PM_{10} AEROSOL MASS AND COMPOSITION IN AND AROUND BERLIN (GERMANY)

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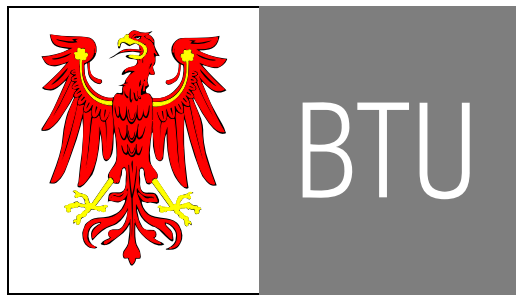


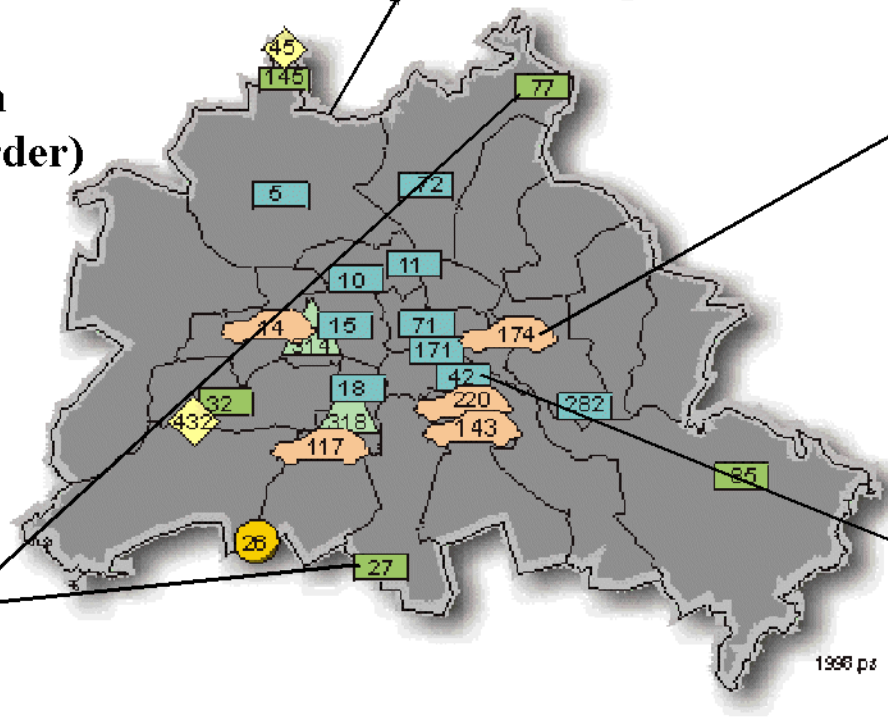
INTRODUCTION

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_{10} 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_{10} pollution limits. These limits were fixed at 50 µg/m^3 for the daily PM_{10} average and at 30 µg/m^3 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 PM10 pollution situation. Identical equipment (High Volume Samplers (Digitel 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^-, NO_3^-. SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^+, Ca^{2+}, 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



Radio tower Frohnau
altitude 320 m above ground

Rural back ground
Paulinenaue (50 km
West to the city border)

Traffic
Frankfurter Allee
(174)

Rural back ground
Hasenholz (50 km
East to the city border)

City back ground
Mariendorf (27)
Buch (77)

Urban background
Nansenstrasse (42)

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 µm.
- 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_2, O_3, NO, etc.)
   - aerosol characteristics (number, size resolution, etc.)
   - meteorological parameters (wind, temperature, etc.)
4. Total PM mass (gravimetric)
5. Chemical analysis
   - inorganic ions (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+})
   - trace metals (Fe, Cu, Zn, etc.)
   - EC (soot)
   - organics (OC, group components, single components)

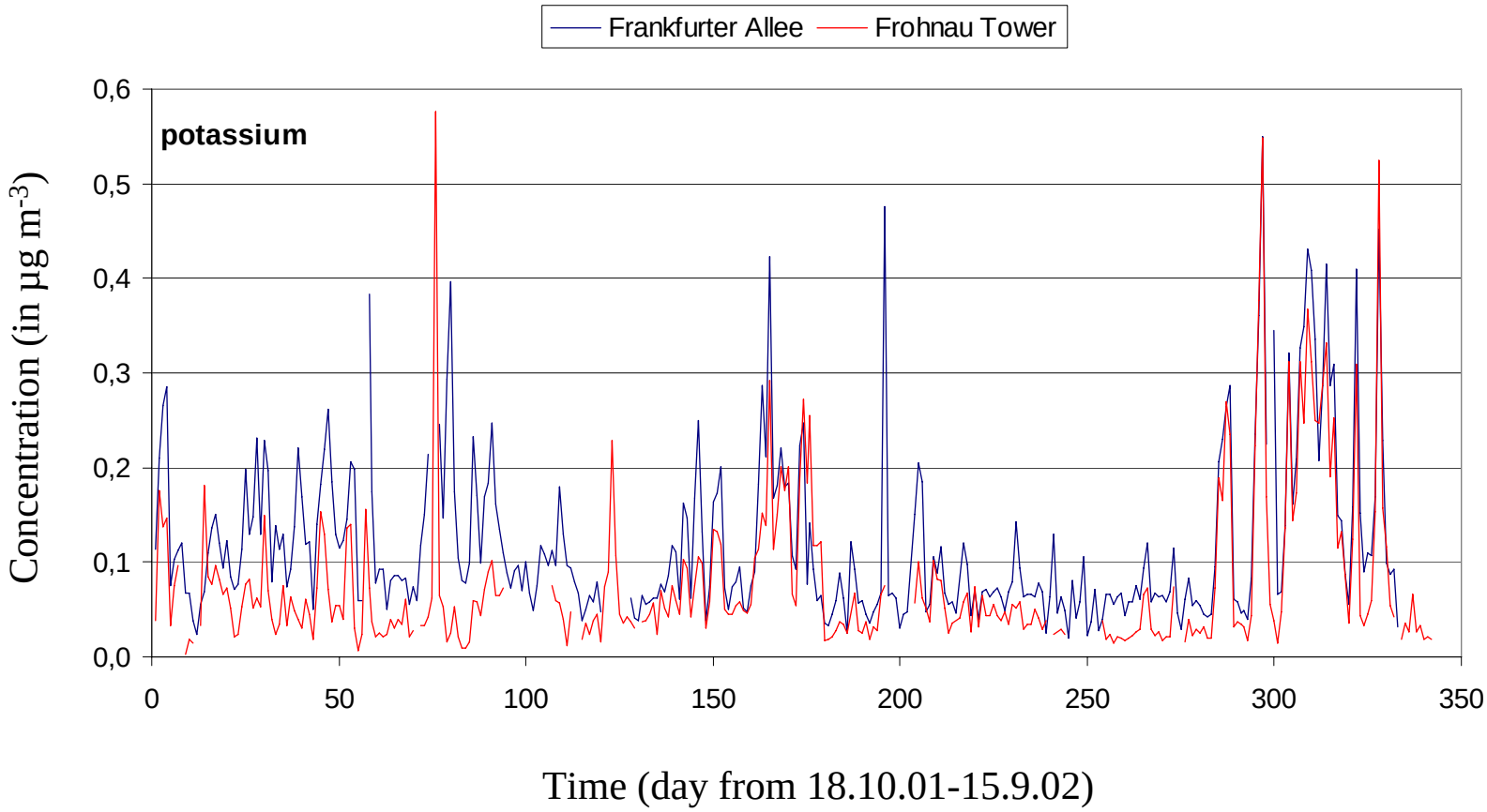
Origin of PM species

PM species	transfer	primary species	source
SO_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	traffic, 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

Analysis of PM data

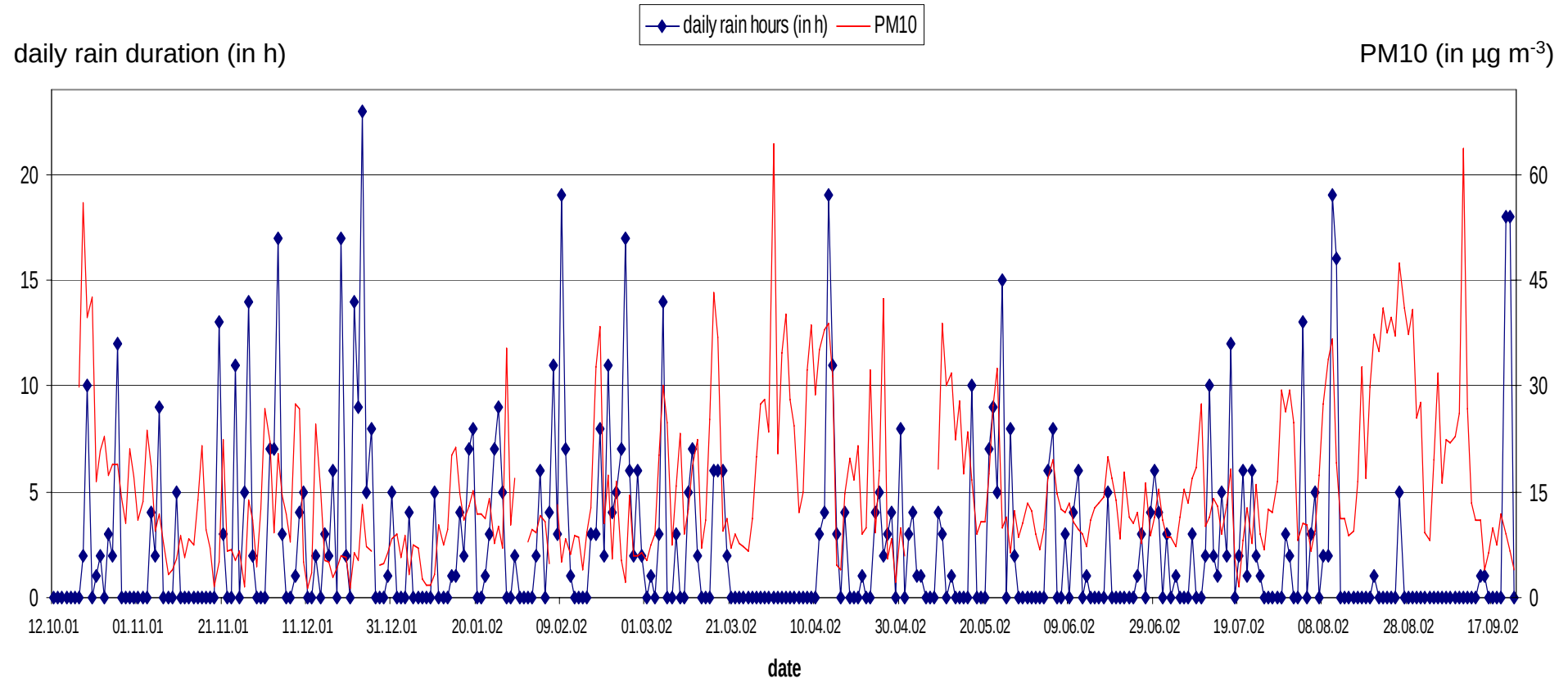
1. Analysis of temporal variation
   - cycles (?): diurnal, seasonal
   - episodes (pollution events, air masses)
   - trends (pollution abatement, climate)
2. Size resolution frequencies (if available)
   - origin of species
3. Correlation between stations (if existing)
   - homogenity of concentration 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)

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



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

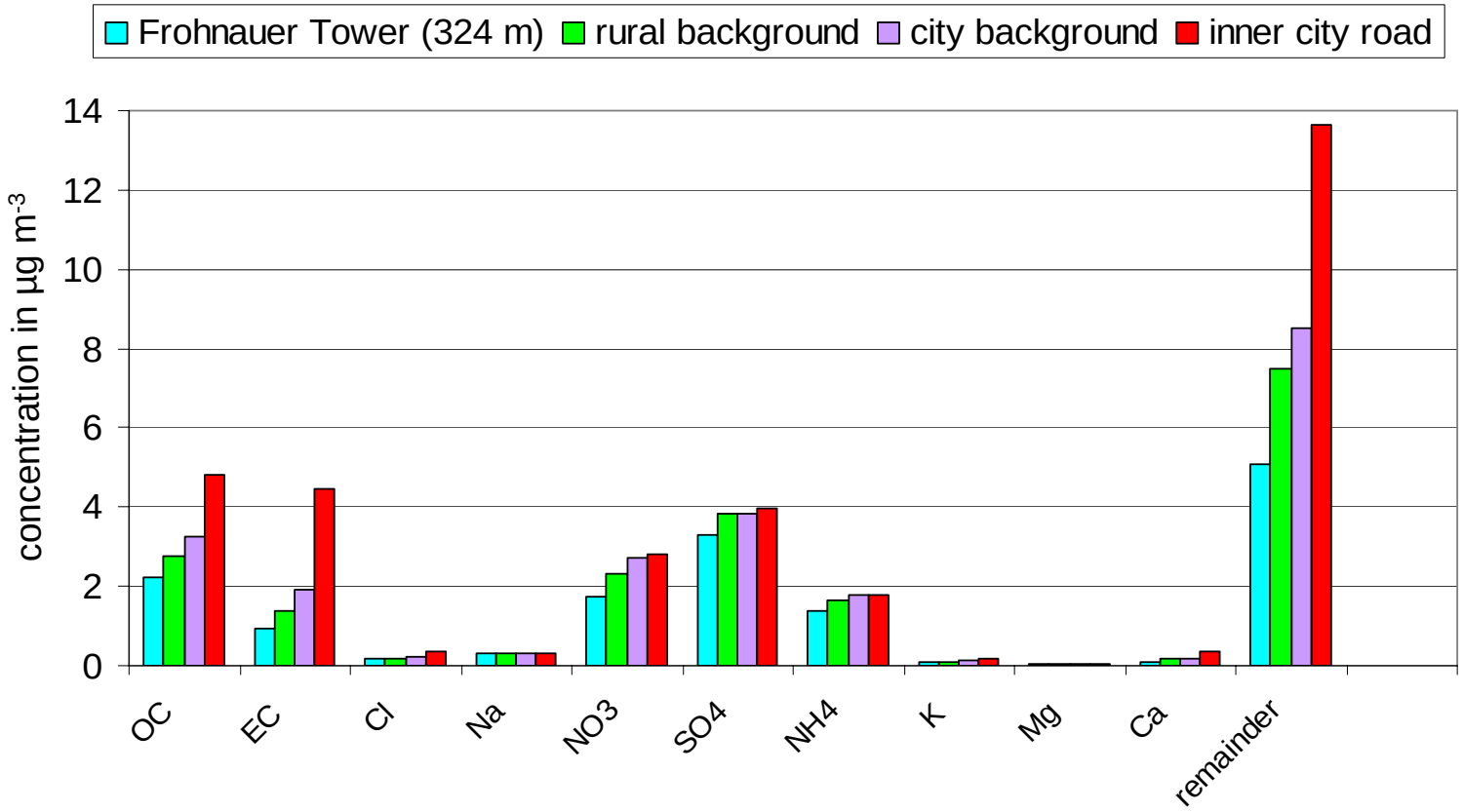
Rain duration and PM10 at Frohnauer Tower



- 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

Chemical composition of PM10 in Berlin/Brandenburg

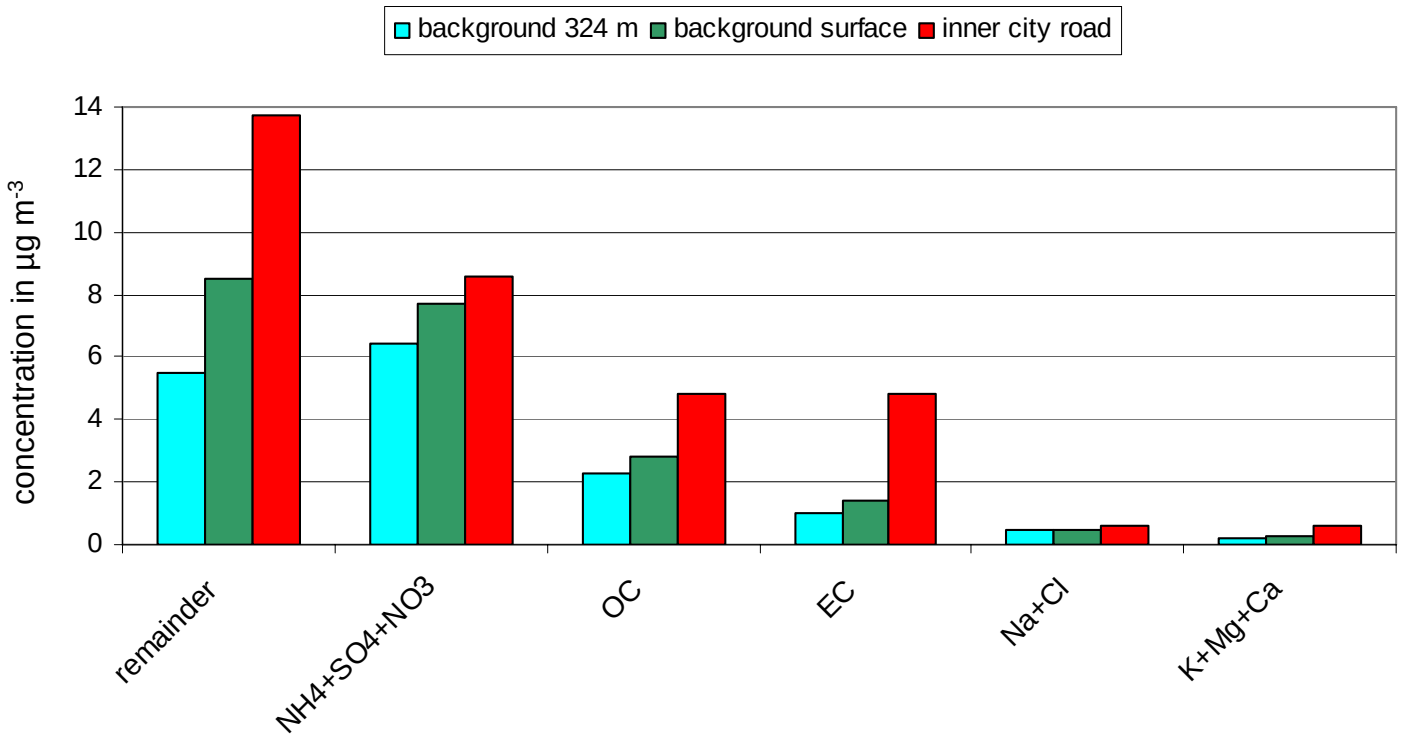
(daily PM High-Vol (digitel) sampling September 2001 – September 2002)



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)

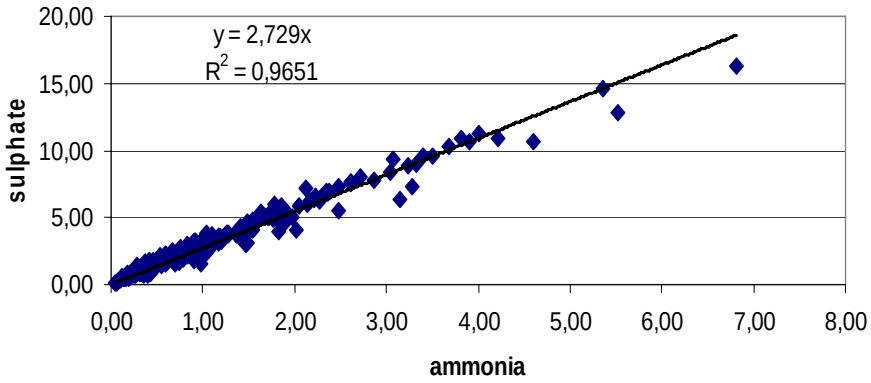


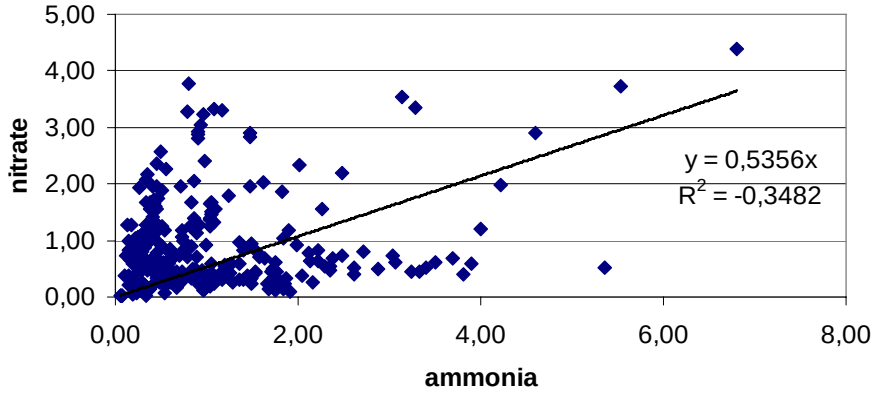
excess road (traffic) contribution: 6.0 µg m^{-3} remainder (probably SiO_2 resuspension)
3.0 µg m^{-3} EC (probably direct emission)
2.5 µg m^{-3} OC (probably SOA from VOC emission)

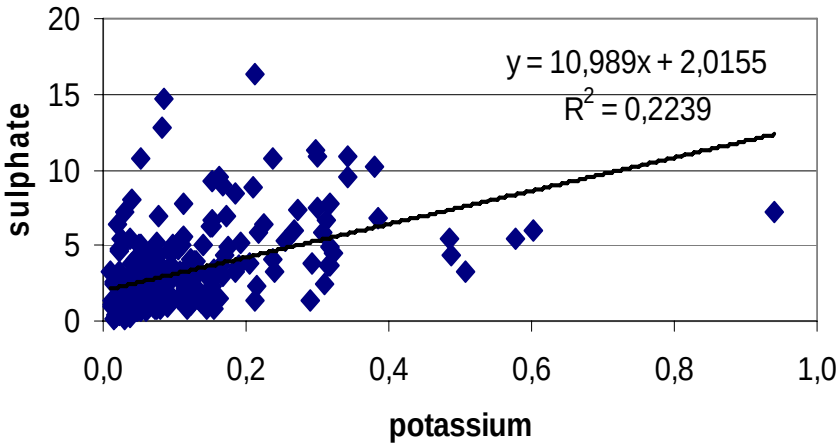
(Note: This excess PM is observed only at very busy streets. Difference between city background and rural background is not significant)

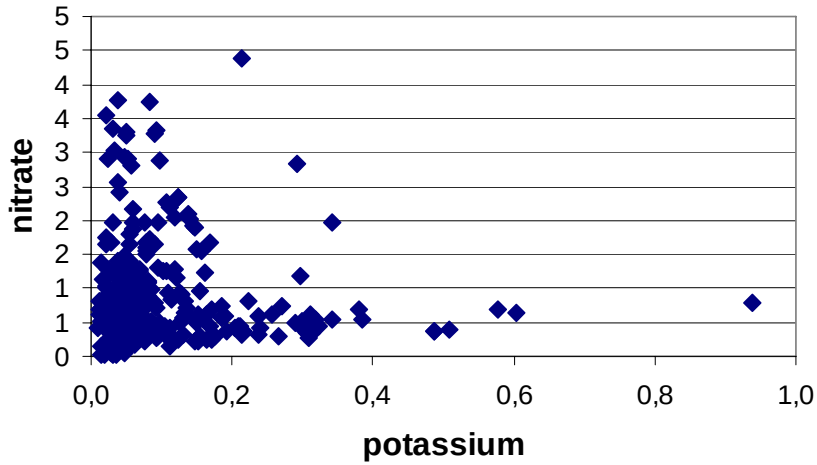
Frohnau Tower: correlations between ions

(concentration basis µg m^{-3})

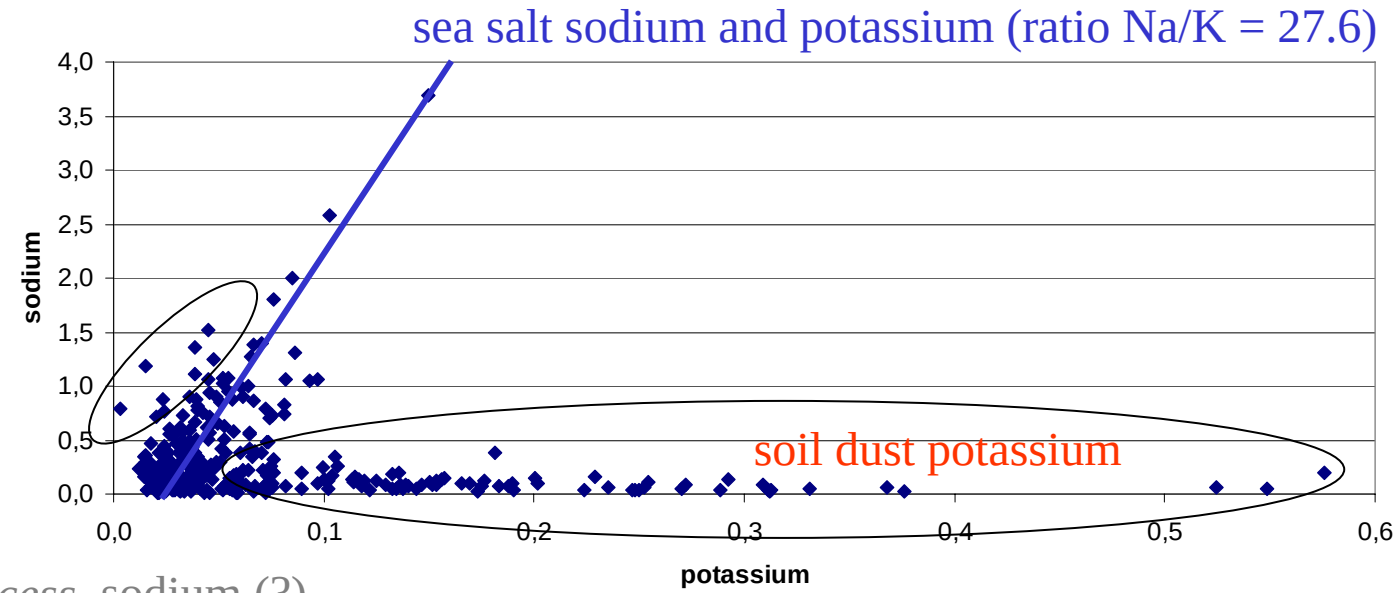








Example for deduction of different origin

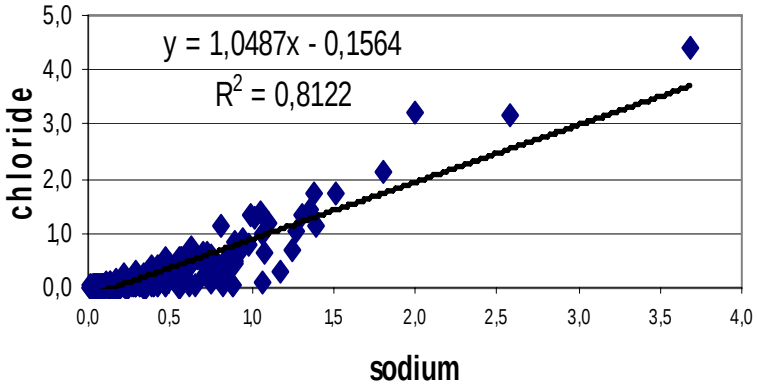


excess sodium (?)

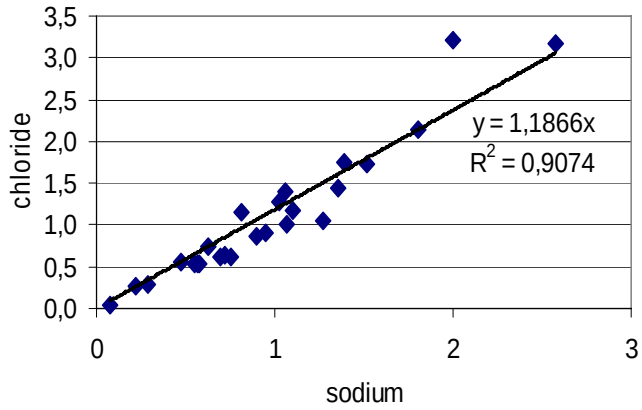
Excess sodium is not likely but could be possible (known from aride soils, flue ash) in small quantities.

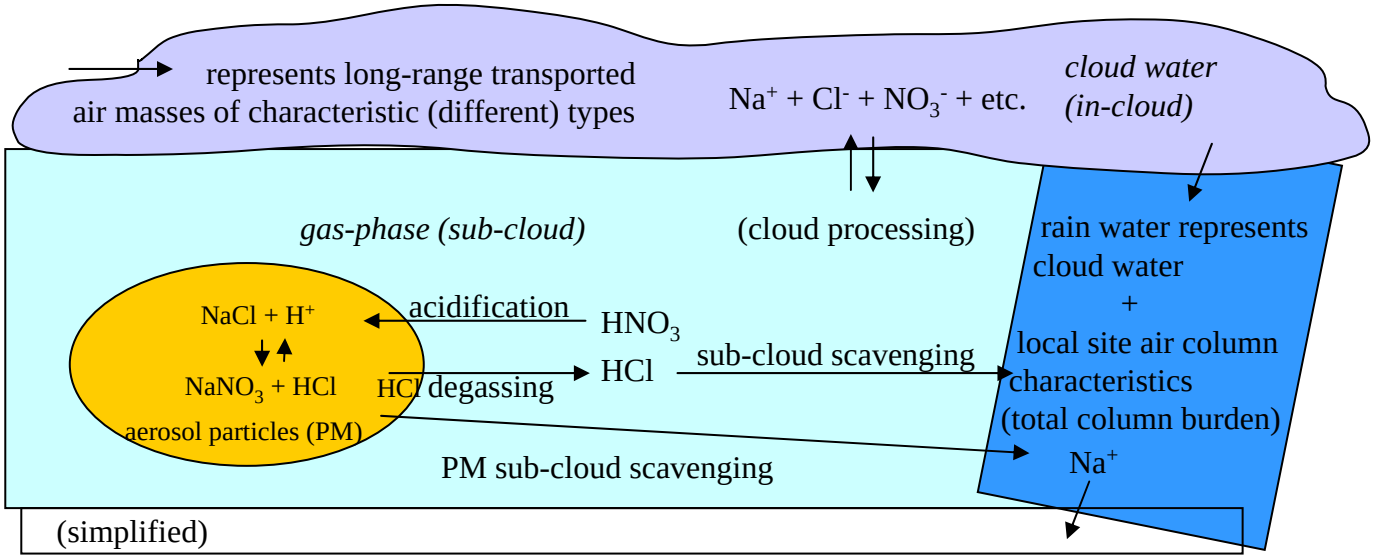
Frohnau Tower: Sea salt species (Na – Cl)

All samples (n = 327)



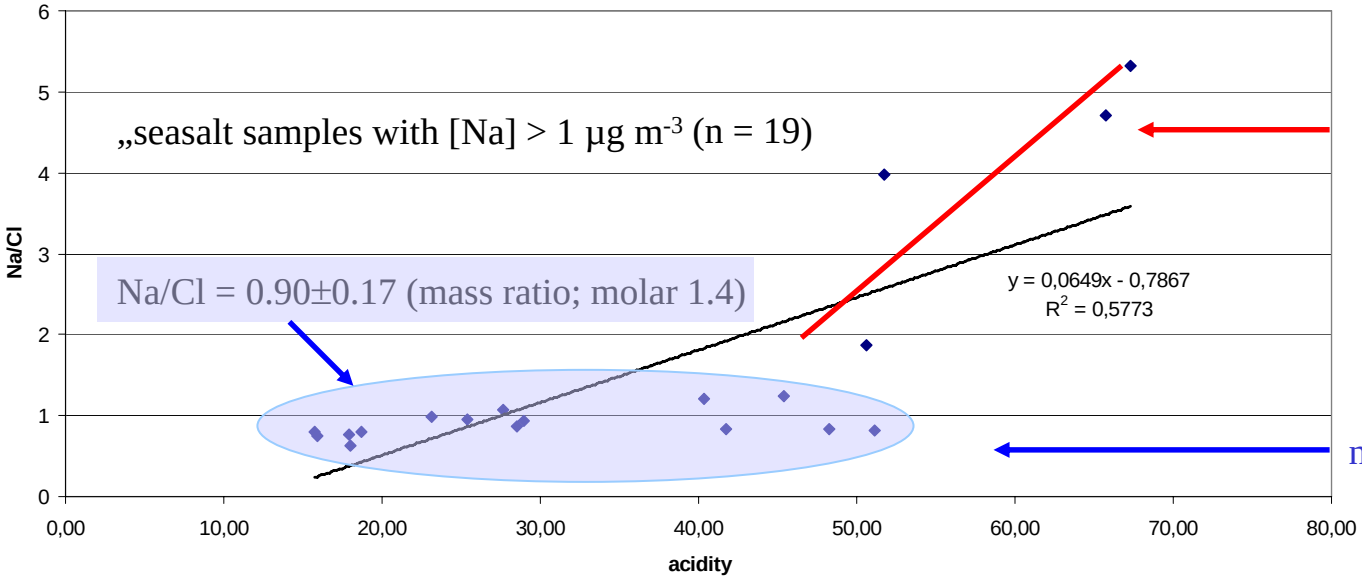
Maritime air masses (n =25)





> 50% Cl lost !

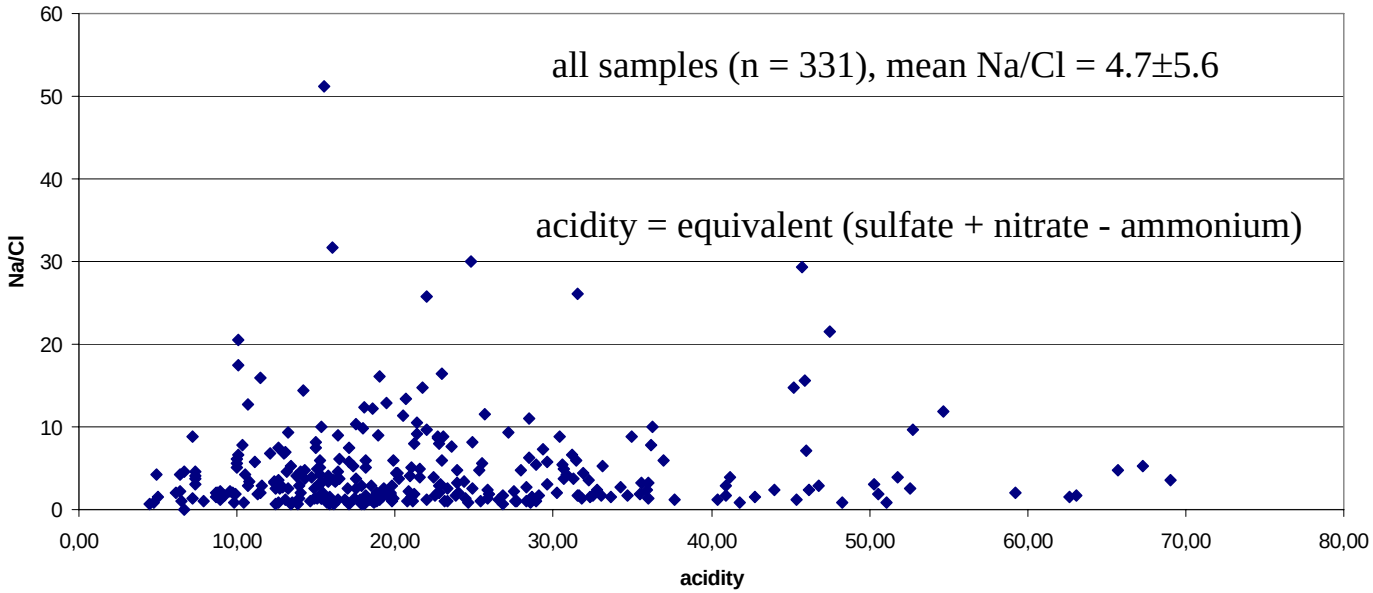
Chlorine degassing from particulate matter?



man-made degassing (?)

natural degassing („standard“)

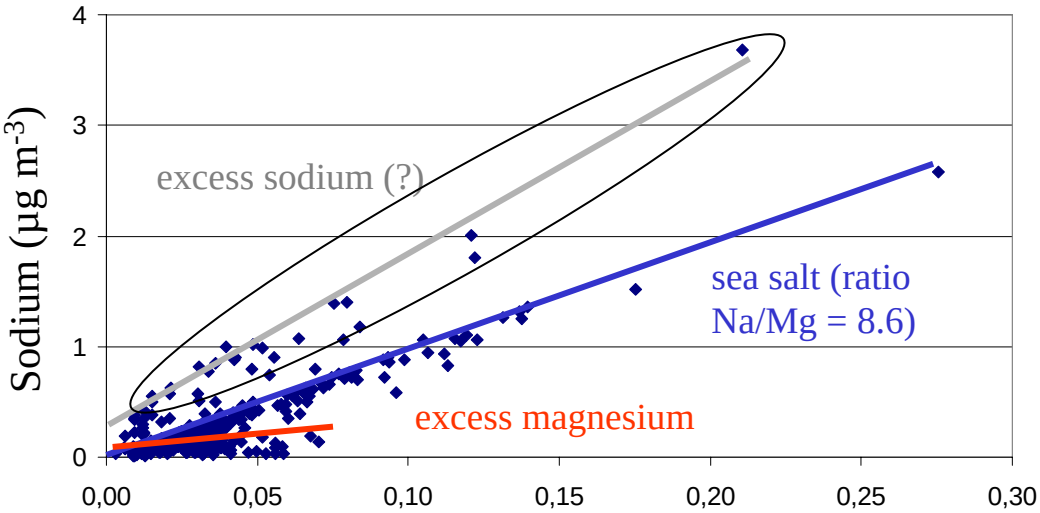
Na/Cl mass ratio



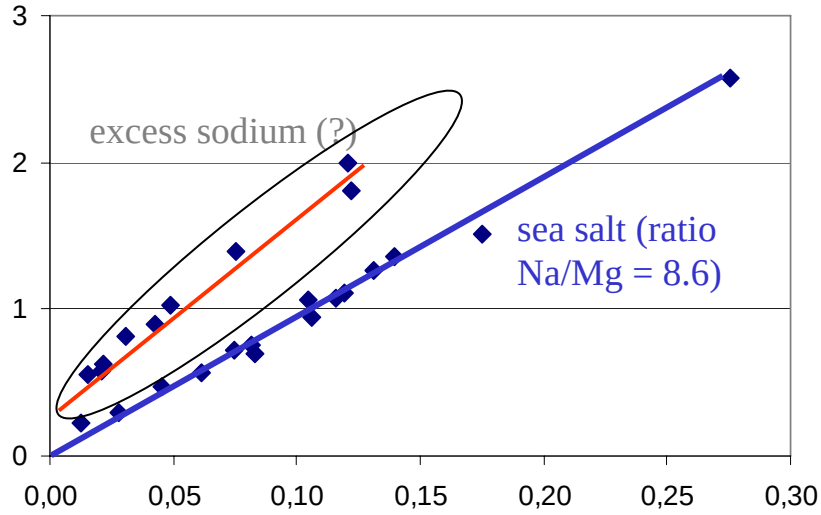
Cl degassing on continental PM samples could be an artefact due to simultaneous particles collection on the filter with different acidity as well as gaseous HNO_3 adsorption.

Frohnau Tower: Sea salt species (Na – Mg)

All samples (n = 327)



Maritime air masses (n =25)



Magnesium (µg m-3)

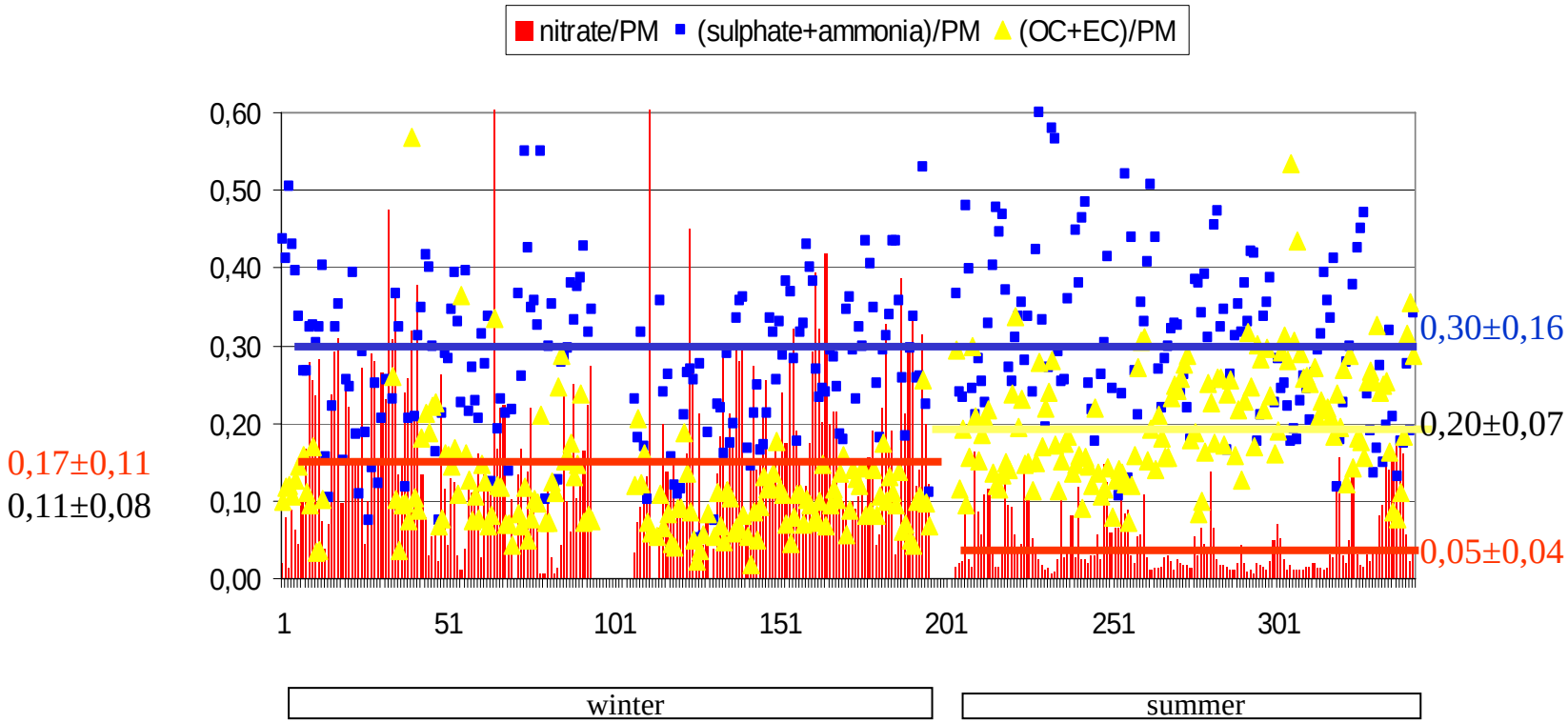
Again a sample collective have been found with high correlation betwen Na and Mg suggesting excess sodium or loss of magnesium. Further studies of those events concerning meteorological influences are needed.

Frohnau Tower: different sample collectives (in mg m^{-3})

Sample collective	n	PM_{10}	OC	EC	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na	K	Mg	Ca
„sea salt“ (maritime)	25	8.1	0.76	0.23	1.11	1.10	1.06	0.32	0.98	0.05	0.09	0.06
„continental“	243	14.3	2.28	0.90	0.13	0.90	3.28	1.15	0.28	0.08	0.04	0.12
„continental“ Na/Cl high	160	13.5	2.05	0.83	0.05	0.85	3.29	1.15	0.24	0.07	0.04	0.11
„continental“ Na/Cl low	91	14.1	1.86	0.95	0.29	0.90	2.84	1.00	0.36	0.08	0.04	0.12

sample collective	n	PM_{10}	OC	EC	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na	K	Mg	Ca
winter	143	10.5	0.6	0.6	0.40	1.22	2.15	0.80	0.47	0.06	0.05	0.07
summer	138	14.8	2.4	0.8	0.08	0.63	3.93	1.32	0.24	0.09	0.04	0.15

Frohnau Tower: Summer-winter ions percentages



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

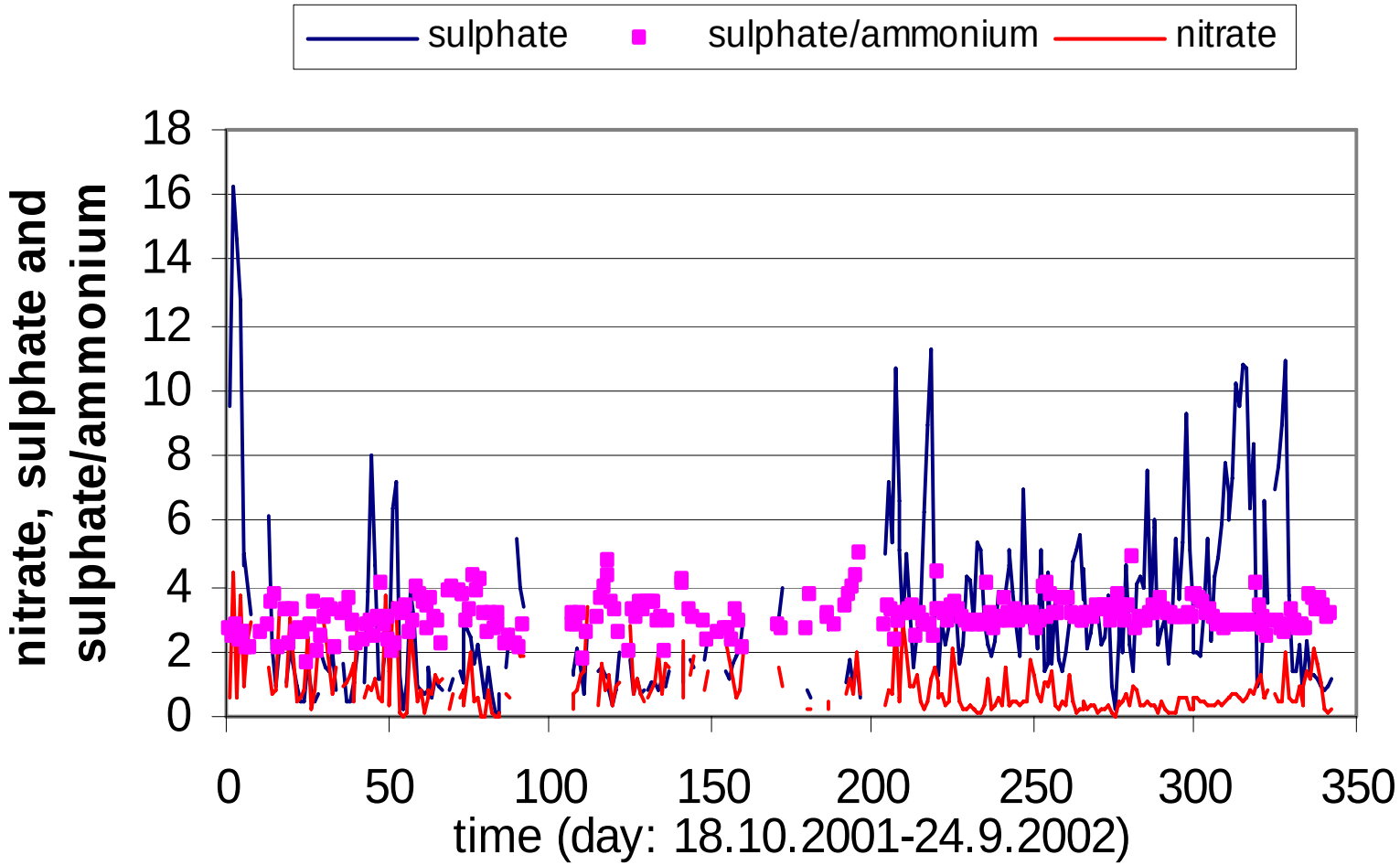
„Acidification“ of PM_{10} (Frohnau Tower)

Equivalent contribution to aeorosol (in µeq m^{-3})

	„continental“	„marine“	
nitrate	14.5	17.7	
nss sulphate	66.8	16.4	
ammonium	63.9	17.8	
calcium	6.0	3.0	
nss-potassium	1.8	0.3	
nss-magnesium	0.8	0.0	
acid difference	8.8	13.0	(mainly by nitrate?)

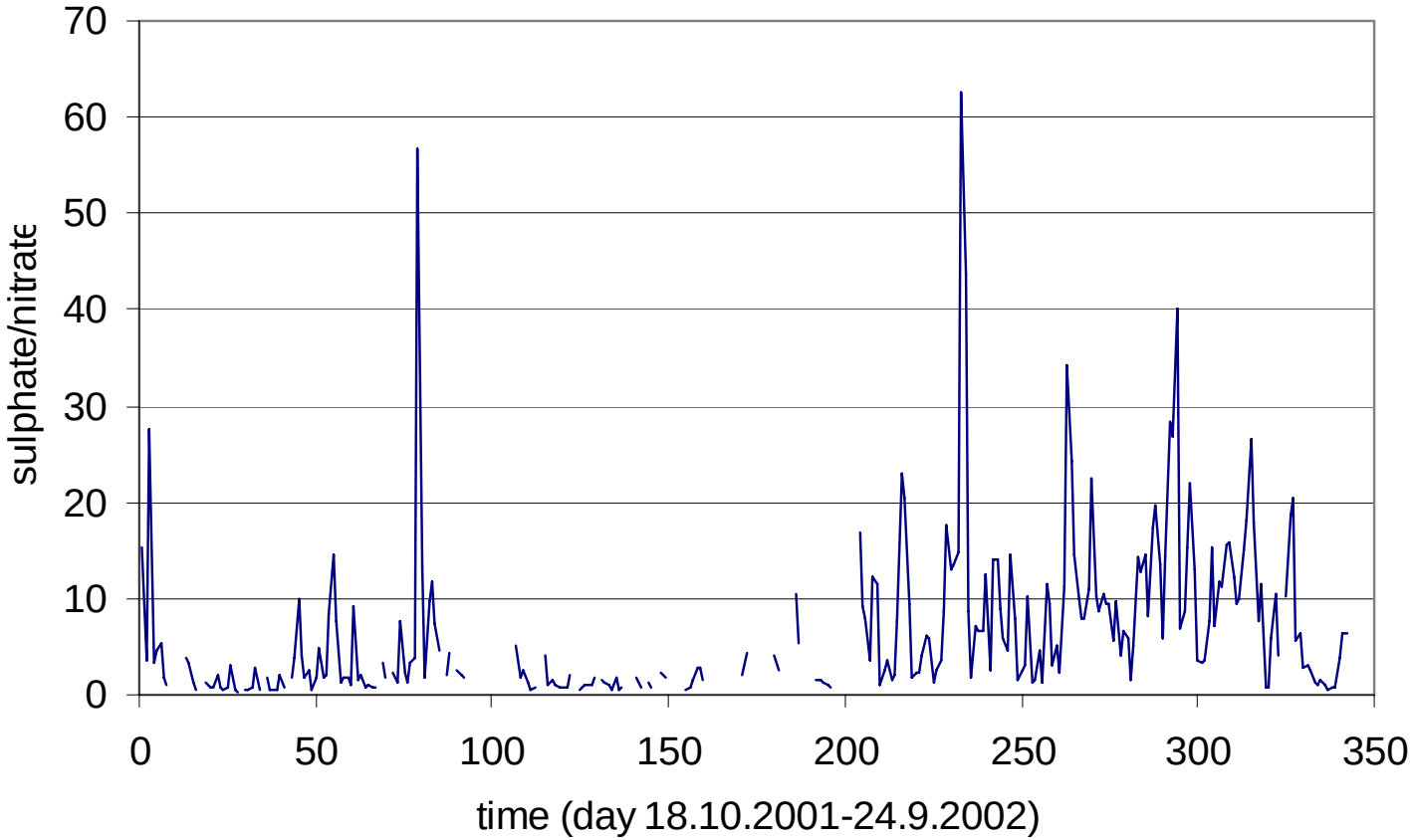
Behaviour of nitrate and sulphate (1)

Frohnau Tower

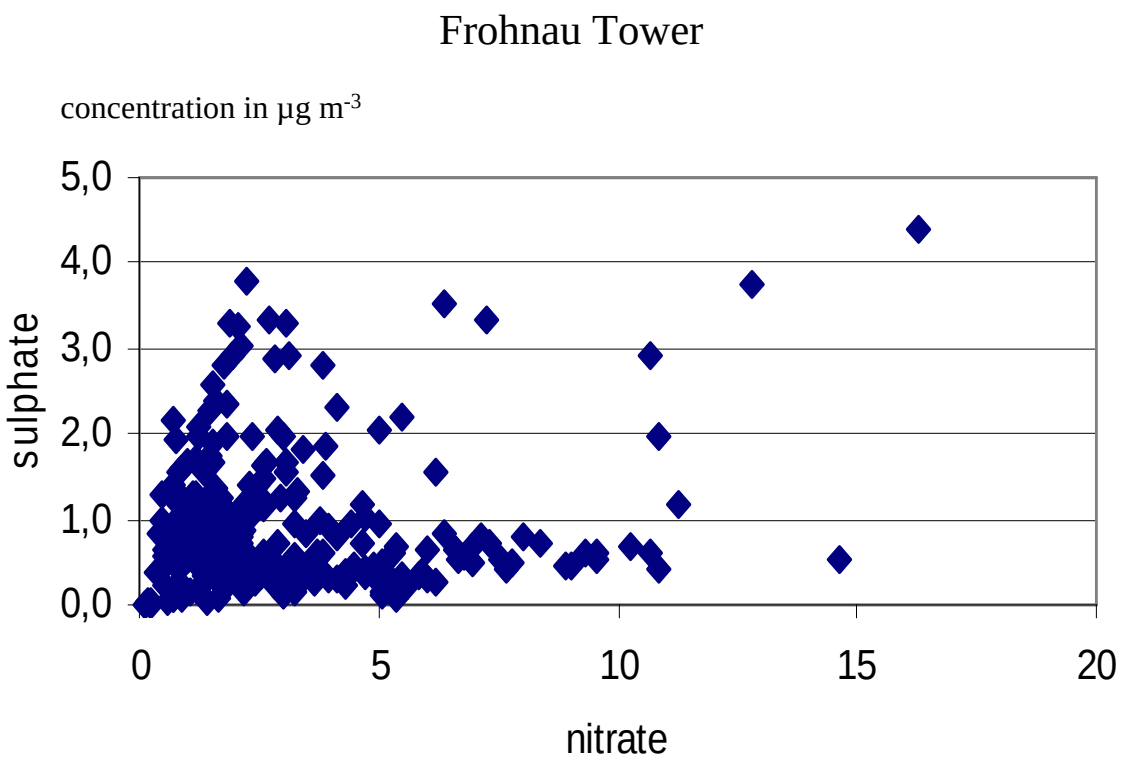


Behaviour of nitrate and sulphate (2)

Frohnau Tower



Behaviour of nitrate and sulphate (3)



- 93% of sulphate being $(NH_4)_2SO_4$
- no correlation between nitrate and sulphate
- sulphate in summer significant larger than in winter, however, sulfate/ammonium ratio shows no seasonal variation

PM chemistry on street level

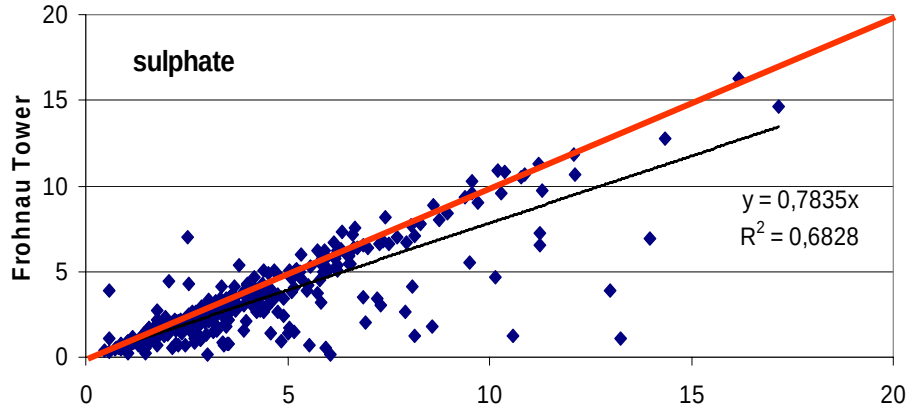
Berlin high traffic area
Berlin low traffic area
Brandenburg suburban

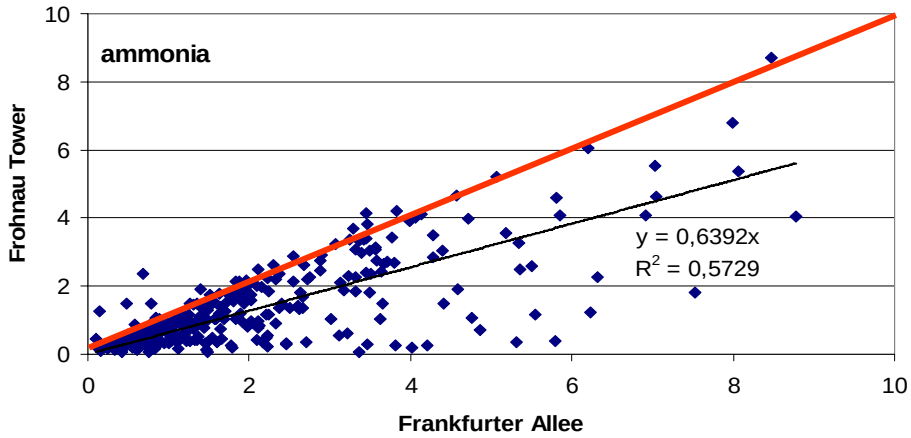
Comparison of means from different stations (in mg m^{-3})

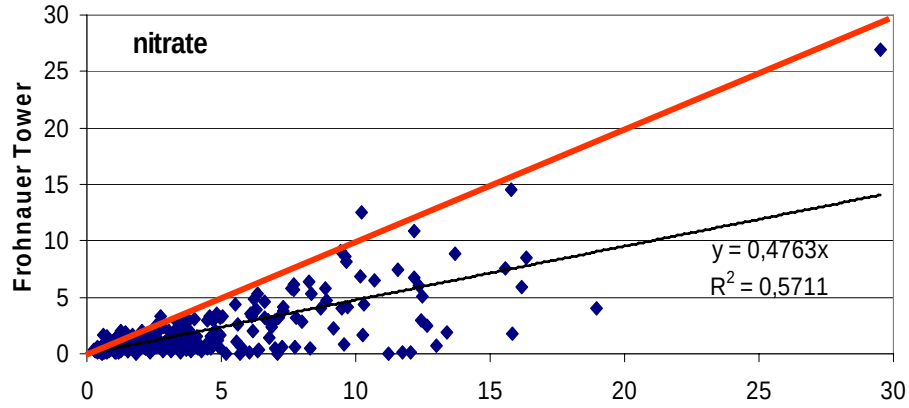
station	PM_{10}	OC	EC	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na	K	Mg	Ca	periode
Frohnau Tower	15,5	2,25	0,94	0,19	1,74	3,32	1,36	0,32	0,08	0,04	0,11	18.10.01-24.9.02
Buch (77)	21,9	3,32	1,78	0,11	1,96	4,25	1,79	0,22	0,11	0,04	0,16	14.9.01-15.9.02
Hasenholz	20,4	2,68	1,40	0,11	1,65	4,04	1,53	0,30	0,10	0,05	0,19	6.2.02-30.9.02
Paulinen-aue	20,1	2,84	1,32	0,21	2,98	3,64	1,76	0,34	0,09	0,05	0,16	4.1.02-15.9.02
Nansenstr. (42)	24,4	3,37	2,15	0,30	2,95	3,62	1,78	0,29	0,14	0,04	0,19	14.9.01-11.11.02
Beuselstr.	31,3	5,35	4,63	0,22	2,04	3,73	1,59	0,18	0,30	0,05	0,32	10.7.02-1.11.02
Frankfurter Allee (174)	34,5	4,27	4,27	0,50	3,59	4,10	1,99	0,34	0,20	0,05	0,42	14.9.01-15.9.02
Group means	21,7 ± 2,0	3,05 ±0,34	1,66 ±0,38	0,19 ± 0,07	2,26 ± 0,66	3,81 ± 0,32	1,69 ± 0,21	0,28 ± 0,06	0,10 ± 0,20	0,05 ± 0,01	0,16 ± 0,03	

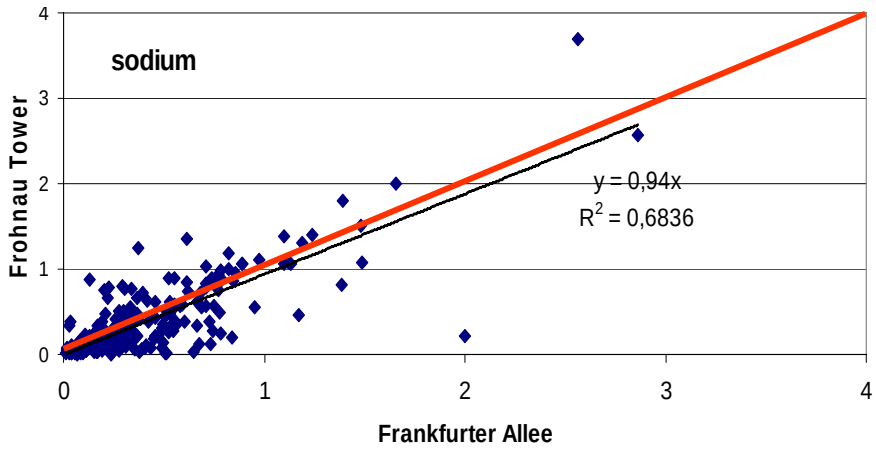
Correlation between tower altitude and street traffic level (1)

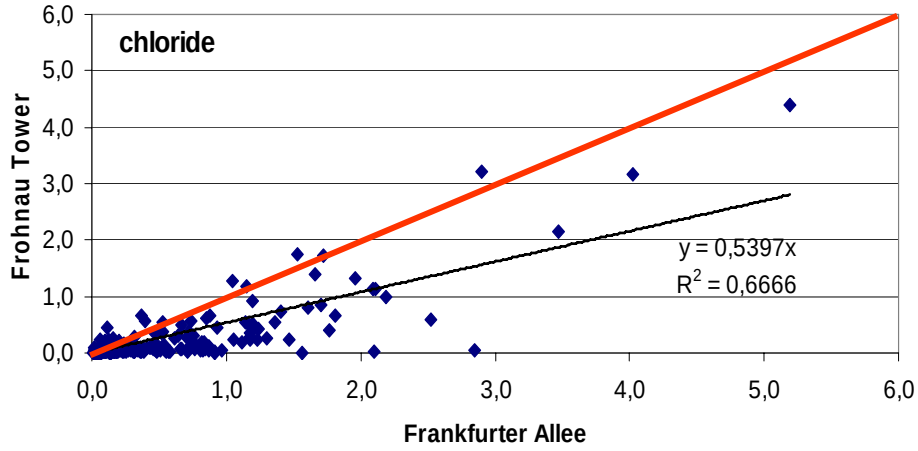
Traffic contribution to nitrate, chloride, ammonium and sulphate is clearly shown. Sodium (seesalt) is homogeneously distributed.



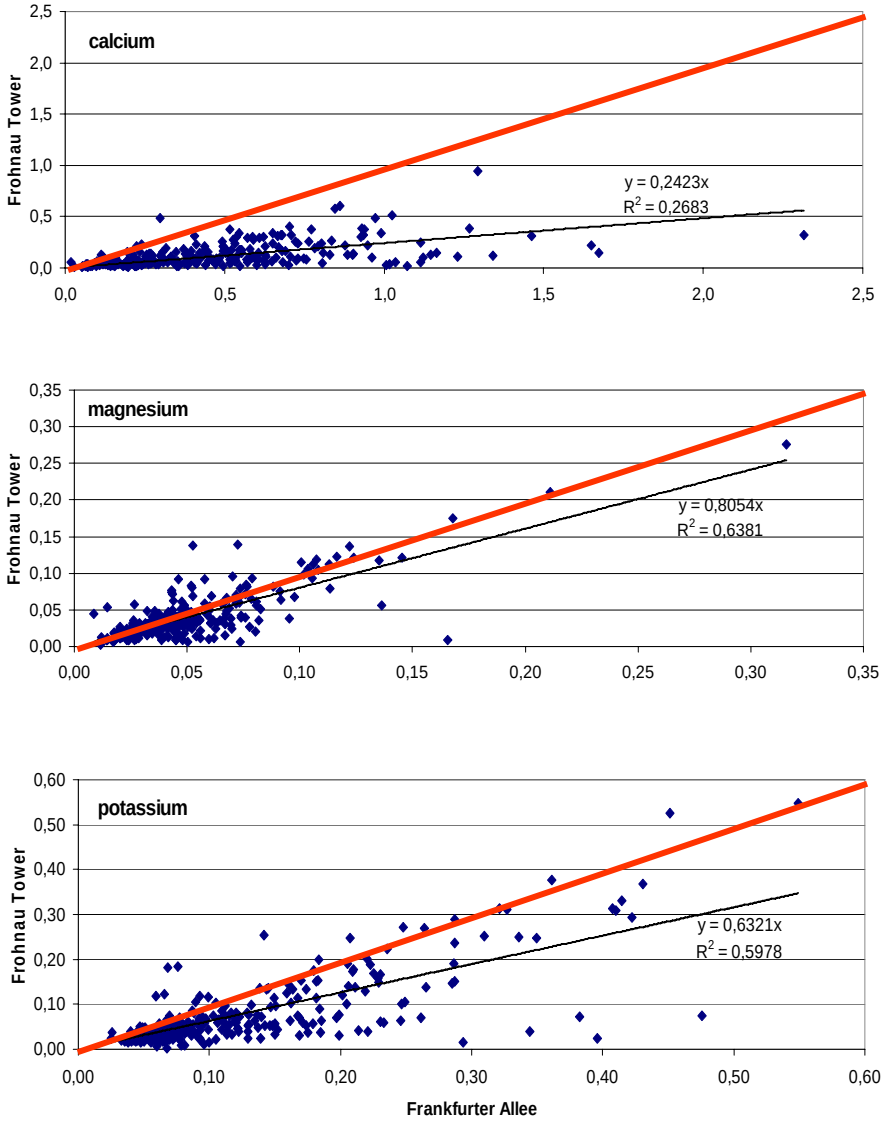








Correlation between tower altitude and street traffic level (2)



Traffic contribution to calcium and potassium is clearly shown. Both species are among resuspension dust. However, potassium as a typical soil constituent, may also of rural origin.

Magnesium (seesalt) is rather homogeneously distributed, but some events with excess magnesium are occurring.

Background level before 1990: 40

Background level around 1995: 20

(reduction due to less coal combustion and desulphurization)

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

Background 20 µg m^{-3}:

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

Road traffic + (10-15) µg 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)

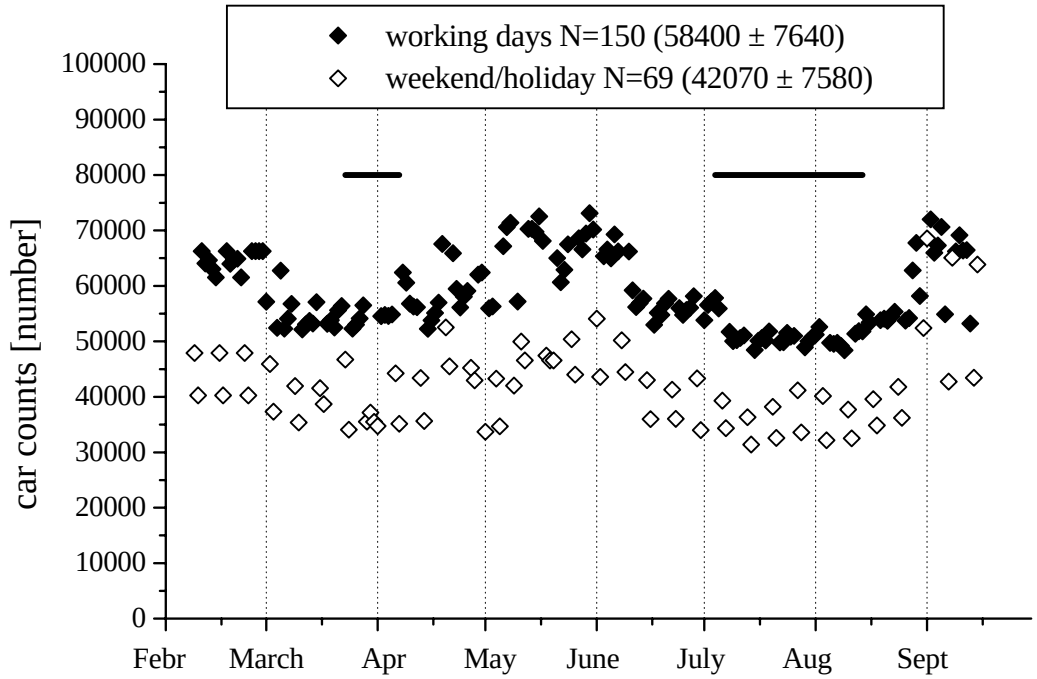
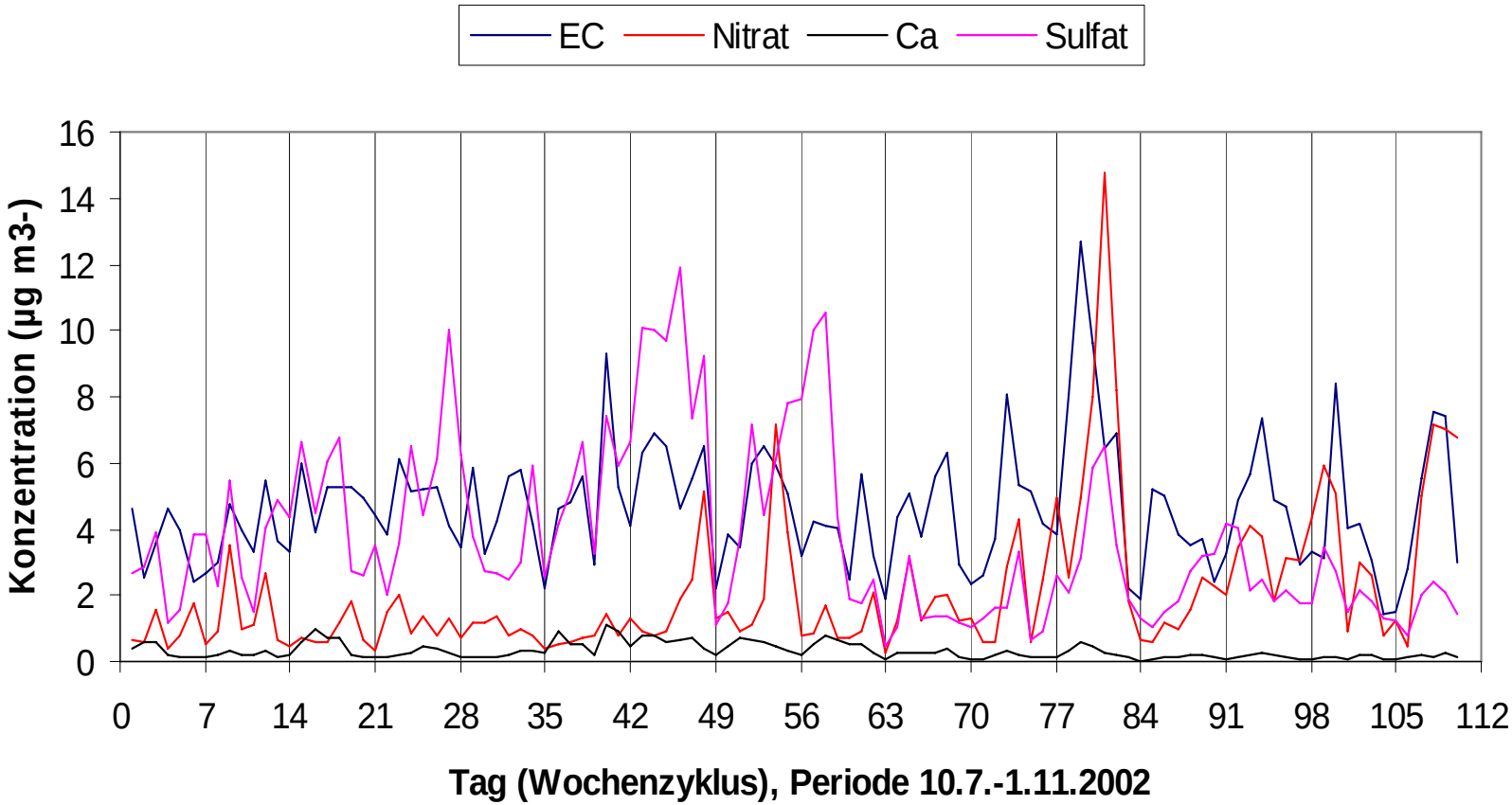


Fig. 1 Number of cars in the city centre in 2002, site Frankfurter Allee (174)

This Figure shows the weekly variations (maximum at working days and minimum at weekend) of the car numbers passing the Frankfurter Allee in both directions

Wochenzyklus Beuselstraße



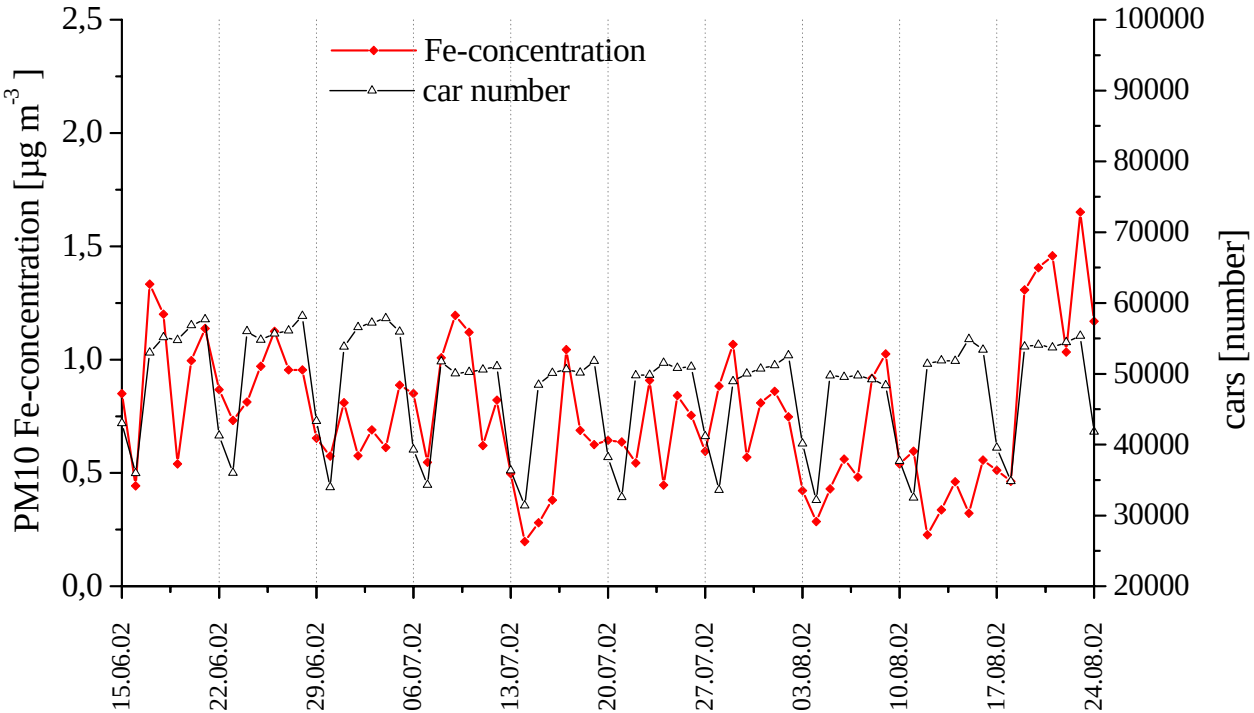


Fig. 2 Fe-PM10 concentration and car-counts at the site Frankfurter Allee in the city centre (June-August 2002)

The iron content of the PM10 aerosol indicates, more than the EC and OC concentrations, that generally the traffic was the main source for the higher aerosol mass concentrations in the city centre (no iron and steel industry in Berlin). There was no linear correlation between the iron concentration and the car numbers, because meteorological effects like rain and strong wind will influence the iron concentration.

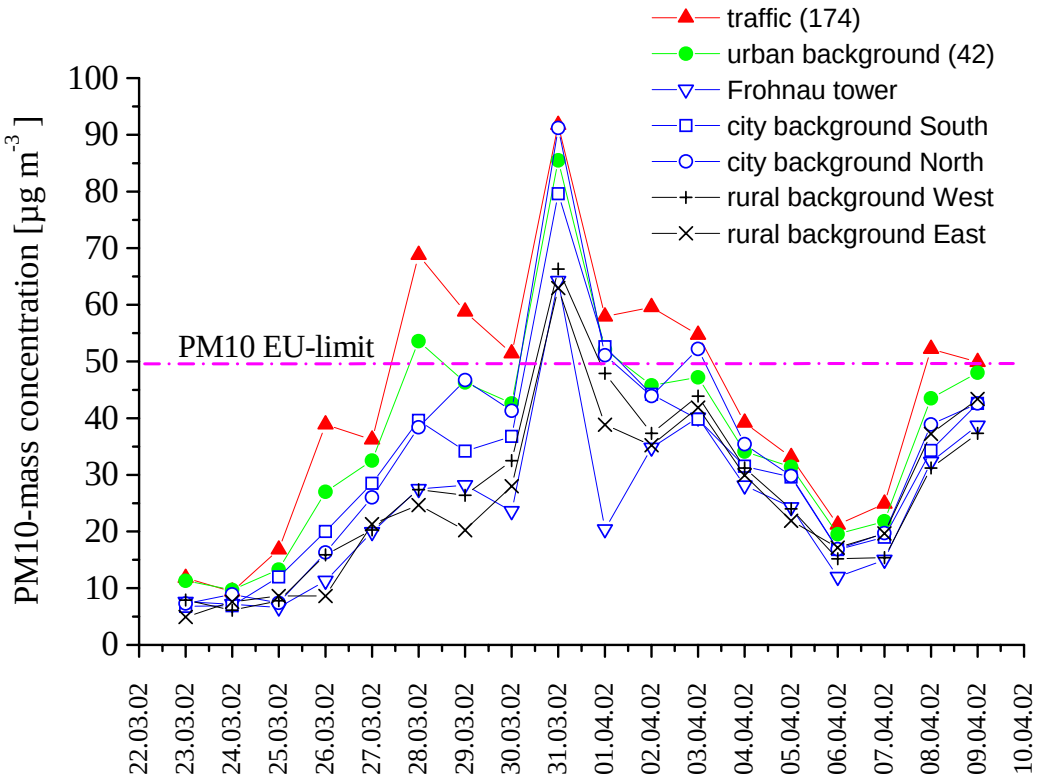


Fig. 3 Exceedence periode in the city during Easter holiday 2002 caused by PM10 import

Altogether 19 limit exceedances and an increasing level of the PM10 mass concentration as well in the city as in the urban and rural background were found. Backward trajectory calculations showed that the air masses had crossed high polluted areas in SE Germany/Europe before reaching Berlin area.

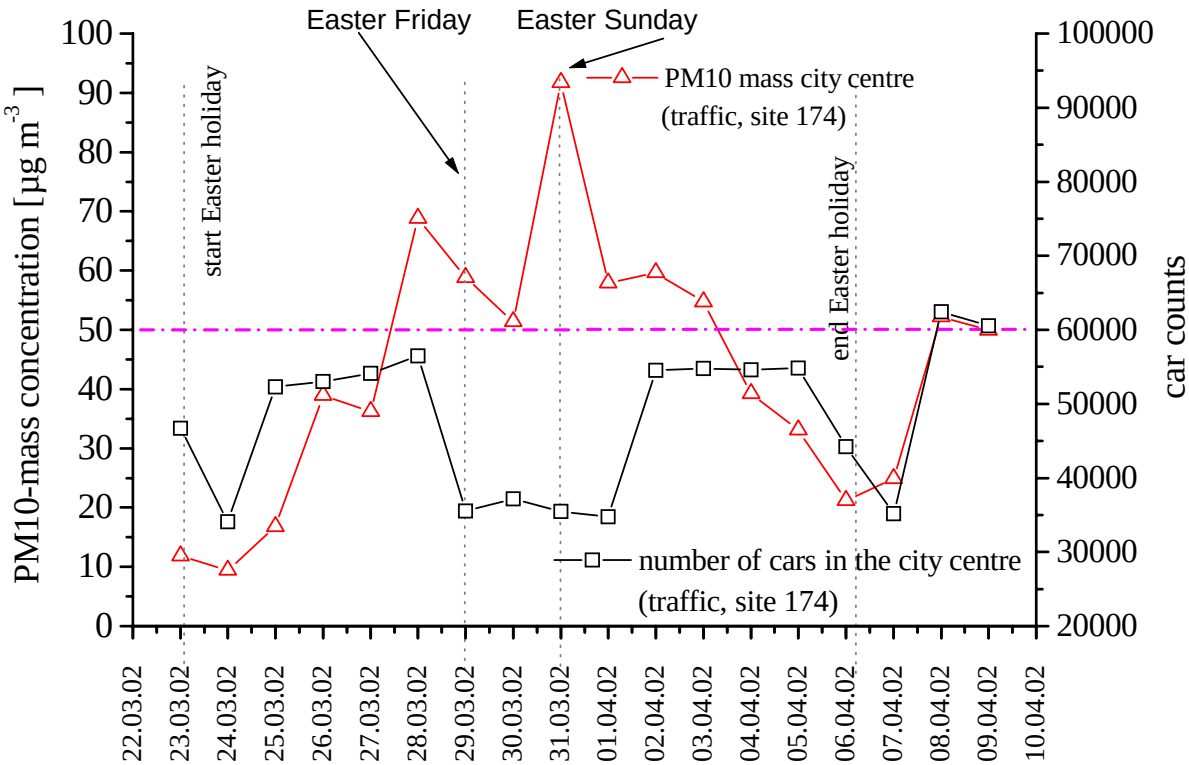


Fig. 4 Exceedence periode with reduced traffic in the city centre during Easter holiday 2002

From March 26 to April 04, 2002 (Easter holiday) a period of high PM10 mass concentrations was observed in Berlin. Especially in the city centre (traffic) seven days were registered in this period with 24h mean values above 50 µg m^{-3}, although the number of driven cars in the city centre was reduced in that time.

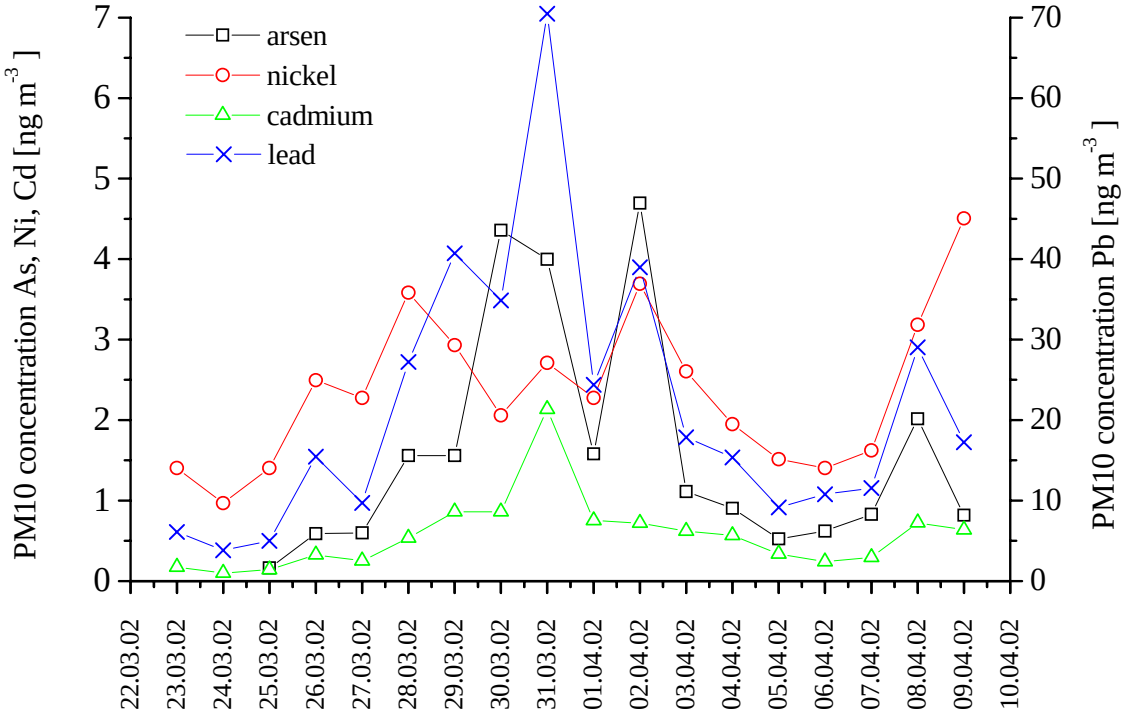


Fig. 5 PM10 aerosol content of As, Ni, Cd and lead at the traffic site (174) during the high polluted period Easter 2002

In the high-polluted period Easter 2002 the concentrations of the heavy metals cadmium, nickel and lead as well as arsenic increased parallel to that of sulphate, nitrate and ammonium (not shown here) in the PM10 aerosol at the traffic site, a further indication for long-range transport of the aerosol particles from high-polluted areas to Berlin.

The emissions of heavy metals and arsenic from industrial processes are in Berlin negligible. Only in winter the combustion of coal and oil will slightly increase the city back ground level. The yearly averages of the Pb, Cd, Ni and As concentrations have practically no gradients from the city centre to the rural background (Figures 6-8). Daily or weekly concentration peaks of all this elements may be an indicator for the import of high-polluted air into the Berlin area.

The yearly averaged concentrations of the toxic and carcinogen elements like Pb (16.3 ng m^{-3}), Cd (0.35 ng m^{-3}), Ni (1.9 ng m^{-3}) and As (1.6 ng m^{-3}) as well as its highest daily concentrations in the PM10 aerosol were in the city centre and in the surrounding areas much lower than the existing or planned pollution limits.

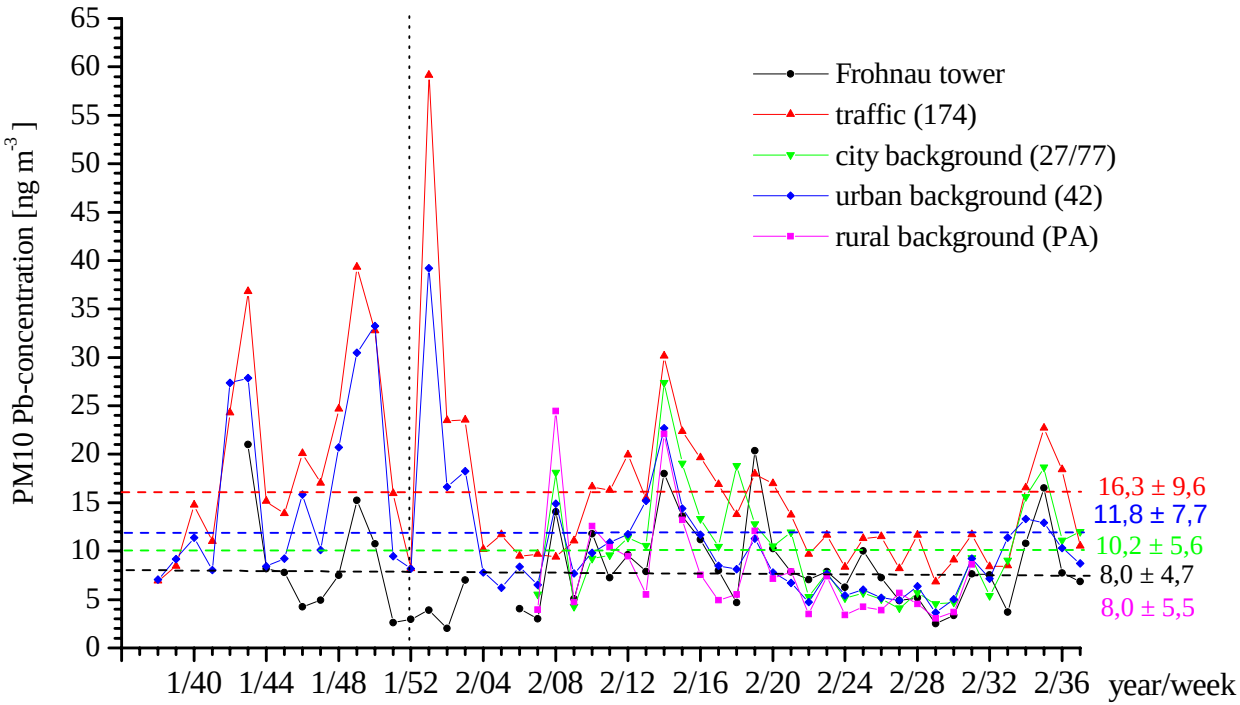


Fig. 6 Weekly and yearly averages of the PM10 Aerosol Pb-concentration at four Berliner sites and in the rural background

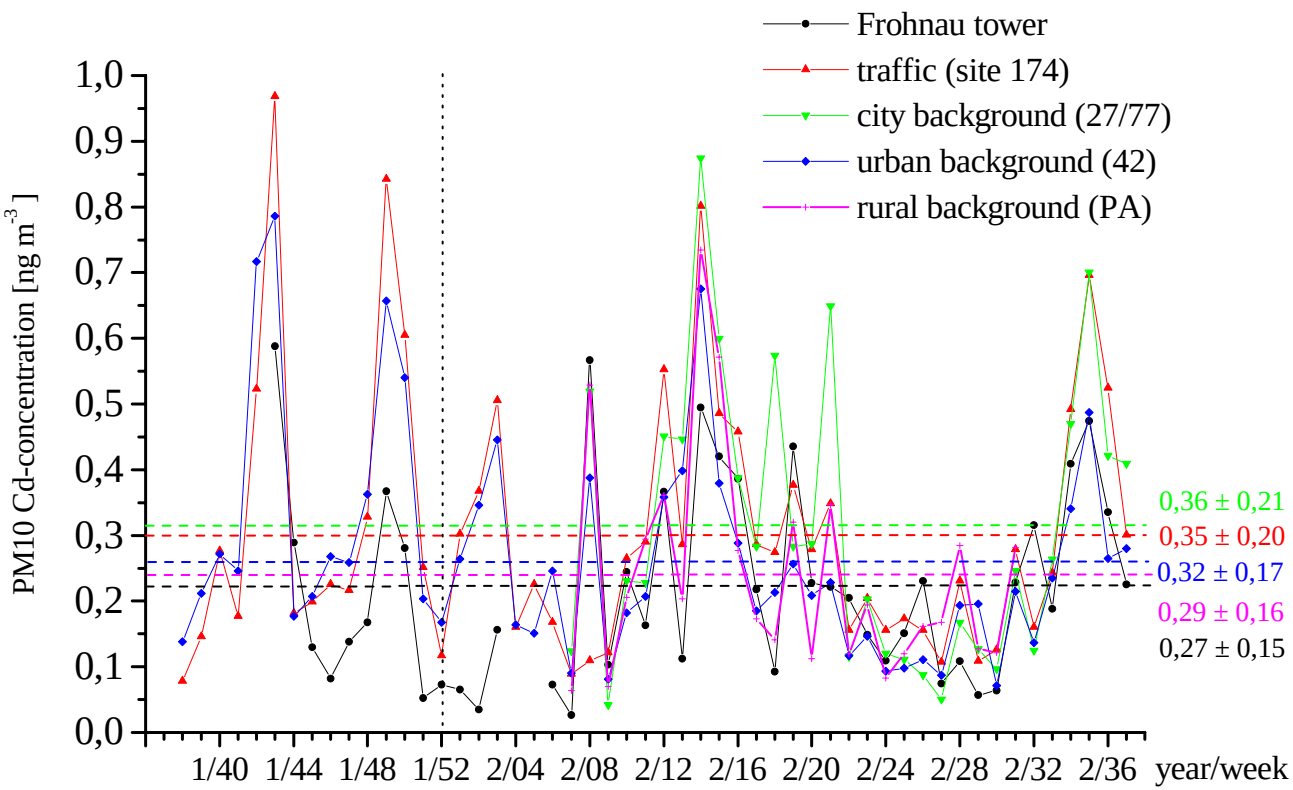


Fig. 7 Weekly and yearly averages of the PM10 Aerosol Cd-concentration at four Berliner sites and in the rural background

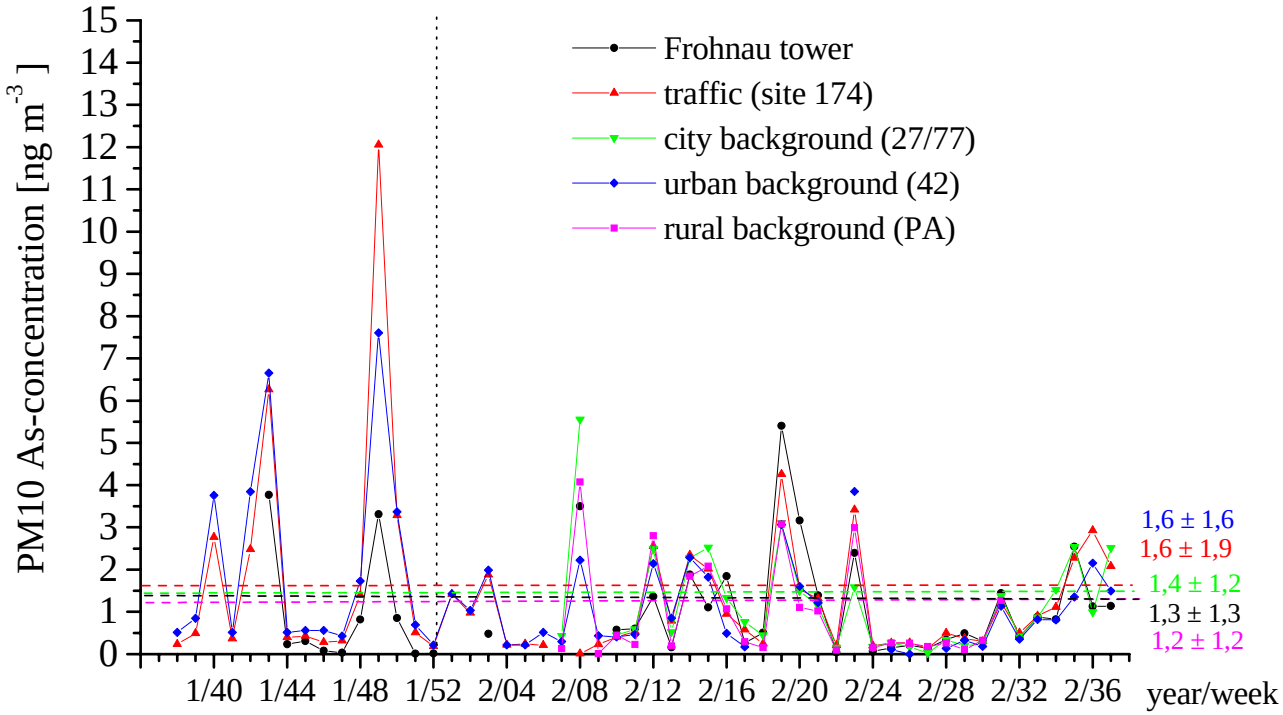


Fig. 8 Weekly and yearly averages of the PM10 Aerosol As-concentration at four Berliner sites and in the rural background

Yearly averages of the Berlin PM10 mass concentration and selected aerosol compounds

Site\Compound	PM10	EC	OC	SO_4^{2-}	NO_3^-	Fe
	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}
Traffic	34,5	4,3	4,3	4,2	3,6	0,7
Urban background	24,4	2,2	3,4	3,6	3,0	0,3
City back ground	22,3	1,8	3,2	3,9	2,4	0,2
Rural back ground	20,4	1,4	2,2	2,8	2,8	0,1

In the main streets of the Berlin city centre the problem with the exceedances of the new EU pollution limits really exist like in the most European big cities. During the one year of measurements we registered PM10 mass exceedances on 56 days in the city centre. Connected with that often also exceedances outside the city centre were registered: on 18 days at the urban background site, on 12 days at the city background sites (periphery) and on 12 days at the rural background sites.

Iron is a main component of the cars brake lining and we found seven times higher concentrations in the city centre compared with rural back ground