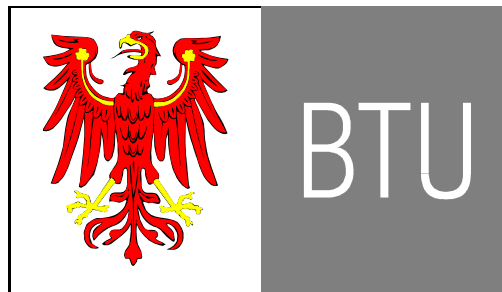


# PM<sub>10</sub> AEROSOL MASS AND COMPOSITION IN AND AROUND BERLIN WITH SPECIAL CONSIDERATION OF TRAFFIC CONTRIBUTION

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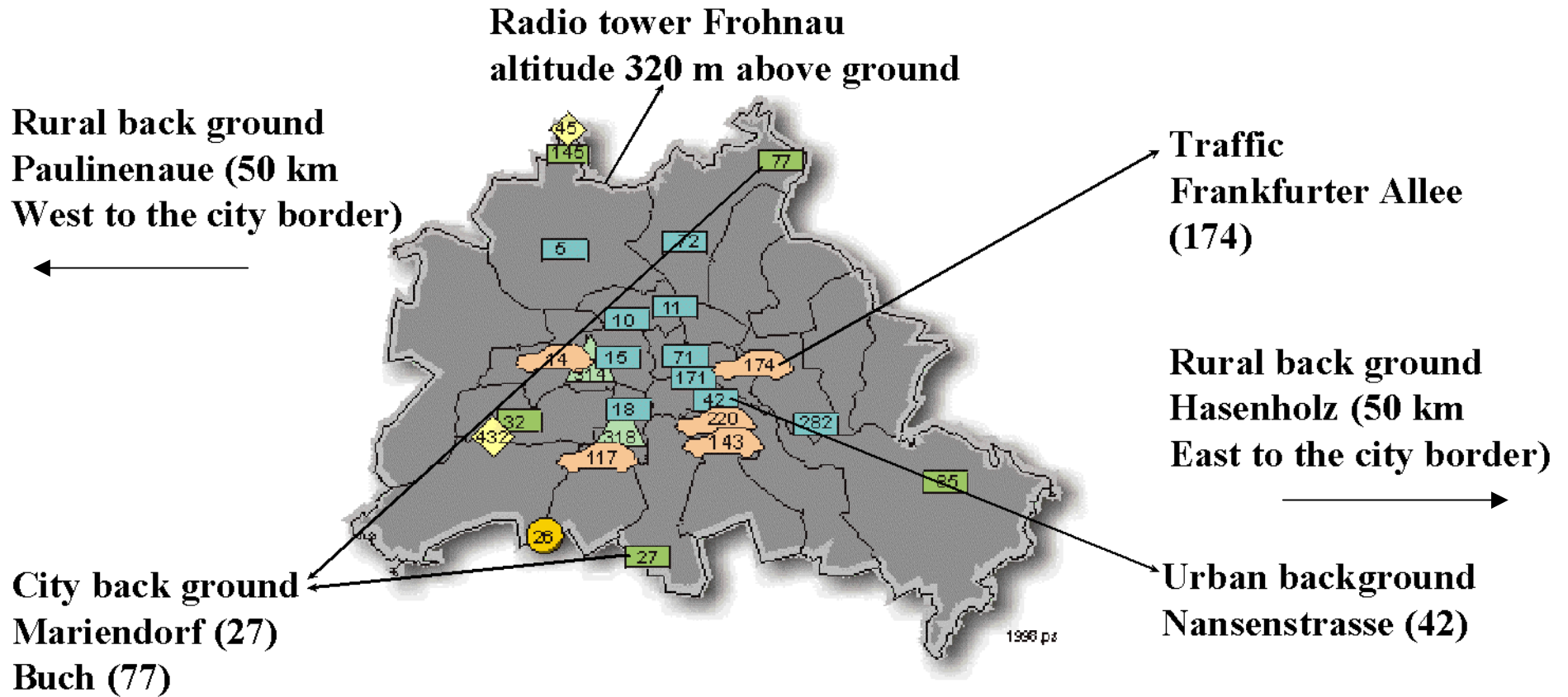
## INTRODUCTION

In city of Berlin (Germany) and in the surrounding area an one year measuring program was designed and carried out from September 2001 to September 2002 to identify the daily PM<sub>10</sub> aerosol mass concentration and its chemical composition. This program was organised by the Berlin government, department of urban development in the background of the new EU air quality directive for the PM<sub>10</sub> pollution limits. These limits were fixed at 50 µg/m<sup>3</sup> for the daily PM<sub>10</sub> average and at 30 µg/m<sup>3</sup> for the yearly average.

## METHOD

From the Berlin Environmental Measurement Network (BLUME) three sites in the city centre and two sites near the city border as well as three sites in the rural environment (Brandenburg) were selected to investigate the PM<sub>10</sub> pollution situation. Identical equipment (High Volume Samplers (Digital DHA 80), quartz fibre filters QF 20 preconditioned at 850° C) was used at all these sites for daily (24 hours) sampling. After exposition the aerosol mass as well as the chemical composition (organic carbon (OC), elemental carbon (EC), Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>+</sup>, Ca<sup>2+</sup>, Fe, Pb, Cd, Ni, As) were detected. Some additional information like meteorological conditions, traffic counts, trace gases and soot measurements were available from the BLUME-Network.

# The area of investigation



## What PM is it?

Different meanings: particulate matter  
suspended particulates  
dust

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

It is a dispersion of all excess-molecular particles  
(with the exception of hydrometeors) in air.

- Particle size range from few nm up to hundreds of  $\mu\text{m}$ .
- Very different chemical composition.
- Different forms and shapes.

# 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

# Experimental approach:

## 1. Fractionized sampling

- Integrated fractions (PM1, PM2.5, PM10, TSP)
- Size resolved

## 2. Sampling periode (time resolution)

## 3. Additional measurements

- trace gases (SO<sub>2</sub>, O<sub>3</sub>, NO, etc.)
- aerosol characteristics (number, size resolution, etc.)
- meteorological parameters (wind, temperature, etc.)

## 4. Total PM mass (gravimetric)

## 5. Chemical analysis

- inorganic ions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>)
- trace metals (Fe, Cu, Zn, etc.)
- EC (soot)
- organics (OC, group components, single components)

# Origin of PM species

PM species	transfer	primary species	source
SO <sub>4</sub> <sup>2-</sup>	transport	seasalt SO <sub>4</sub> <sup>2-</sup>	ocean
	gas-phase oxidation ( $\tau \approx 1$ d) aqueous-phase oxidation (cloud processing)	SO <sub>2</sub>	combustion of fossil fuels
NH <sub>4</sub> <sup>+</sup>	fast gas-to-particle transformation	NH <sub>3</sub>	fertilizing, livestock, traffic (?), industry
NO <sub>3</sub> <sup>-</sup>	multi-step gas-phase oxidation ( $\tau \approx 1-2$ d)	NO	traffic, combustion, industrial high-temperature processes
Cl <sup>-</sup>	transport	seasalt Cl <sup>-</sup>	ocean
	fast gas-to-particle transformation	HCl	coal combustion, incineration
Na <sup>+</sup> , Mg <sup>2+</sup>	transport	seasalt Na <sup>+</sup>	ocean
K <sup>+</sup> , Mg <sup>2+</sup>	transport	K <sup>+</sup>	soil
Ca <sup>2+</sup>	transport	Ca <sup>2+</sup>	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

# 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)

- homogeneity 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

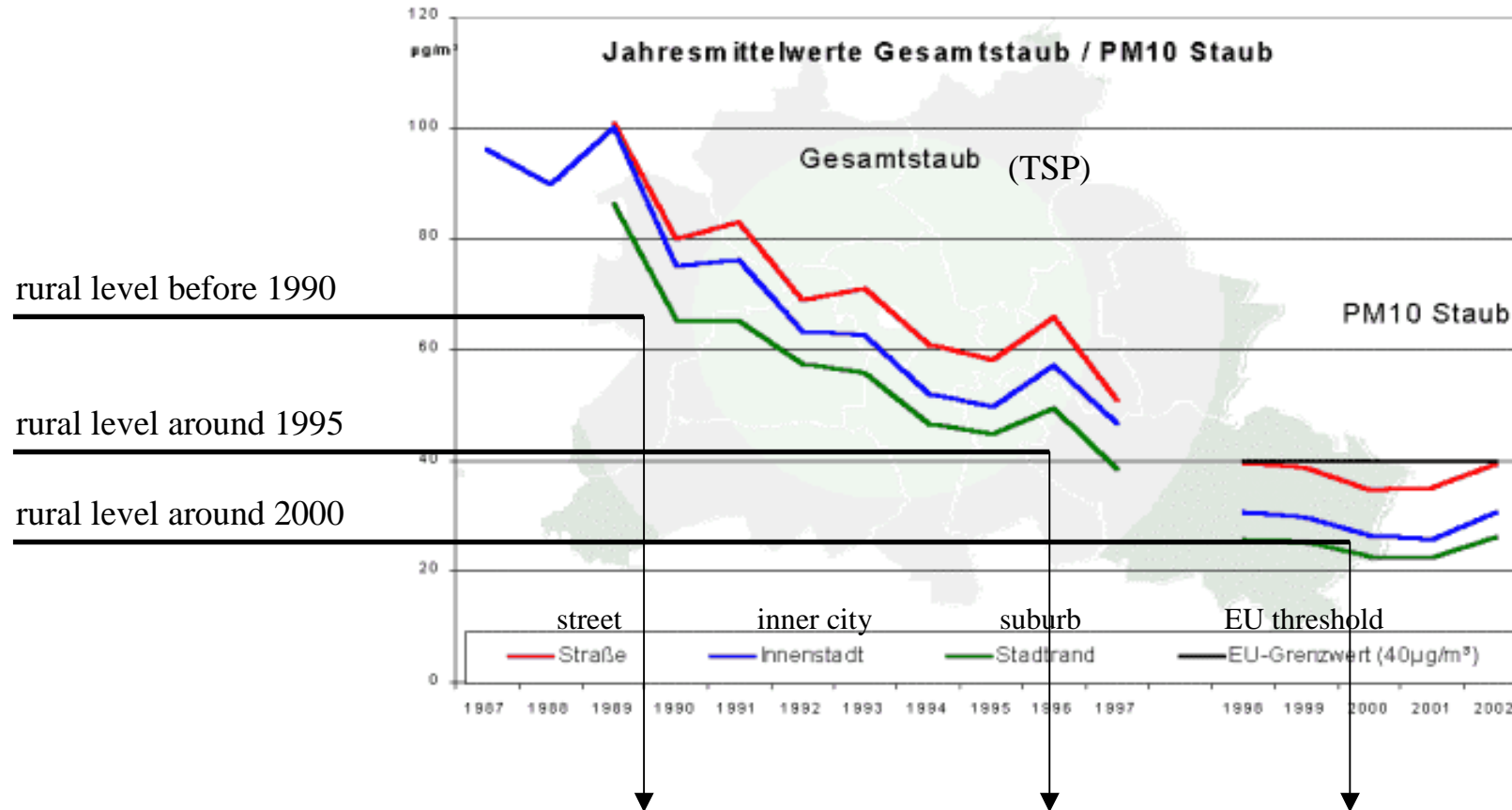
## 5. Correlation with meteorological parameters (if measured)

- characteristics of transport and (partly) transformation

## 6. Correlation with traffic data (if available)

# Berlin trend of SPM

Annual mean of TSP / PM<sub>10</sub> (in  $\mu\text{g m}^{-3}$ )



## Mean PM10 concentration in Berlin-Brandenburg (typically even for Germany)

In  $\mu\text{g m}^{-3}$

Site characteristics	Berlin-Brandenburg (2001/2002)	UBA network (2001-2006)
Tower (324 m) suburb	16	-
Rural background	20	19 $\pm$ 3
City background	23	27 $\pm$ 2
Traffic influenced (road)	35	36 $\pm$ 3

PM10 chemical composition: mean concentrations, percentage and difference

component	Concentration (total and percentage)			Excess (in $\mu\text{g m}^{-3}$ )	
	Rural background	City background	Traffic road	City excess <sup>a</sup>	Traffic excess <sup>b</sup>
Total PM10 (in $\mu\text{g m}^{-3}$ )	20	23	35	3	12
Unsoluble fraction	41	40	43	1	5
Seasalt (Na + Cl + Mg)	2	2	3	0	1
K + Ca	1	1	1	0	1
Sulphate	20	15	12	0	0
Ammonium	8	8	6	0	0
Nitrate	9	11	10	0.3	0.5
OC	13	14	13	② 1	2
EC	7	9	12	② 1	2.5
total	100	100	100	3	12

<sup>a</sup> difference between rural and city background

<sup>b</sup> difference between city background and traffic road

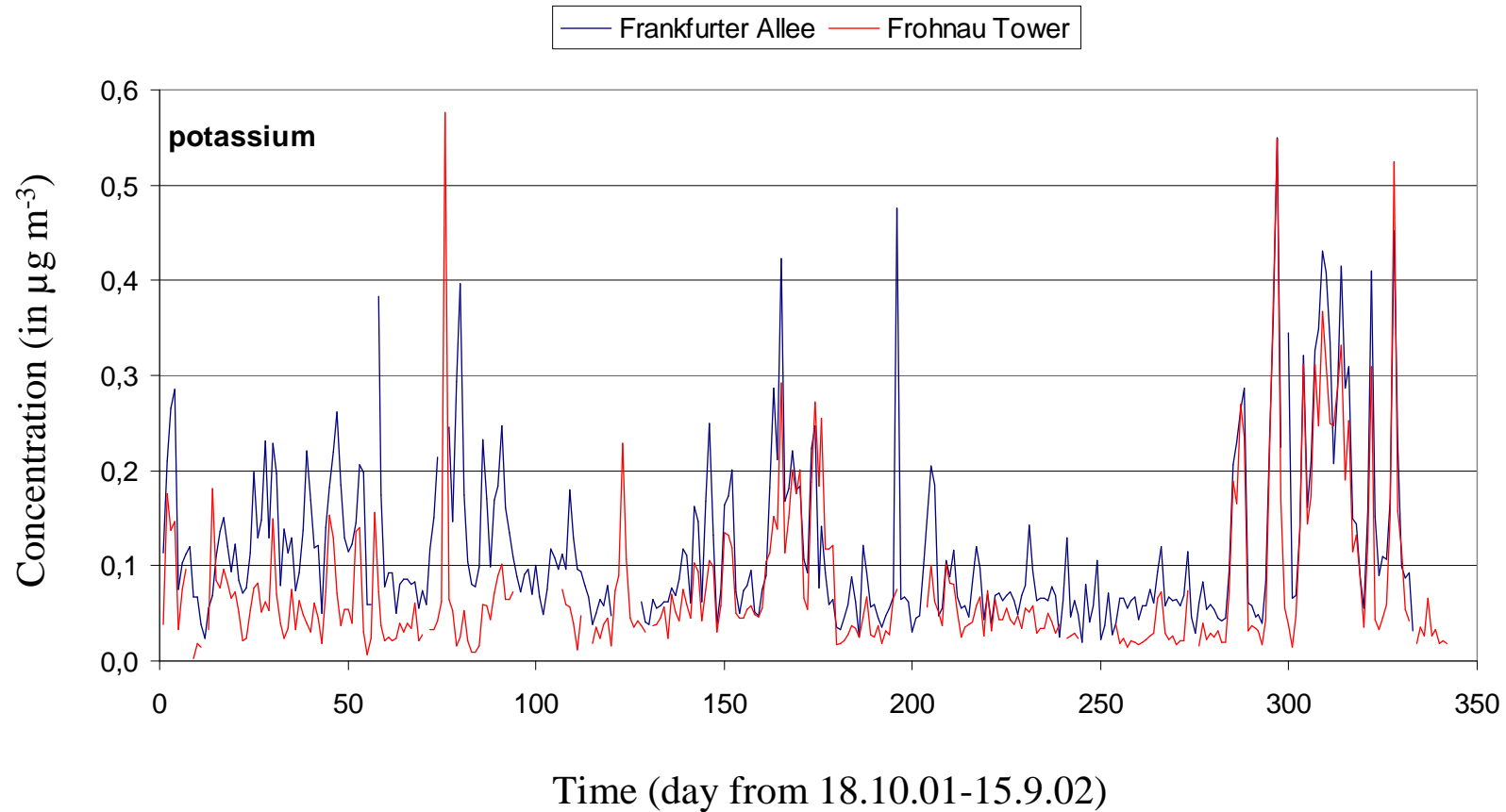
## Staubbelastung einschl. ausgewählter Inhaltsstoffgruppen [ $\mu\text{g m}^{-3}$ ]

Standort	PM <sub>10</sub>	OC+EC <sup>a</sup>	Rest <sup>b</sup>
174 (Frankfurter Allee)	34,5	4,7	14,3
42 (Neuköln)	24,4	5,4	9,5
27 (Marienfelde)	21,9	5,0	8,0
77 (Buch)	22,6	4,8	8,1
Frohnauer Turm (324 m Höhe)	15,5	3,2	5,1
Beuselstraße	31,3	9,5	13,0
Paulinenaue	20,1	4,3	6,7
Hasenholz	20,4	4,0	8,3

<sup>a</sup> organisches Material + elementarer Kohlenstoff (Ruß)

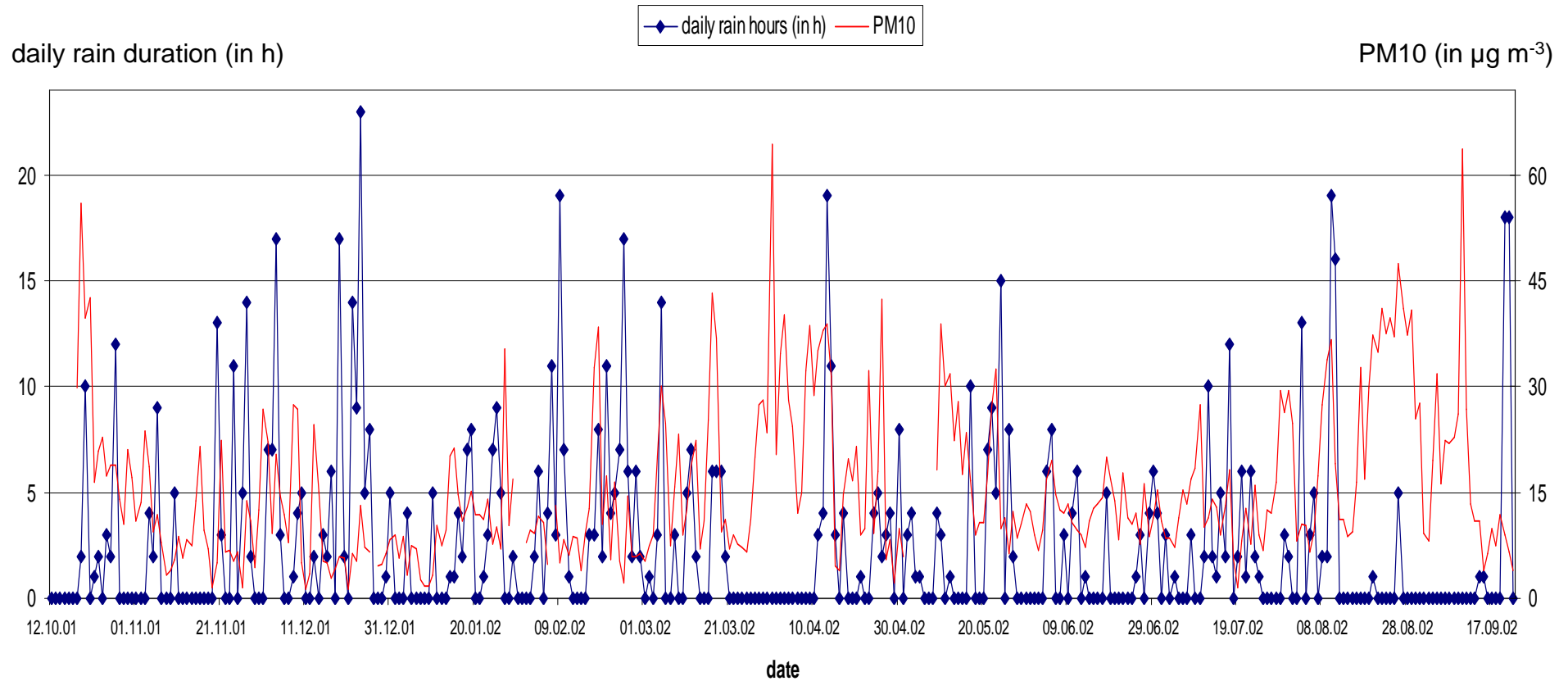
<sup>b</sup> nichtanalyzierter mineralischer Rest (insb. Silikate)

# Time variation of a soil dust component ( $K^+$ )



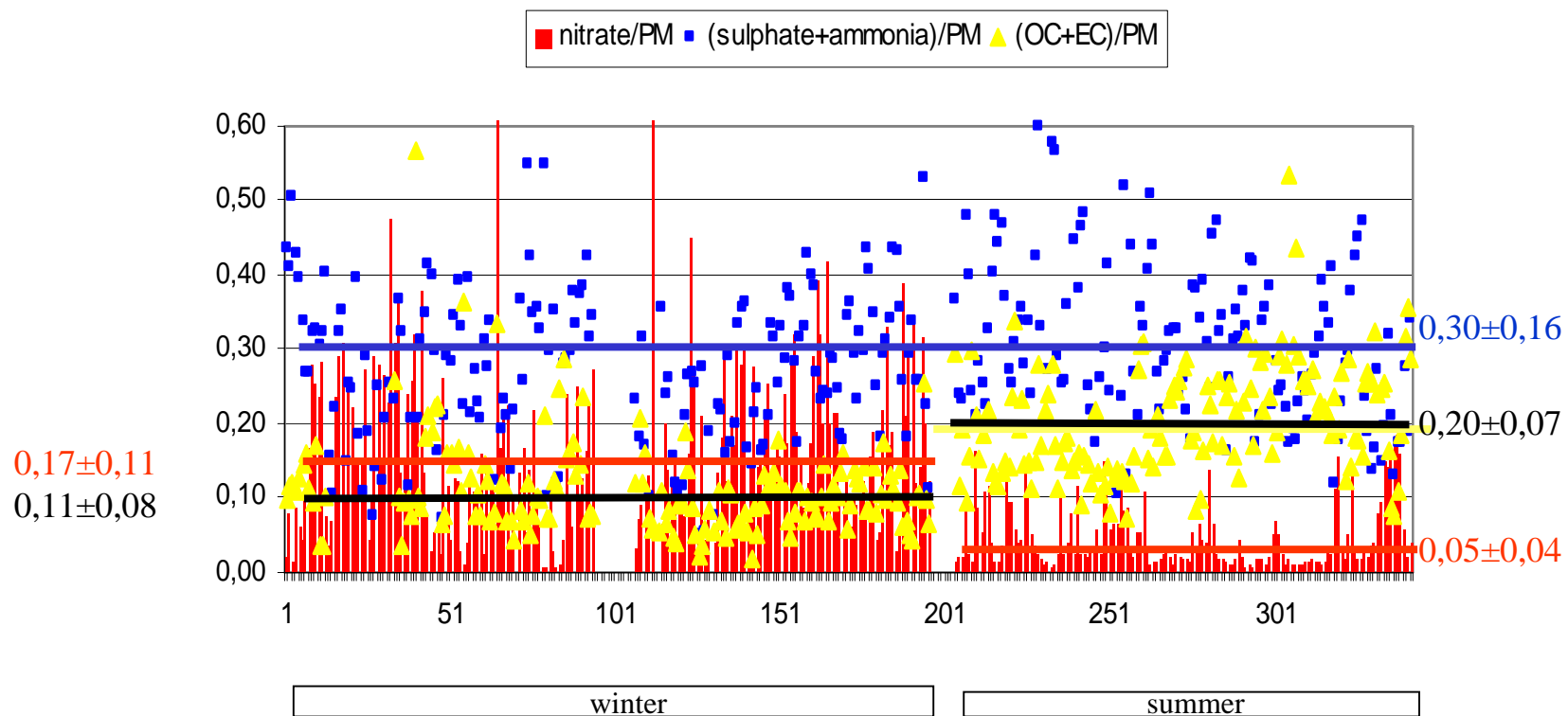
Concentration variation determined only by meteorological parameters influencing source strength and transport (wind speed, wind direction, precipitation, soil humidity).

# Rain duration and PM10 at Frohnauer Tower



- anticorrelation is clearly seen (wet deposition of PM)
- dry periode duration leads to an PM10 increase
- however, some other parameters (air mass) determines the PM level too

# Frohnau Tower: Summer-winter ions percentages



# Summer-winter variation in background PM10

Less PM<sub>10</sub> in winter (or vice-versa more in summer):

species	Concentration in $\mu\text{g m}^{-3}$	Percentage based on annual mean
less PM10	4.3	25
less OC	1.8	120
less sulphate	1.8	60
less remainder <sup>a</sup>	1.2	25
less EC	0.2	30
less calcium	< 0.1	70
more seasalt <sup>b</sup>	0.6	80
more nitrate	0.6	60

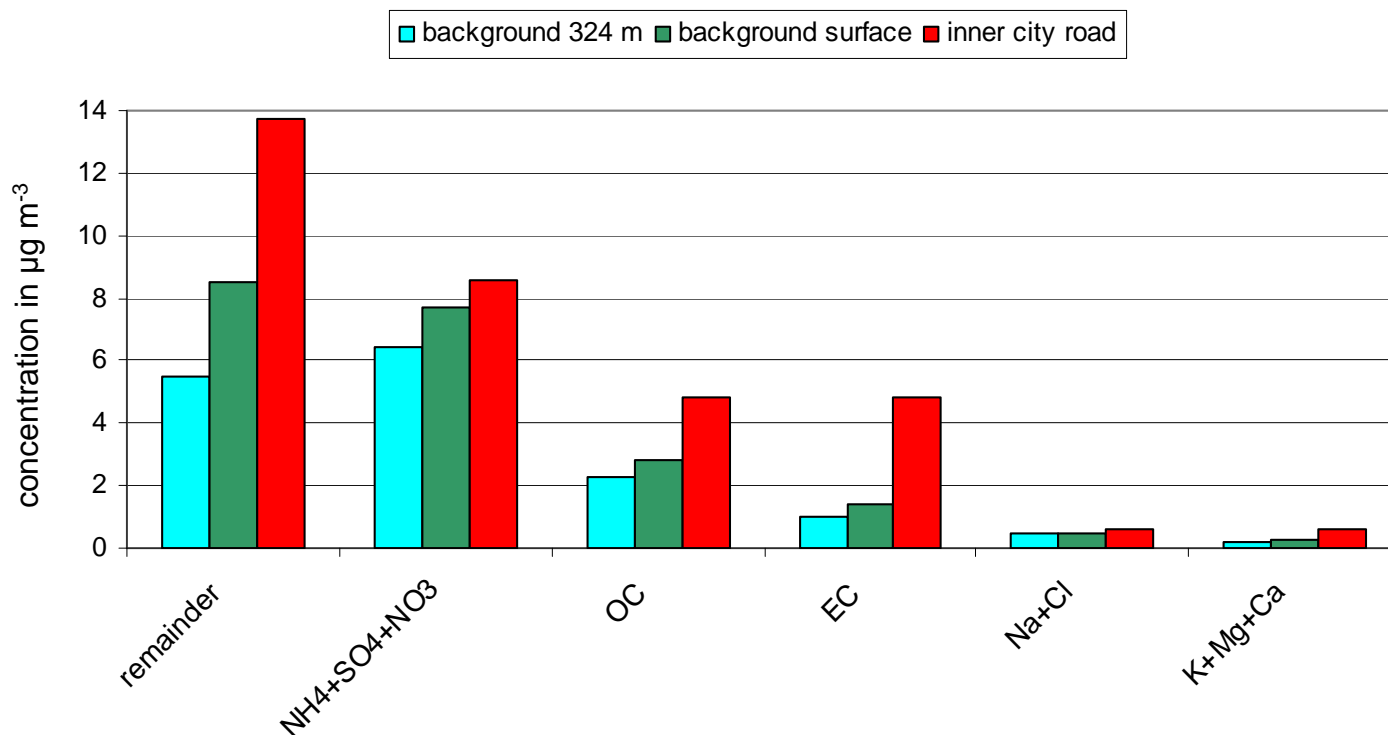
<sup>a</sup> not analyzed, i.e. insoluble fraction

<sup>b</sup> Na + Cl + Mg

**Conclusions:** In winter less photochemistry and hence less secondary PM (OC and sulphate) but also different air masses (west and no southeast) explaining differences in Ca, seasalt, nitrate and likely EC by long-range transport. Less soil dust due to wet surface.

# Group contribution to PM10 (Berlin/Brandenburg)

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



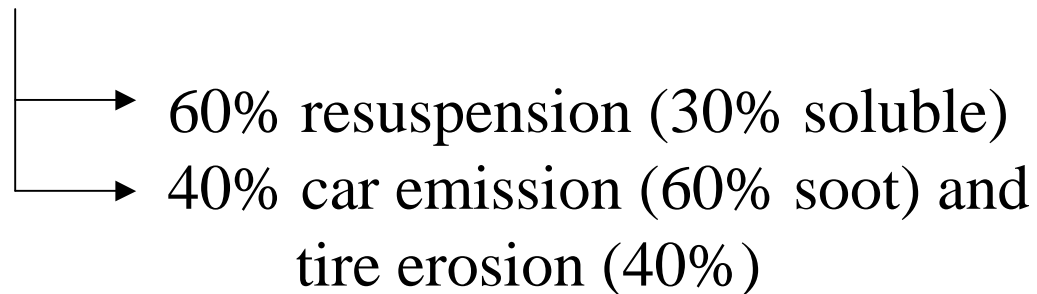
excess road (traffic) contribution: 6.0 µg m<sup>-3</sup> remainder (probably SiO<sub>2</sub> resuspension)  
3.0 µg m<sup>-3</sup> EC (probably direct emission)  
2.5 µg m<sup>-3</sup> OC (probably SOA from VOC emission)

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

# PM Conclusions:

City background: 80-90% from long-range transport  
10-20% from city sources

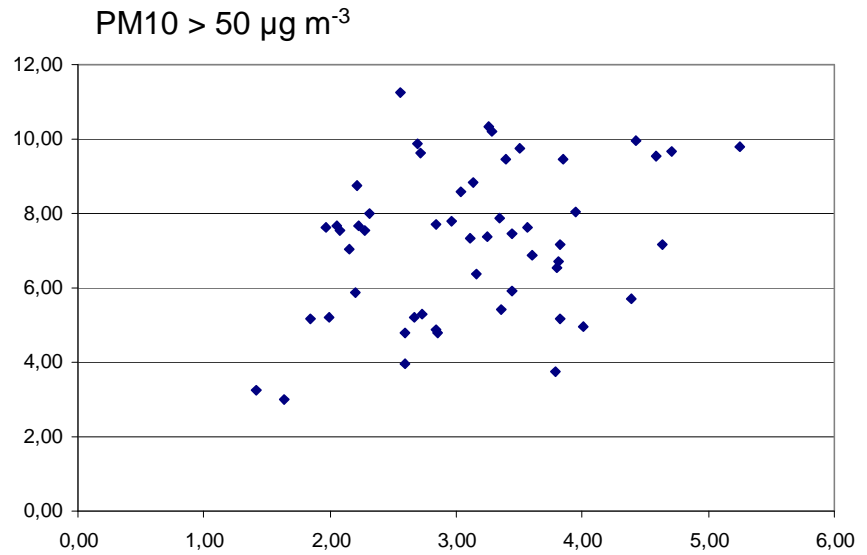
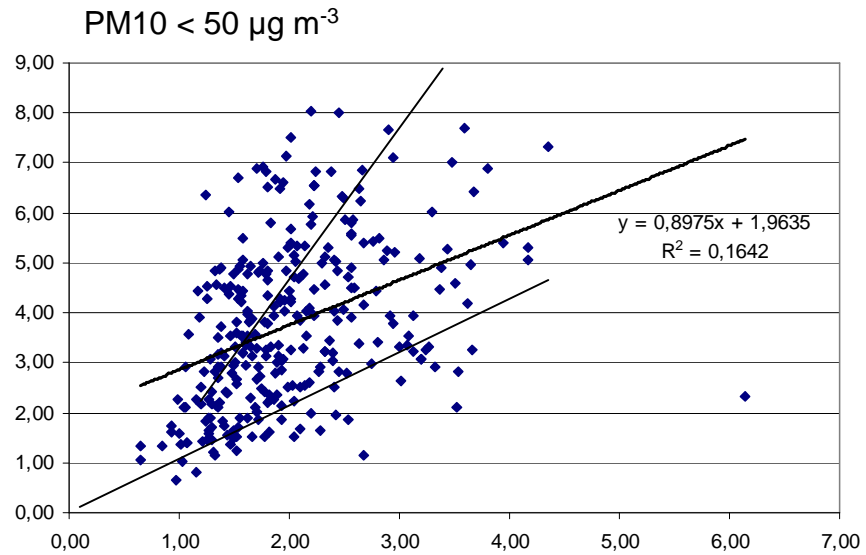
Traffic (road) : 60% from long-range transport  
10% city background  
30% local traffic contribution



Only 5-10% of street PM ( $2-3 \mu\text{g m}^{-3}$  soot) under principal technical air pollution control. Exceedance  $> 50 \mu\text{g m}^{-3}$ , however by

- a) dust resuspension in dry periods and
- b) long-range transport episodes

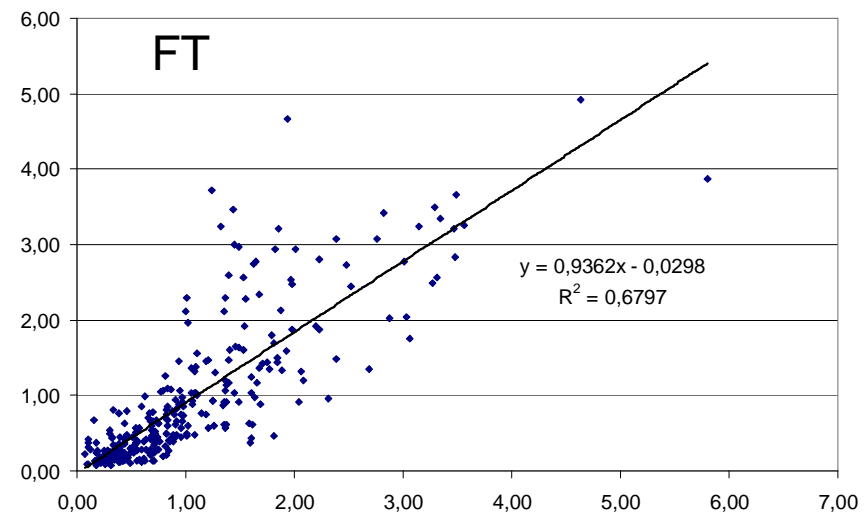
## 174 (Frankfurter Allee)



## EC (y) mit OC (x)

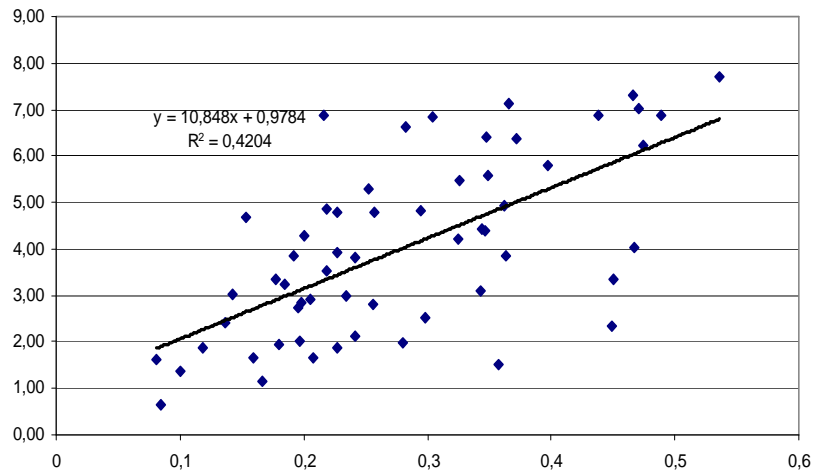
Die gute Korrelation zwischen EC und OC am FT (Hintergrund) bedeutet „gemeinsame Quelle“ und/oder „gemeinsamer Transport“ aus der Ferne.

Die schlechte bzw. fehlende Korrelation an der Straße bedeutet „Entkopplung“ und „Überlagerung“



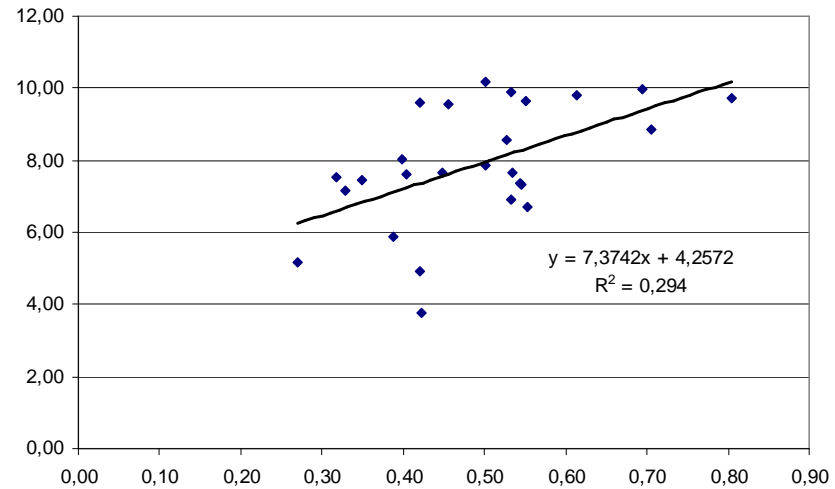
PM<sub>10</sub> < 50 µg m<sup>-3</sup>

174



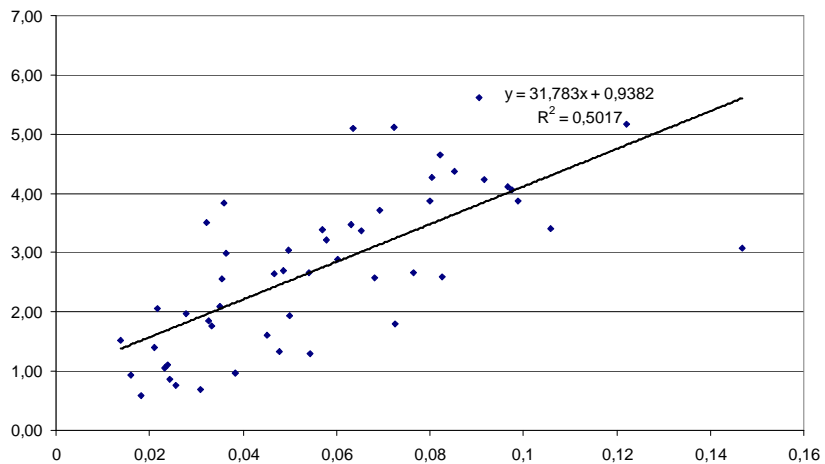
PM<sub>10</sub> > 50 µg m<sup>-3</sup>

EC mit Fe

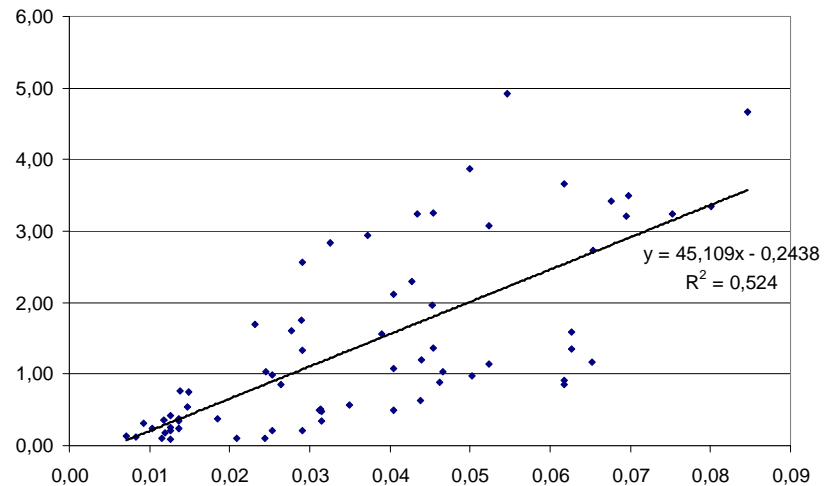


Eisen als Tracer für Kfz (?). Für Fe = 0 (nicht verkehrsverursacht) EC-Hintergrund von 0,5. Bei Überschreitungsepisoden jedoch EC = 4,3 µg m<sup>-3</sup>

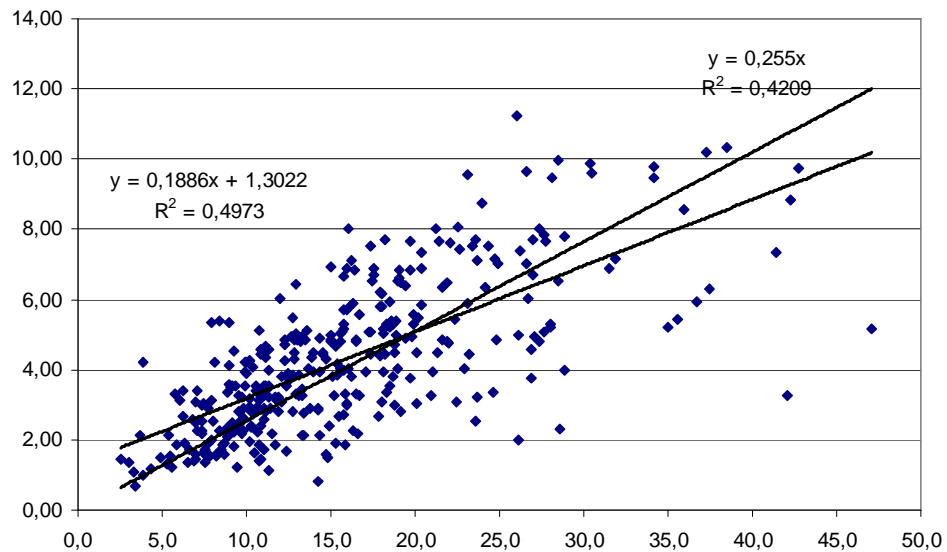
27



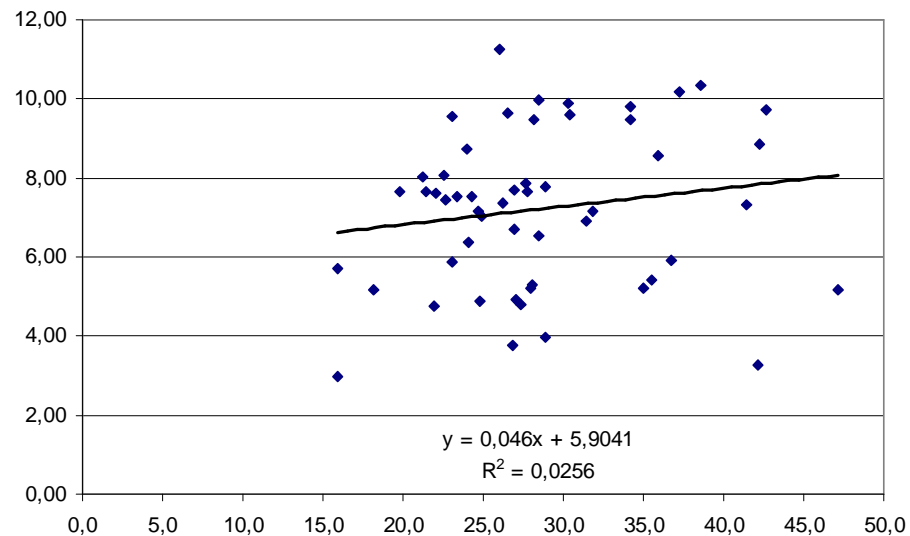
FT



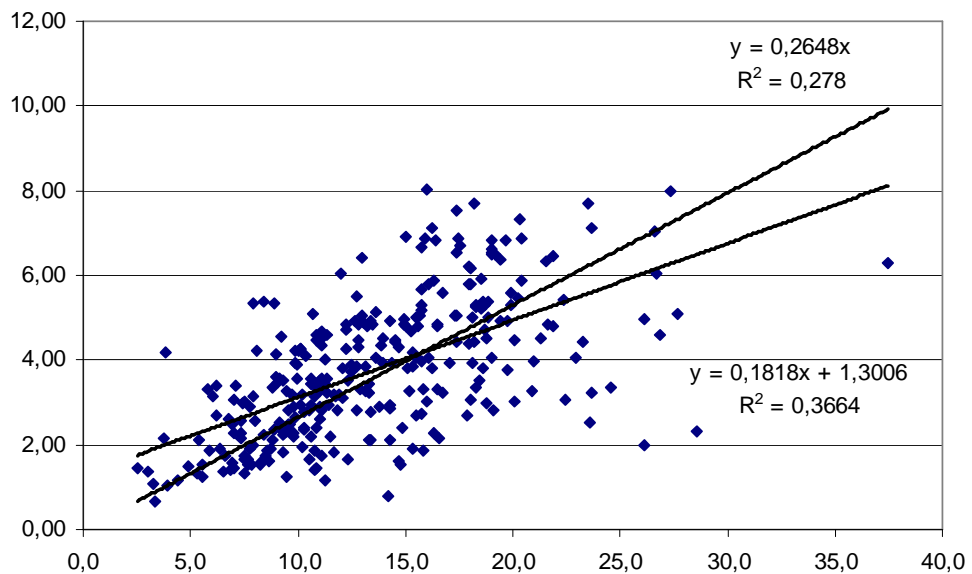
Alle Werte



Werte > 50  $\mu\text{g m}^{-3}$



Werte < 50  $\mu\text{g m}^{-3}$



Frankfurter Allee

Korrelation EC mit Rest

## Air mass and seasonal influence (concentration ratios)

	continental/maritime	winter/summer
Ammonia	3.6	0.7
Sulphate	3.1	0.5
Nitrate	0.8	1.9
Chloride	0.3	2.0
Sodium	0.1	5.0
Calcium	2.0	0.5
Sodium/chloride	2.4	0.4
Sulphate/ammonia	0.8	0.9
Sulphate/nitrate	3.8	0.3
Nitrate/ammonia	0.4	0.3

Nitrate large scale distributed; in winter larger than in summer

Ammonium sulphate continental and in summer larger than in winter

Chloride loss in summer and continental air masses larger

Summer-winter difference probably due to different air mass climatology

## Comparison of low and high dust Events

	PM10 < 50 $\mu\text{g m}^{-3}$						n
	PM	OC	EC	Fe	remaining	SO4 + NO3 + NH4	
FT (324 m)	15,1±10,1	0,9±0,9	0,9±0,9	0,04±0,02	5,1±4,7	6,3	322
27	20,4±10,5	1,6±0,8	1,7±1,1	0,06±0,03	7,2±5,6	7,6	340
174	29,1±10,1	2,0±0,7	3,8±1,6	0,28±0,11	12,0±5,4	7,8	301
	PM10 > 50 $\mu\text{g m}^{-3}$						
FT (324 m)	61,3±4,6	2,7±1,6	2,7±1,2	0,07±0,02	18±7	29,1	3
27	56,7±7,9	2,9±1,4	4,2±1,2	0,08±0,01	29±12	16,9	15
174	62,9±10	3,0±0,9	7,1±2,1	0,49±0,12	25±7	20,5	53
$\Delta$ (excess)	30-35	1-1,5	2,5-3	0,03-0,15	13-22	10-23	

## Conclusions:

- Concentration variation determined only by meteorological parameters influencing source strength and transport
- 93% of sulphate being  $(\text{NH}_4)_2\text{SO}_4$
- no correlation between nitrate and sulphate
- sulphate in summer significant larger than in winter, however, sulfate/ammonium ratio shows no seasonal variation
- Nitrate large scale distributed; in winter larger than in summer
- Ammonium sulphate continental and in summer larger than in winter
- Chloride loss in summer and continental air masses larger
- OC/EC in Summer by a factor 2 larger than in winter
- Exceedance given by long-range transport