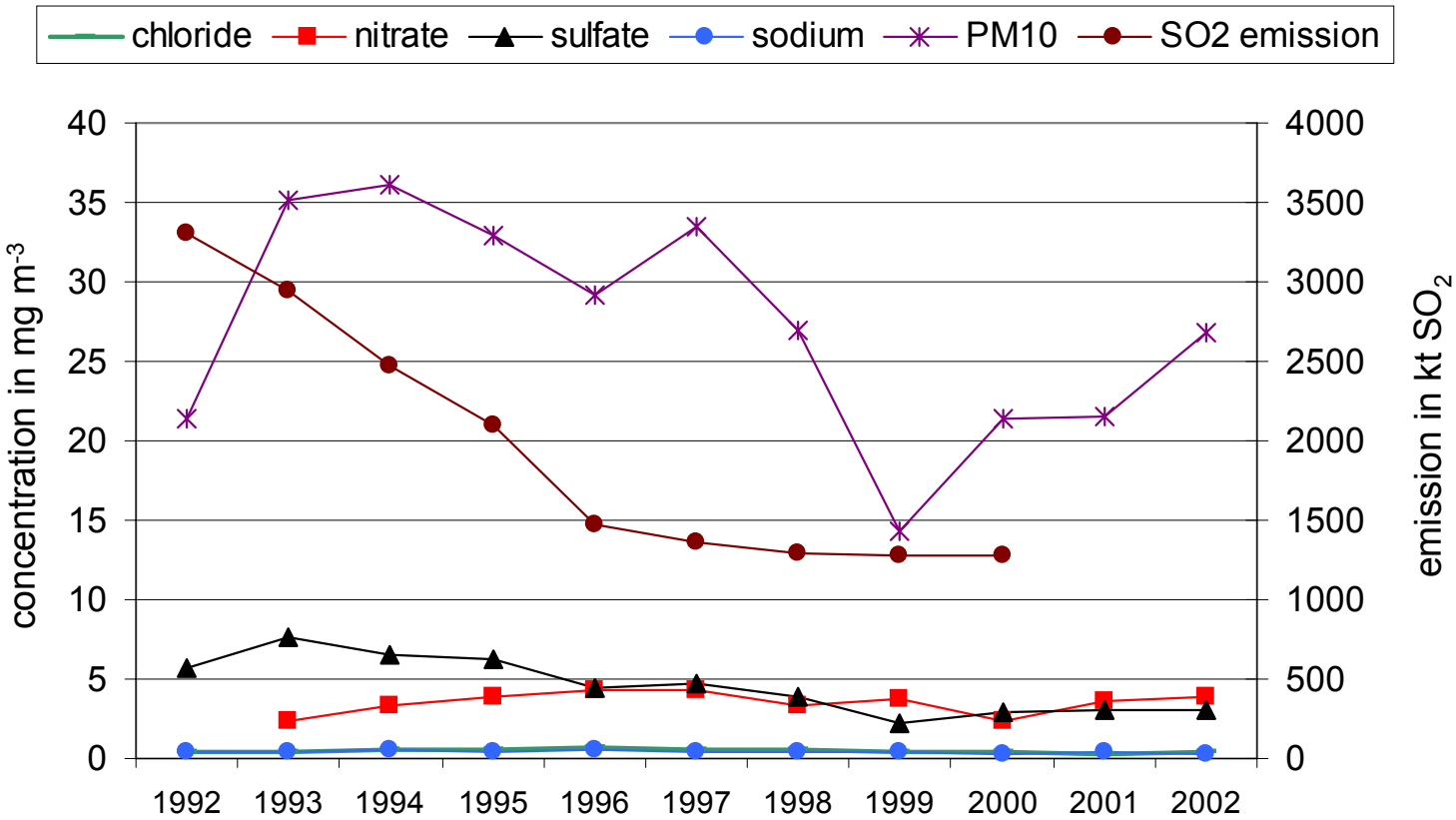
SPM trend at some East German background stations

Zingst: Baltic Sea coast (sea side resort)
Neuglobsow: Mecklenburg farm land background
Schmücke: Mountain background (900 m a.s.l. in Thuringia
Melpitz: industrial background (25 km NE from Leipzig)

a: German unification (collaps of Eastern Germany)
b: full introduction of power plant desulphurization



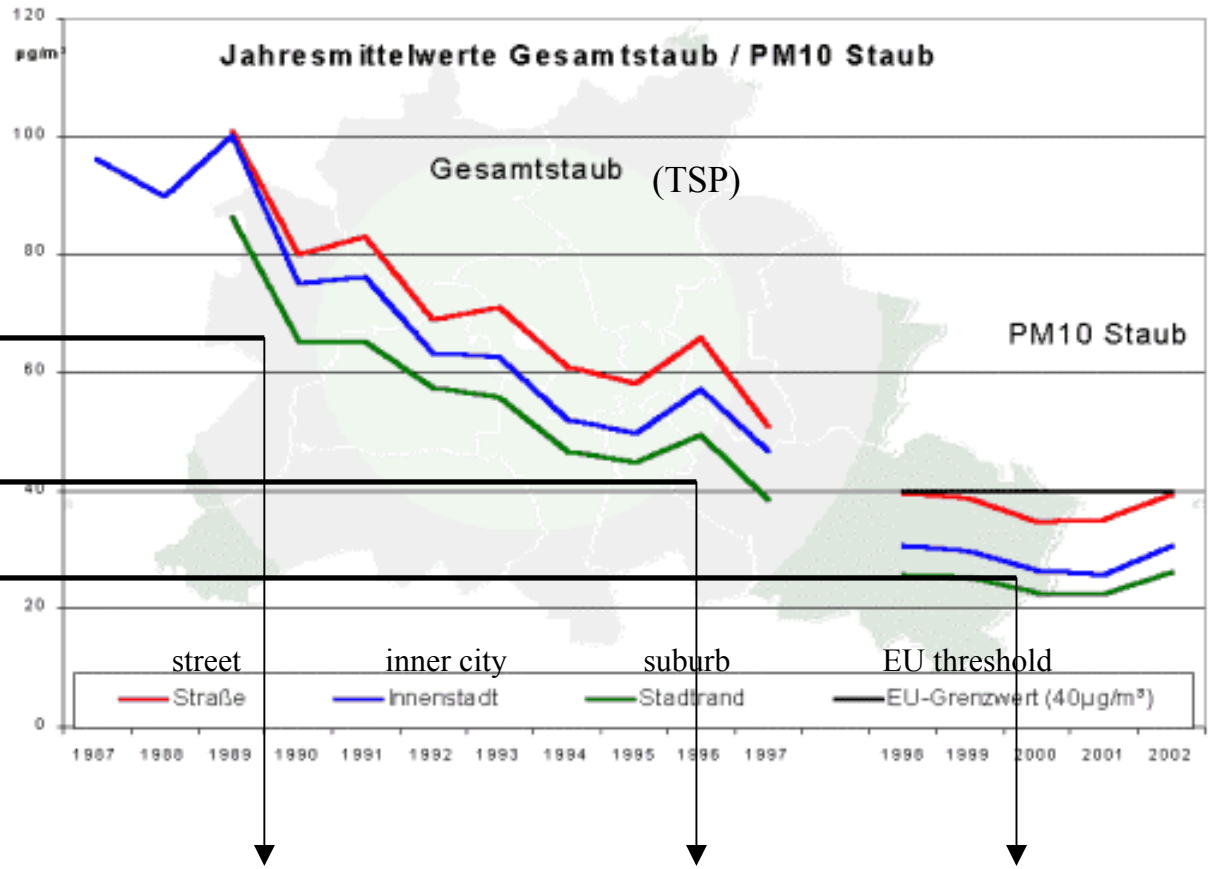
PM10 trend at Melpitz (near Leipzig)



Reduction 1993/1997→1998/2002:	SO_2 emission	44%	996 kt
	PM sulfate	49%	2.8 mg m^{-3}
	PM10	29%	9.2 mg m^{-3}

Berlin trend of SPM

Annual mean of TSP / PM_{10} (in µg m^{-3})



rural level before 1990

rural level around 1995

rural level around 2000

street

inner city

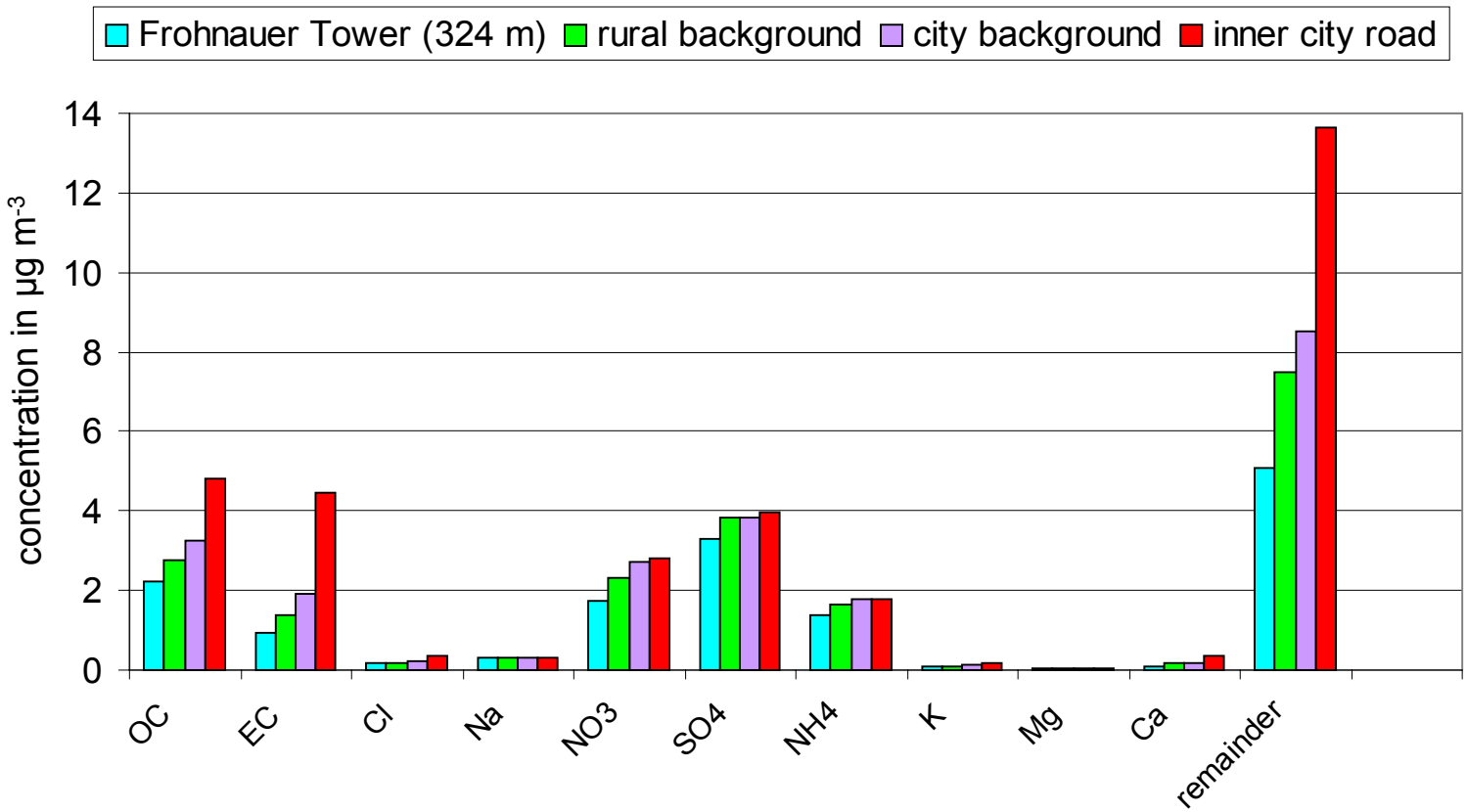
suburb

EU threshold

Conclusion: Berlin PM10 nowadays is given by the background figure

Chemical composition of PM10 in Berlin/Brandenburg

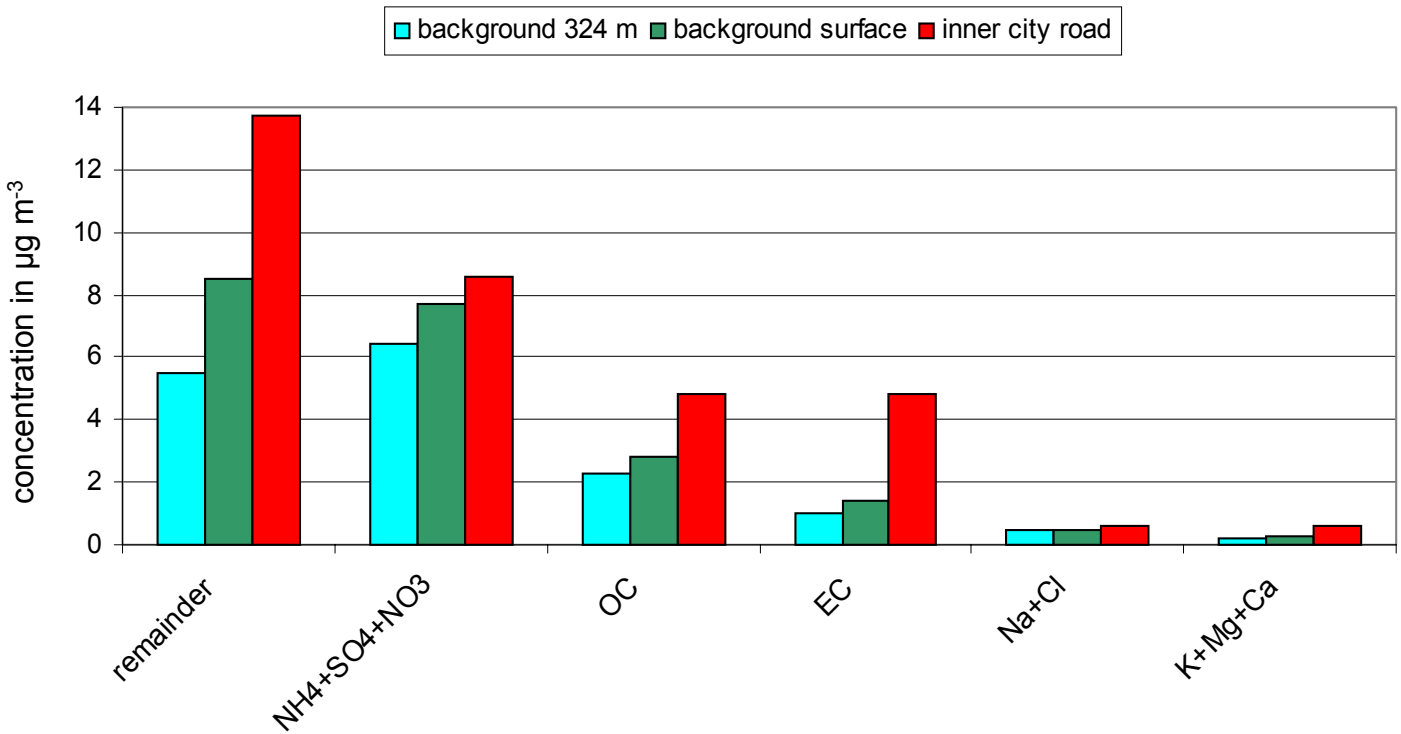
(daily PM High-Vol (digitel) sampling September 2001 – September 2002)



PM10 concentration:	Frohnauer Tower	15.5
	rural background	20.3
	city background	23.0
	inner city road	32.9

Group contribution to PM10 (Berlin/Brandenburg)

(daily PM High-Vol (digitel) sampling September 2001 – September 2002)



excess road (traffic) contribution: 6.0 µg m^{-3} remainder (probably SiO_2 resuspension)
3.0 µg m^{-3} EC (probably direct emission)
2.5 µg m^{-3} OC (probably SOA from VOC emission)

(Note: This excess PM is observed only at very busy streets. Difference between city background and rural background is not significant)

Background level before 1990: 40

Background level around 1995: 20

(reduction due to less coal combustion and desulphurization)

Mean PM10 ($\mu g\ m^{-3}$):		
	Frohnauer Tower (324 m)	15.5
	rural background	20.3
	city background	23.0
	inner city road	32.9

Background 20 $\mu g\ m^{-3}$:

7-8 remainder (SiO_2?)
1 seasalt
2.5 OC
1 EC
2 nitrate
4 sulfate
1 ammonium

Road traffic + (10-15) $\mu g\ m^{-3}$:

6-11 resuspension (SiO_2?)
1 OC
3 EC

Exceedance:

+ 10-15 dry periode
+ 5-10 eastern air masses

- meteorological variations cause higher PM levels
- local abatement limited (< 4 mg m^{-3} for OC + EC only)