Ultrafine Particles (UFPs) Chemical Content - Some Basics and Measurements in Saxonia -

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Overview

- Introduction, size scale and time scale
- Sampling of UFPs, impactor characterisation

Regional studies: Chemical Content and what can be learned from it

- Melpitz: UBA/EMEP studies, MINT
- The Leipzig LfUG I
- The FAT project in Leipzig and Melpitz
- The Dresden LfUG II project

Conclusion

10.1098/rsta.2000.0670

THE ROYAL SOCIETY

The chemical composition of atmospheric ultrafine particles

By Glen R. Cass[1], Lara A. Hughes[2], Prakash Bhave[2], Michael J. Kleeman[3], Jonathan O. Allen[2] and Lynn G. Salmon[2]

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Size and Time Regime

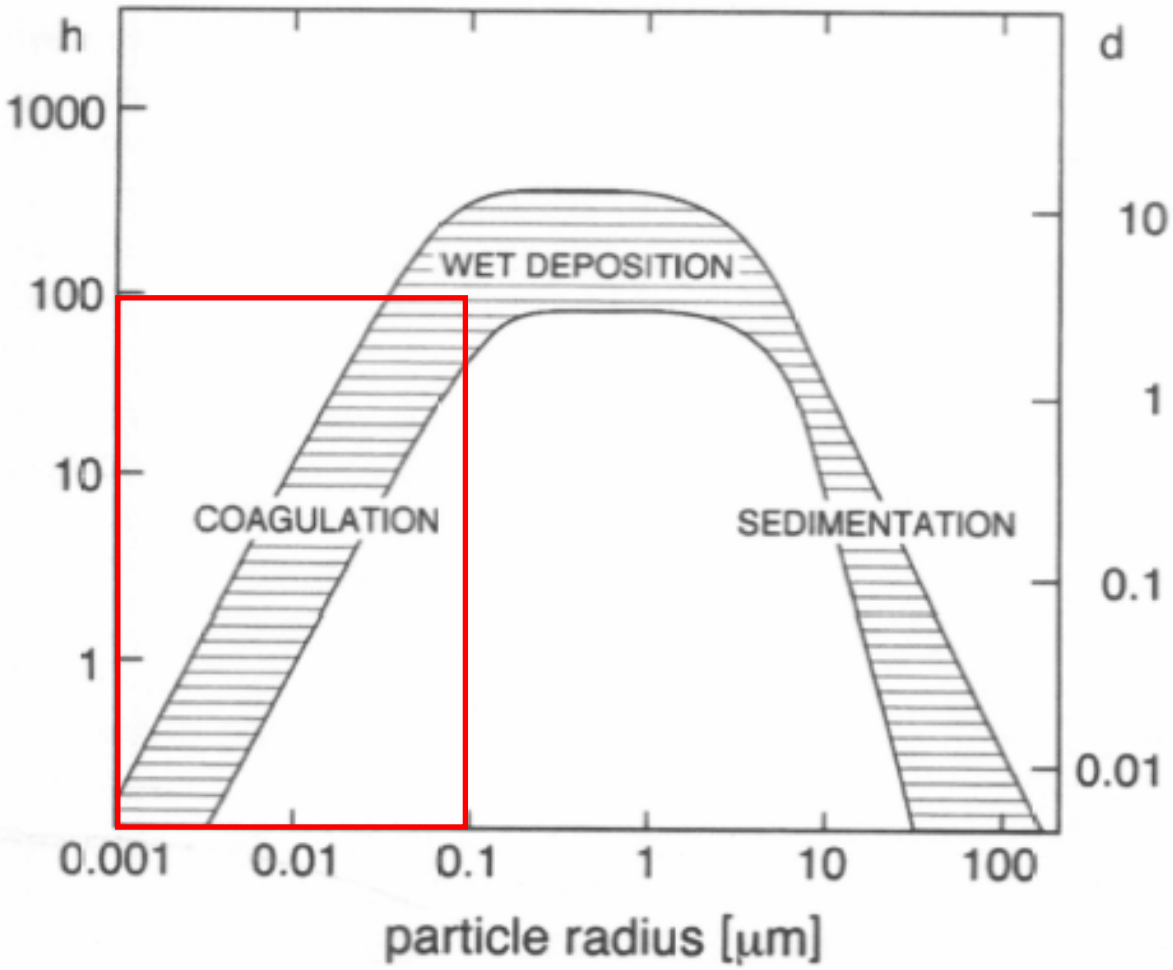


Fig. 3.11. Range of residence times of the tropospheric aerosol as a function of particle size. The leading processes are indicated (adapted from Warneck, 1988).

Tropospheric Aerosol Size and Lifetime: An early and very popular consideration, after Jaenicke (1978), here fm Zellner

RECENT RESULTS FOR PITTSBURGH (Gaffney, Nancy A. Marley, and Mary M. Cunningham, "Natural radionuclides in fine aerosols in the Pittsburgh area." *Atmospheric Environment*, 38, 3191-3200 (2004).)

URBAN AREAS – AGES RANGE FROM 10-50 Days

Apparent Ages for Aerosols – NETL

Sample	SIZE(μm)	CORR. AGE (days)
PA1	<1	17
PA2	>1	11
PA5	<1	19
PA6	>1	20
PA9	<1	21
PA10	>1	12
PA11	<1	18
PA12	>1	15
PA13	<1	30
PA14	>1	27
PA17	<1	10
PA18	>1	30
PA21	<1	12
PA22	>1	25
PA25	<1	24
PA26	>1	32
PA29	<1	31
PA30	>1	46

OK SO WHAT IS CAUSING THIS?

–PRECIPITATION - WASHOUT

– SULFATE, NITRATE- Soluble - 10 Days

(Gaffney, et.al, "Measurement of ^{7}Be and ^{210}Pb in Rain, Snow, and Hail." *J. Applied Meteor.* **33** 869-873 (1994).)

> 10 Days Aerosol Lifetimes!

Something Hydrophobic- Less Soluble

BLACK CARBON?

A slide fm **Jeffrey S. Gaffney** and Nancy A. Marley, Atmospheric Research Section Environmental Research Division, Argonne National Laboratory

Table 2. The integrated particle ages derived from the calculated lifetimes. Ages derived by extrapolation are marked in greyscale

Size (μm)	0-1 km	4-8 km	8-13 km	Units
0.003	885	20	13	Seconds
0.005	2400	285	222	Seconds
0.01	2.5	2	2	Hours
0.02	6.8	20	24	Hours
0.05	20	122	180	Hours
0.08	1.3	7.9	12.7	Days
0.1	1.5	9.0	15.2	Days

Atmos. Chem. Phys., 2, 133–145, 2002

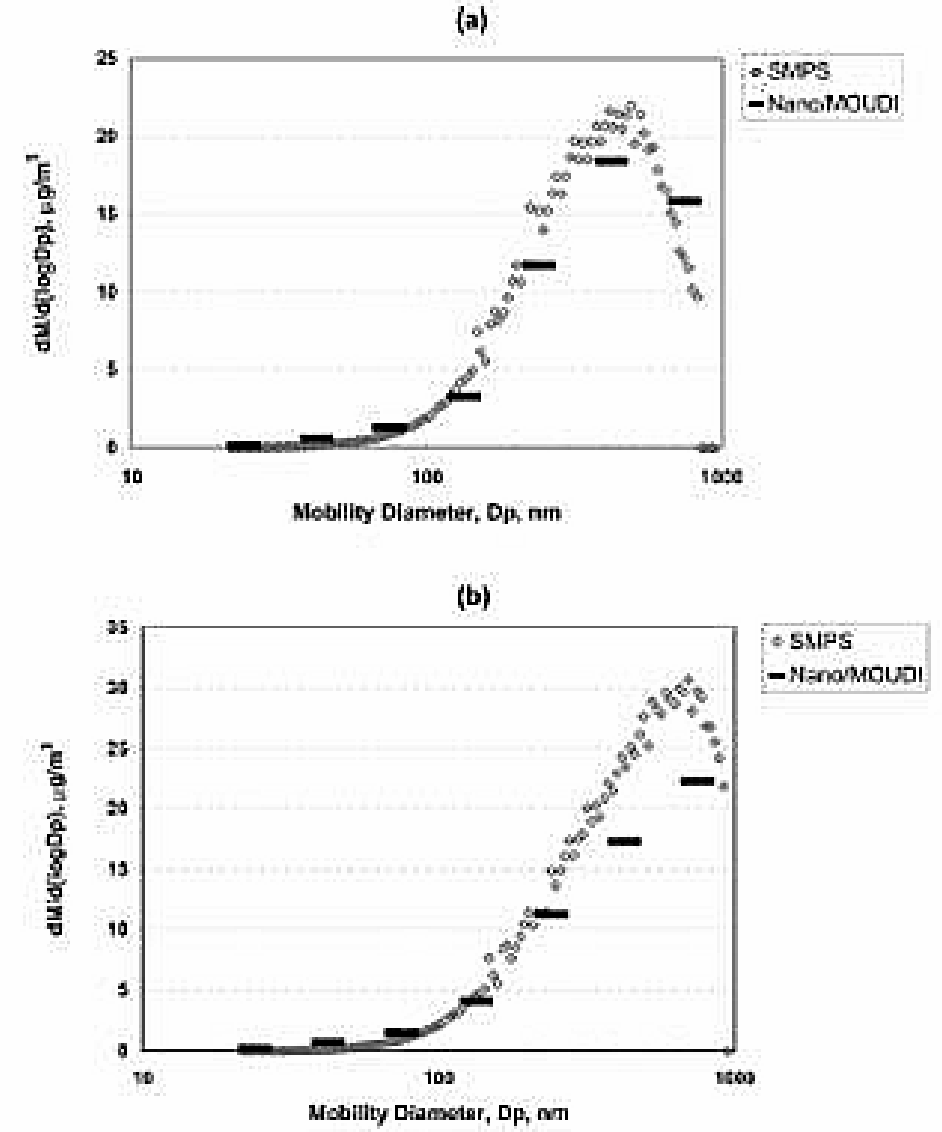
A model study based on particle size measurements in INDOEX.
Grey: Extrapolated

Particle Size [μm]	τ (Williams et al)	Spatial Range [km]
0.003	885 s	**3**
0.005	2400 s	**7**
0.01	2.5 h	**27**
0.02	6.8 h	**73**
0.05	20.0 h	**216**
0.08	1.3 d	**337**
0.1	1.5 d	**389**

Particle lifetimes fm Williams et al. APCD, 2002, Estimated average windspeed 3 m/s

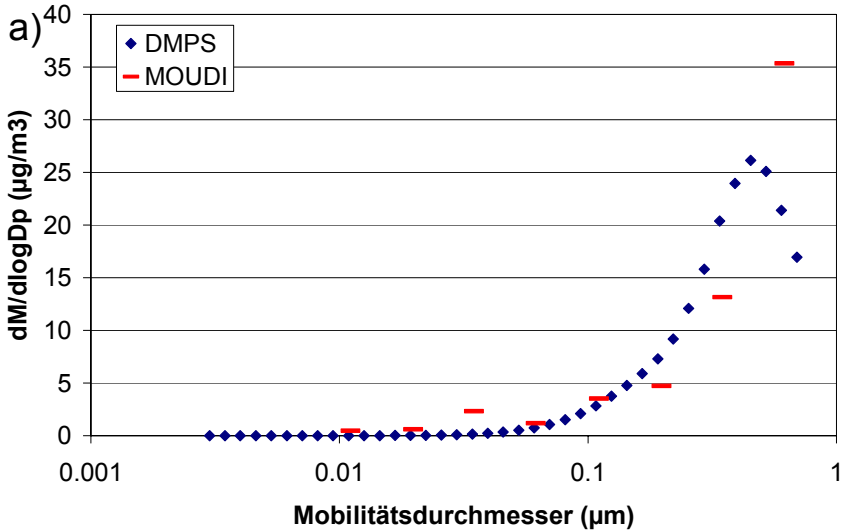
Sampling

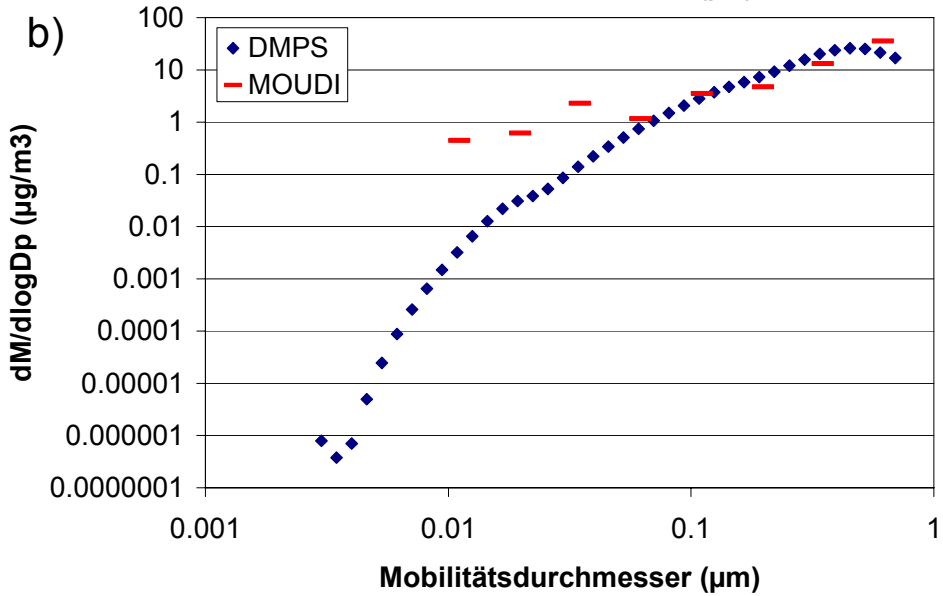
(i) The „nano-Moudi“ Impactor



Fm Sardar et al. (2005), mass size distributions fm SMPS and MOUDI /nanoMOUDI, averaged over 2 weeks sampling at (a) University of Southern California, near Los Angeles, and (b) University of California – Riverside, 90 km east of von Los Angeles.
For the conversion r = 1,6 g cm^{-3} and spherical geometry were assumed.

Sardar et al (2005): Reasonable Agreement between nano-Moudi and SMPS

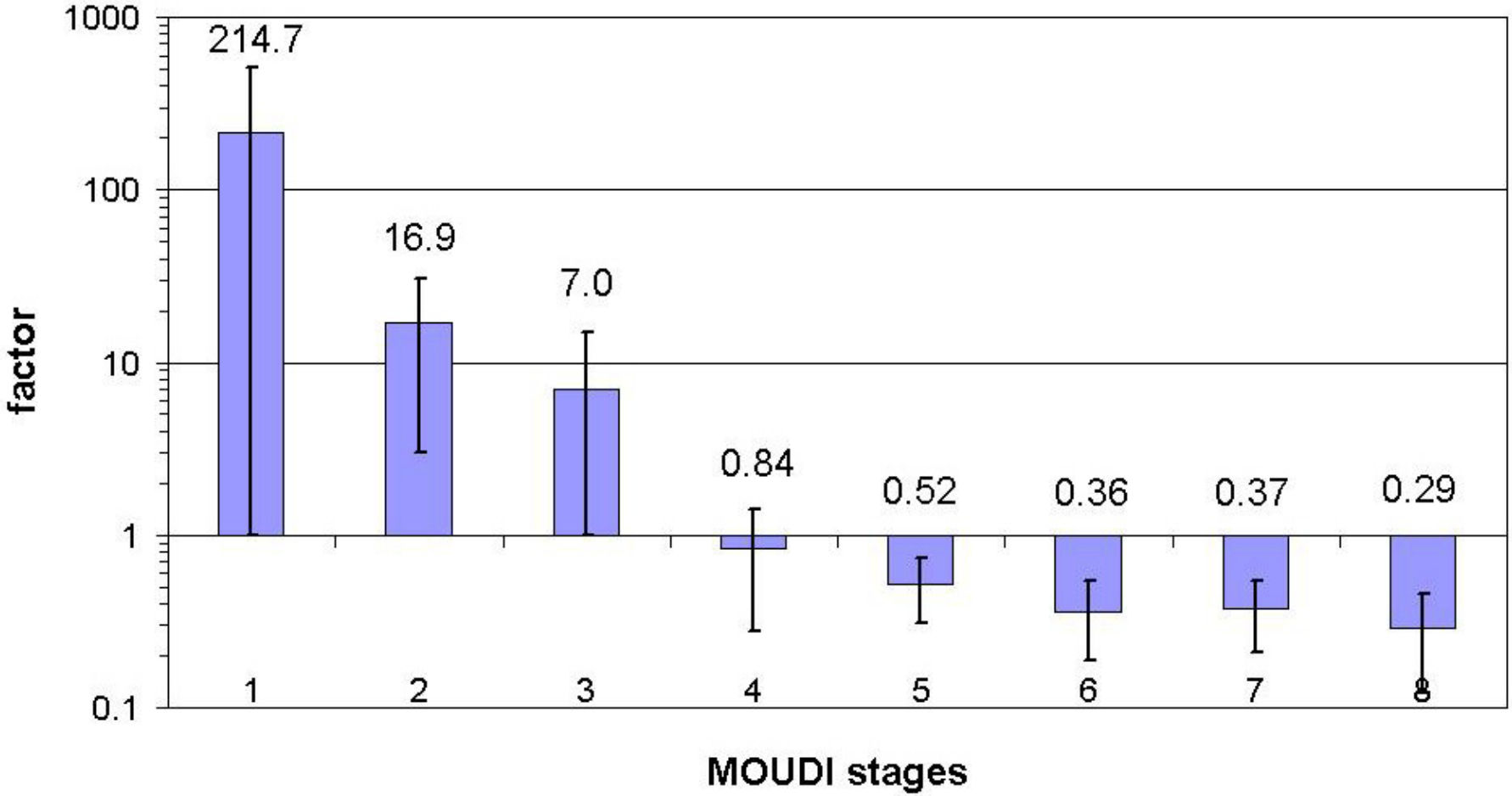




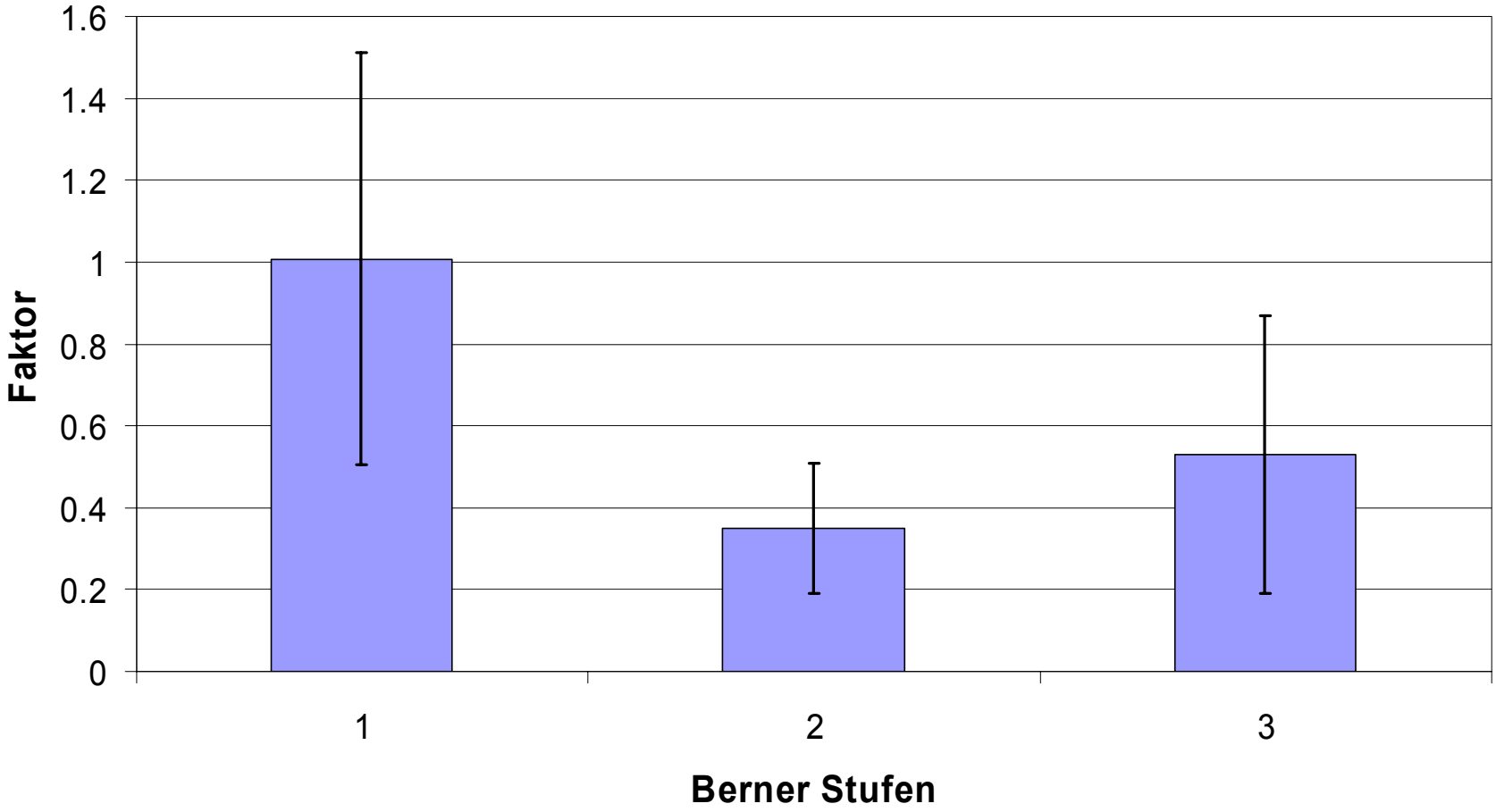
(a) Mass size distributions fm DMPS-Data, averaged over the MOUDI-sampling intervals

and

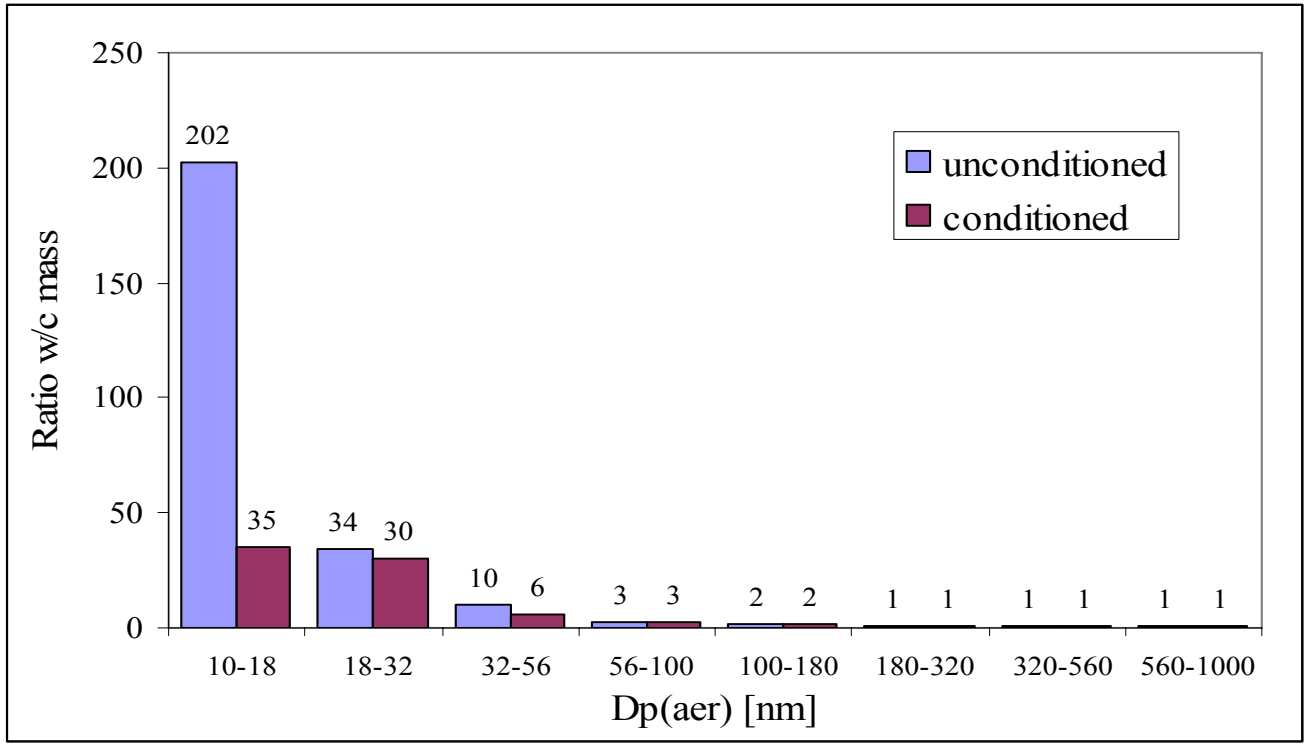
(b) Mass concentrations on the auf MOUDI-stages plotted at the mean particle diameter for each stage.



Particle masses on the MOUDI-stages compared to masses calculated fm DMPS data. As an average (n=30 comparison runs) there is a factor of more than 200 mass difference on the smallest nanoMOUDI stage !



Comparison DMPS vs Berner-Impactor (BI), stages 1-3



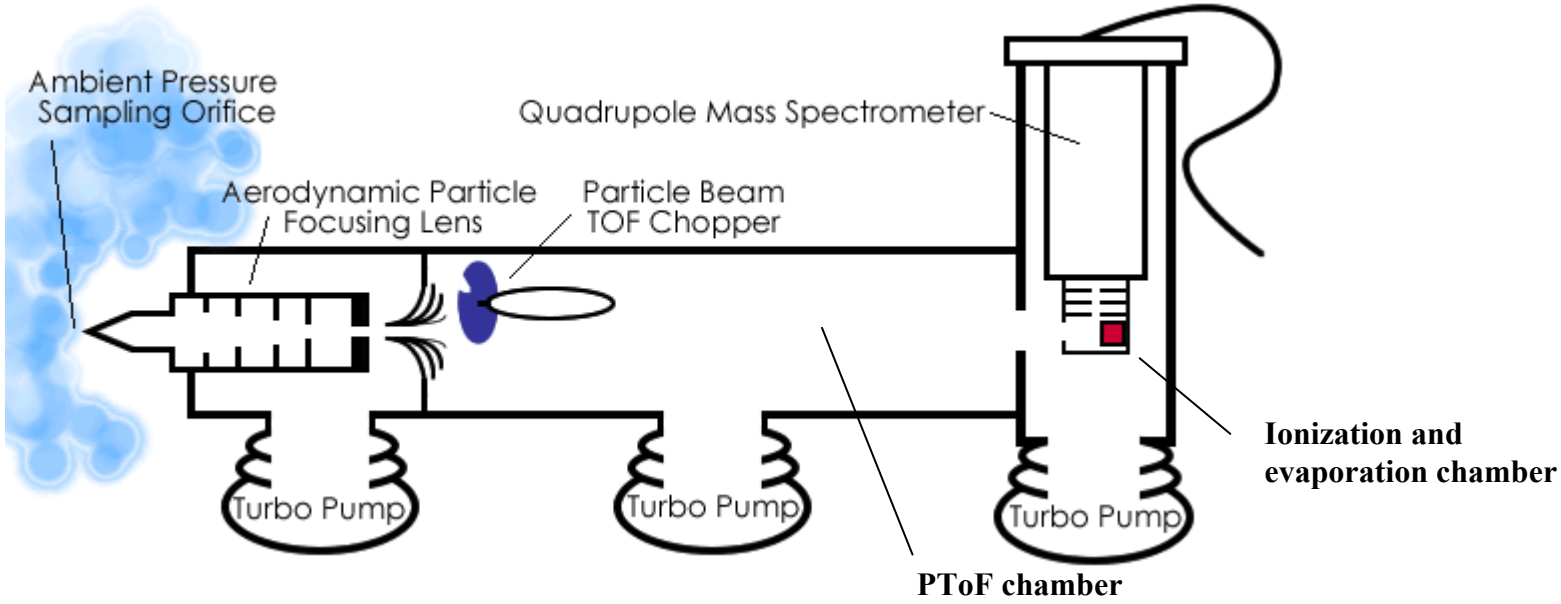
High PM(weighted)/PM(measured) rations for the smallest particles is possibly due to bounce-off of larger particles during sampling.

Therefore, RH was kept constant at RH = 60 % (Conditioning)

Conditioning for RH = 60 % decreases the difference form > 200 to 35

PM(weighted)/PM(calculated) for unconditioned sampling vs conditioning to 60% RH

(ii) Online Measurements : The Aerodyne Mass Spectrometer (AMS)



- Aerodynamic lens: focus particle in a narrow beam
- Chopper: 2 positions, block or not the particle beam (MS-mode, chemical information) or chop it (PToF mode, size distribution)
- PToF chamber: allow size distribution
- Evaporation at 600°C
- Ionization by electron impact source at 70eV
- detection: Quadropole or ToF mass spectrometer

AMS principle of work

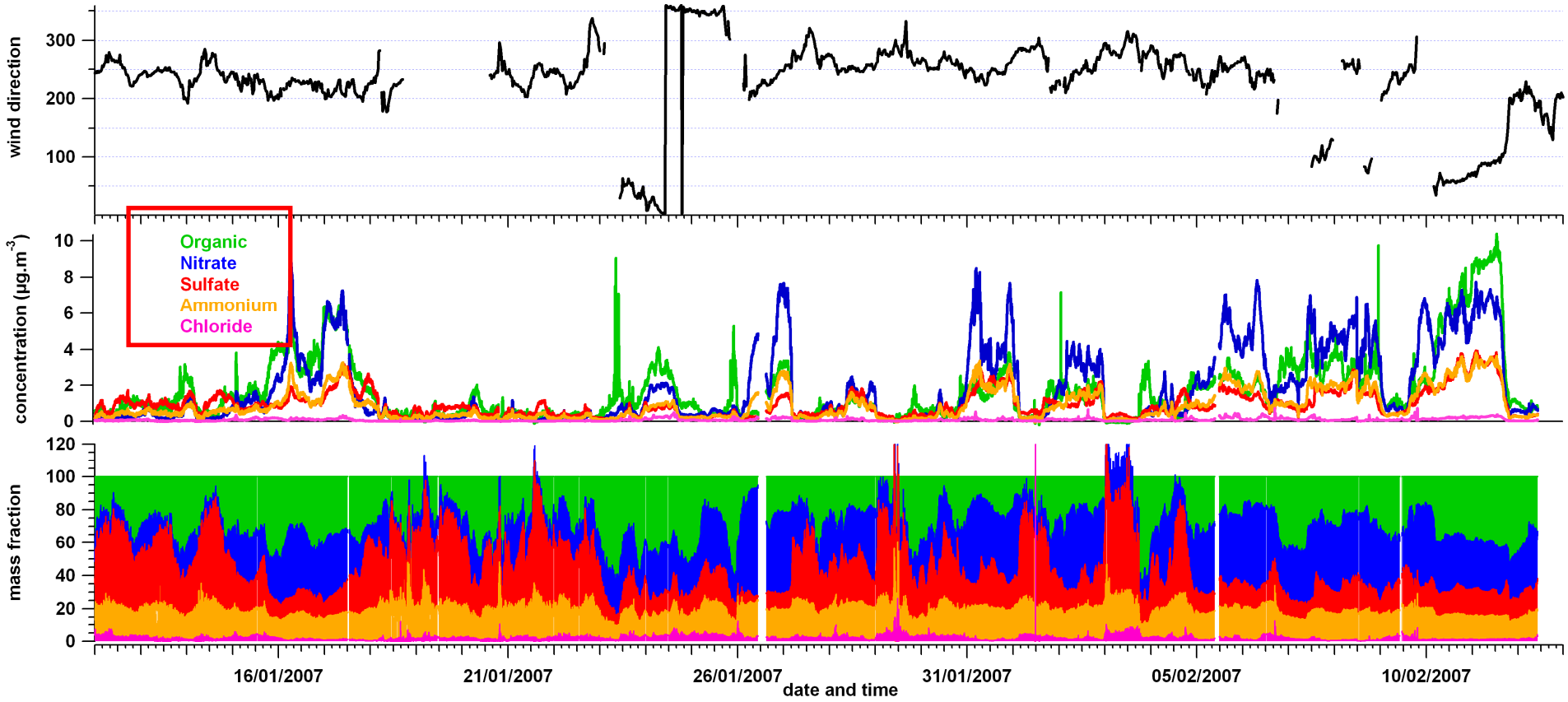
Courtesy of J. Jimenez from AMS web page (http://cires.colorado.edu/~jjose/ams.html)

Advantage

- High time resolution (up to 30s)
- chemical composition and size distribution measure at the same time
- Direct analysis without separation
- High sensitivity (0.01µg/m3)
- Universal ionization source allow MS comparison with MS data base

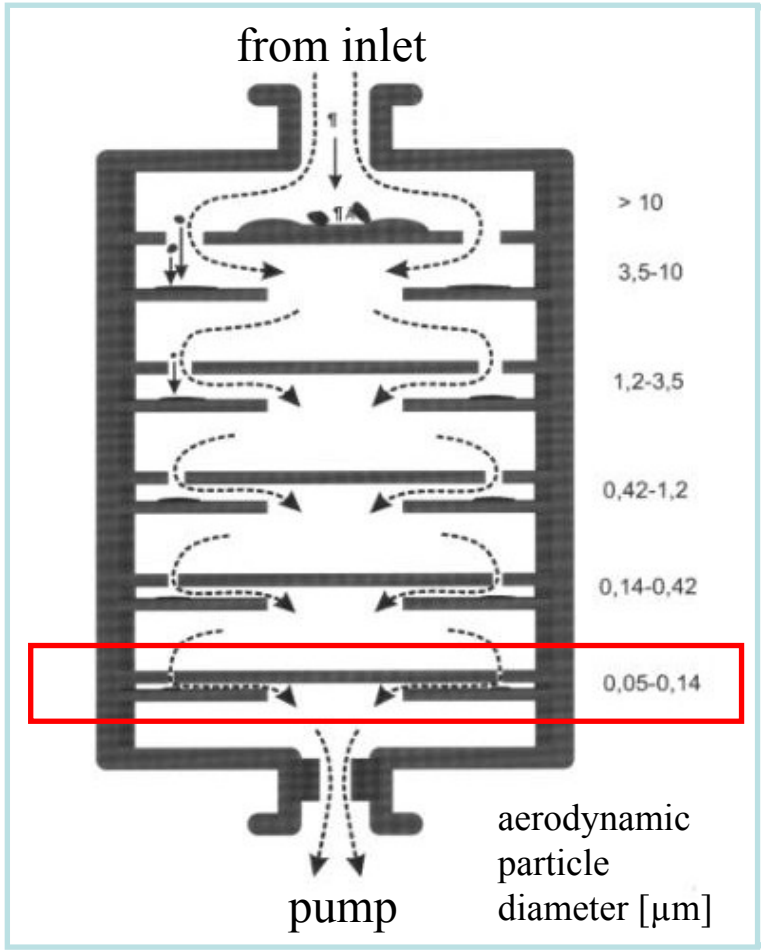
Disadvantage

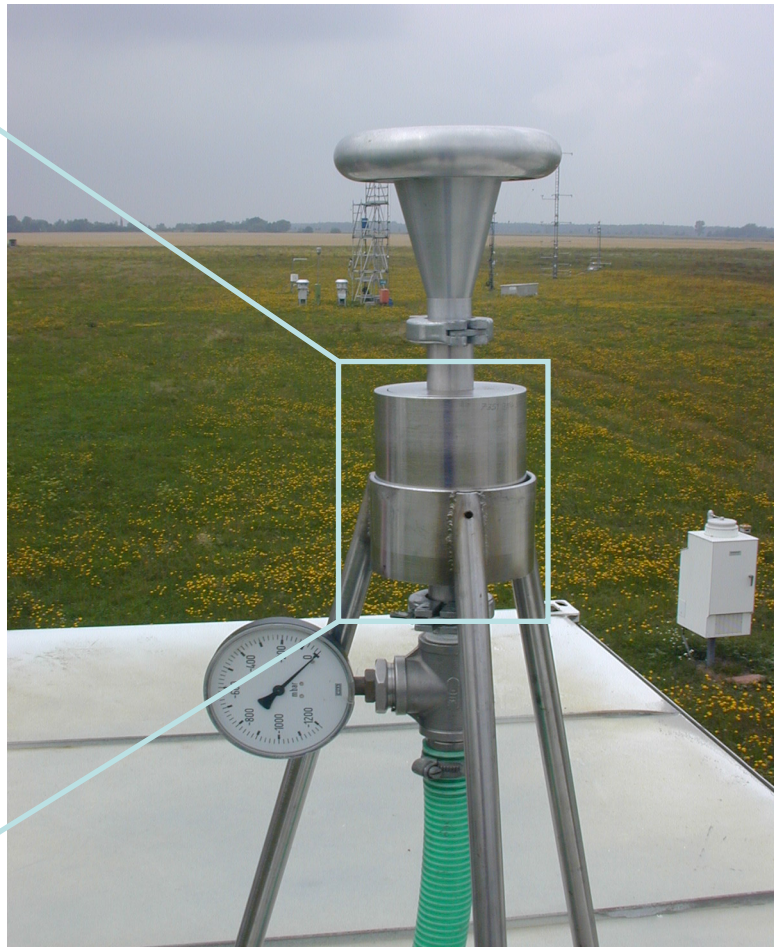
- Only non refractory compounds are detected (crustal material, soot, sea-salts, metals are not detected)
- high fragmentations of the molecule by the ionization source



AMS results: time profiles and mass fraction at Melpitz

(iii) Classical:
The Berner Impactor (BI)





Low-pressure cascade impactor, flow rate 4.5 m^3/h Aluminium impaction foils

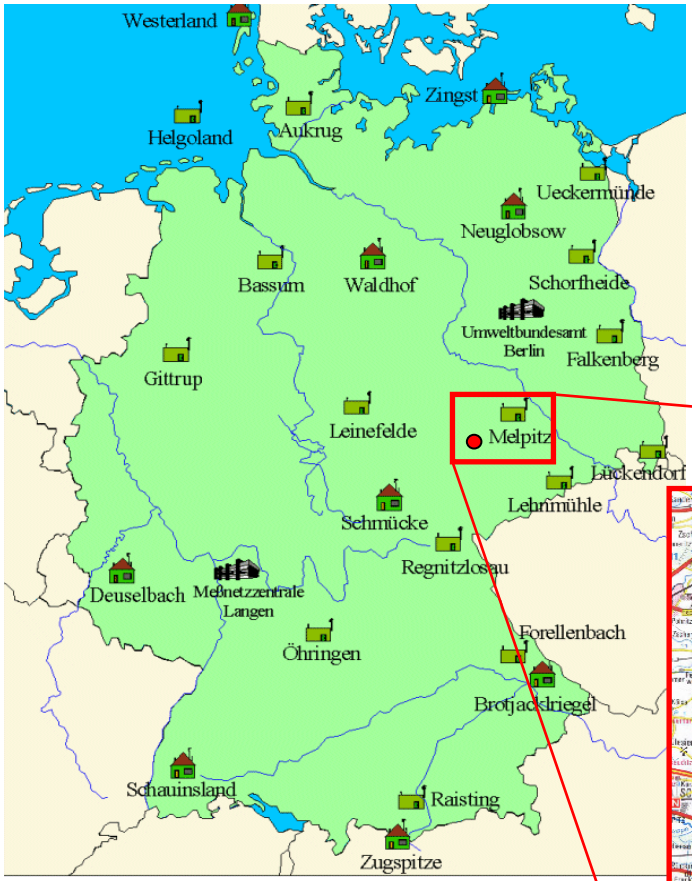
Our work horse up to now: The BERNER 6-stage impactor

BI-6 stage No	Size Range	BI-11 stage No	Size Range
---		1	0,015 – 0,03
---		2	0,03 – 0,06
1	0,05 – 0,14	3	0,06 – 0,125
2	0,14 – 0,42	4	0,125 – 0,25
3	0,42 – 1,2	5	0,25 – 0,5
4	1,2 – 3,5	6	0,5 – 1,0
5	3,5 – 10,0	7	1,0 – 2,0
6	> 10,0	8	2,0 – 4,0
---		9	4,0 – 8,0
---		10	8,0 – 16,0
---		11	> 16,0

6 and 11 stage Berner Impactor (BI) size ranges for comparison

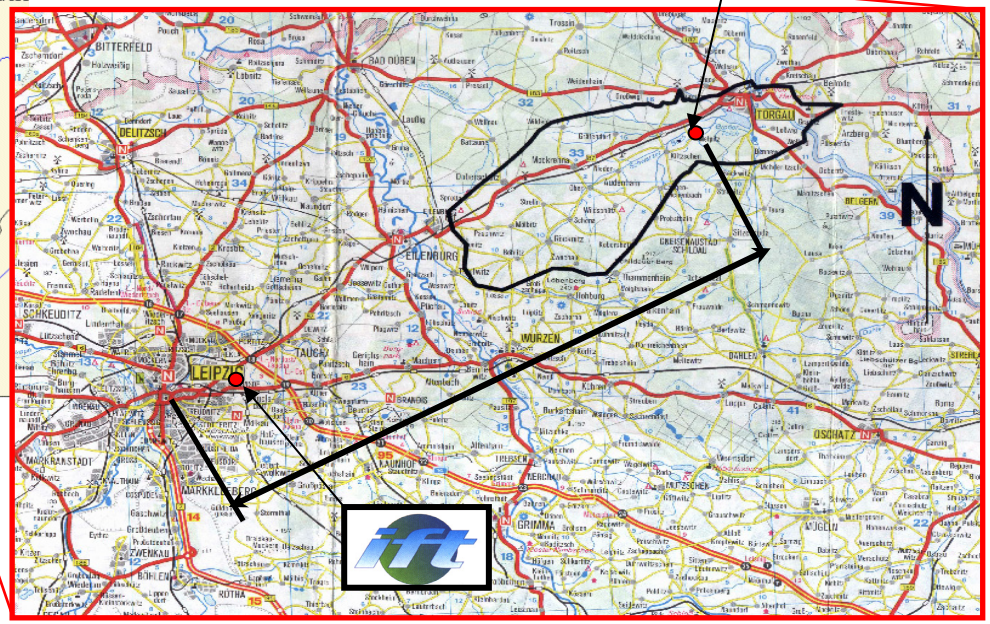
Melpitz:

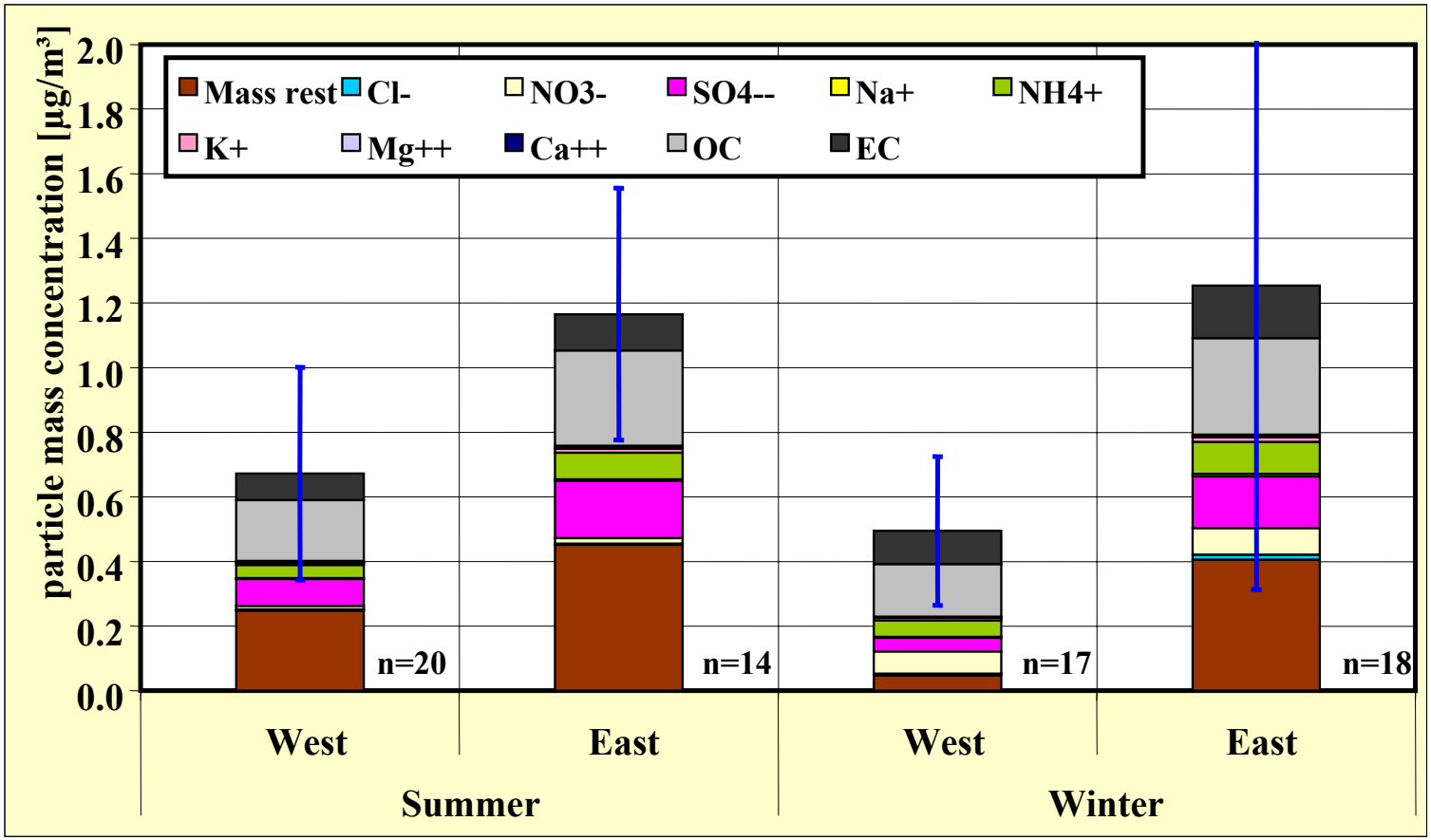
Current UBA-EMEP Measurements



Distance:
Leipzig (downtown) to Melpitz
about 50 km
(12°56‘ E, 51°32‘ N,
Altitude 86 m above see level)

Melpitz site

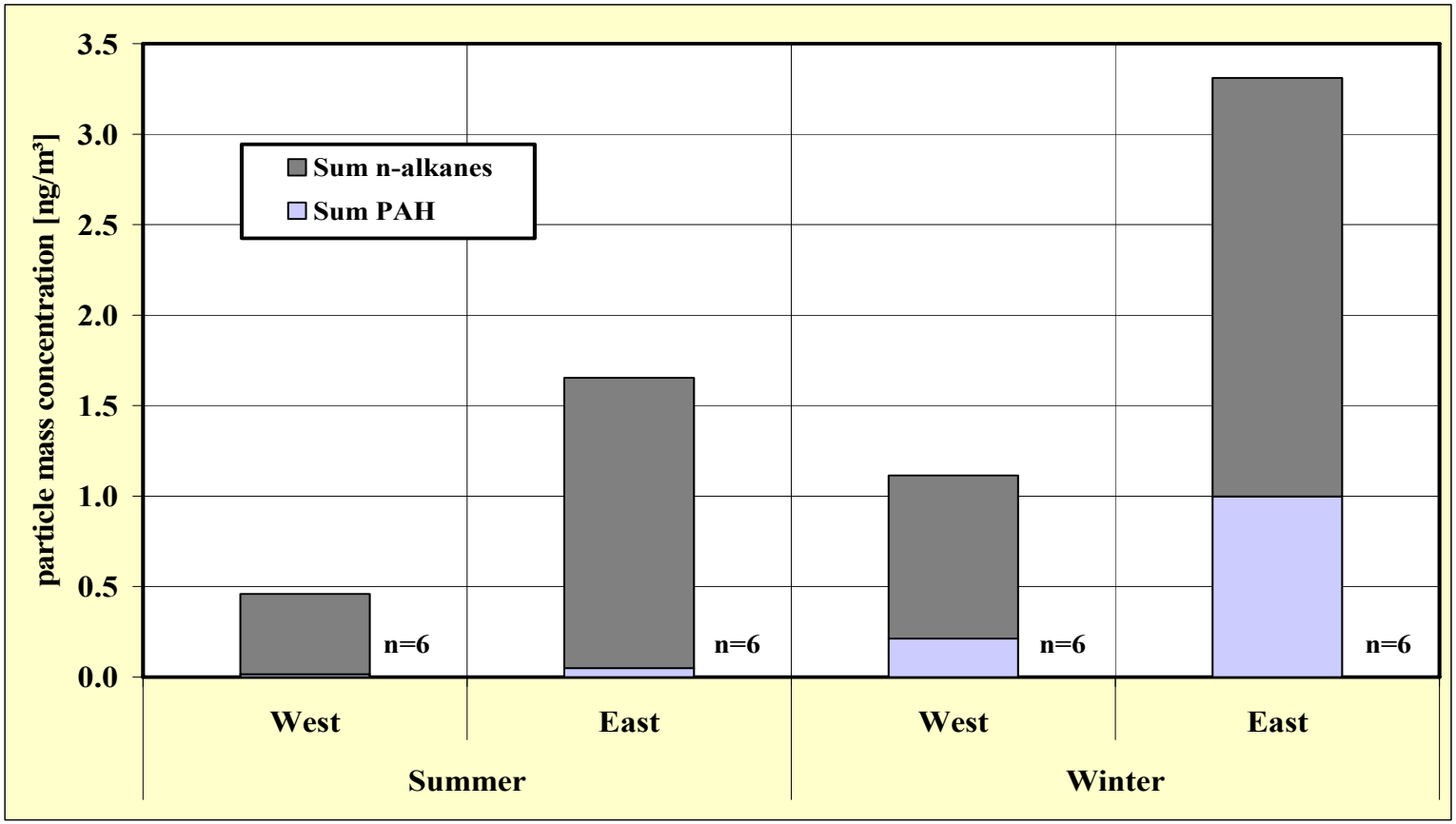




Melpitz site, BI stage 1 only dP = 0.05-0.14 µm (means for summer 2004, 05, 06 and winter 2004/05, 05/06, 06/07 differentiated for air mass transport from west and east)

Water soluble ions, OC, EC and unidentified mass (absolute)
One standard deviation as mass error is shown.

Organics

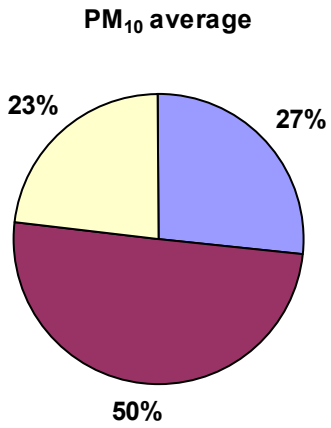


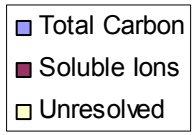
Melpitz site, BI results stage 1 only dP = 0.05-0.14 µm (means for summer 2004, 05, 06 and winter 2004/05, 05/06, 06/07 differentiated for air mass transport from west and east)

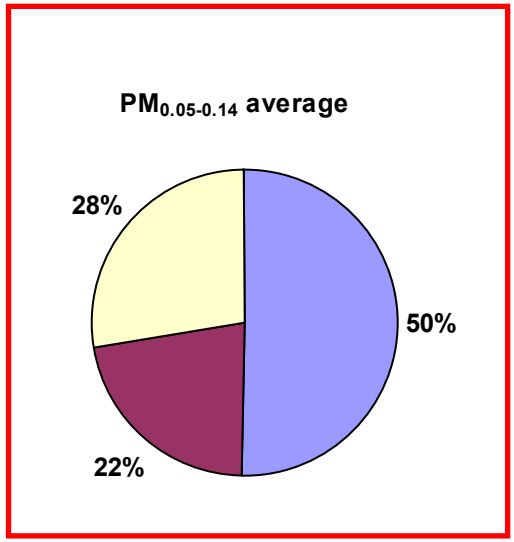
Sum n-alkanes and sum PAH's (absolute)

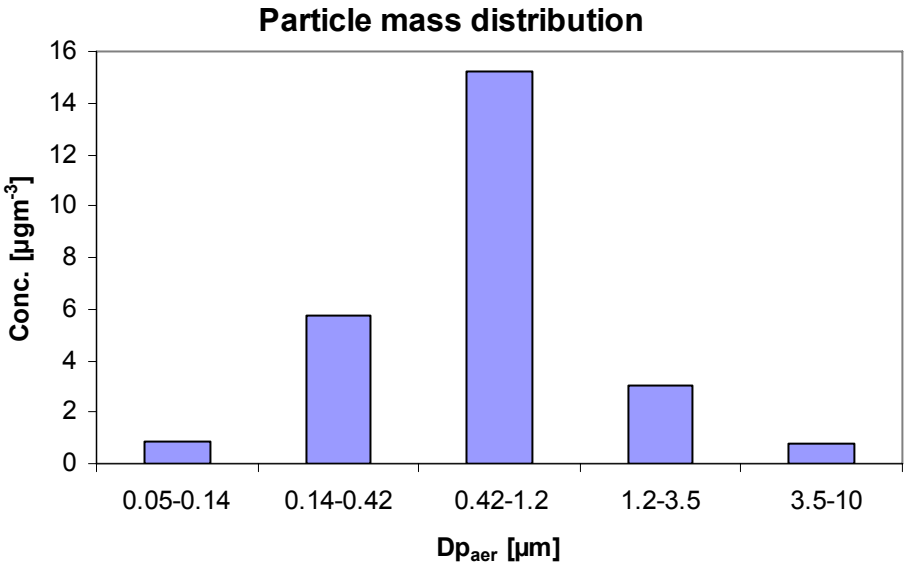
MINT

„Melpitz Intensive (1999/2000)“









MINT: Comparison of UFP and PM_{10} composition

Organics

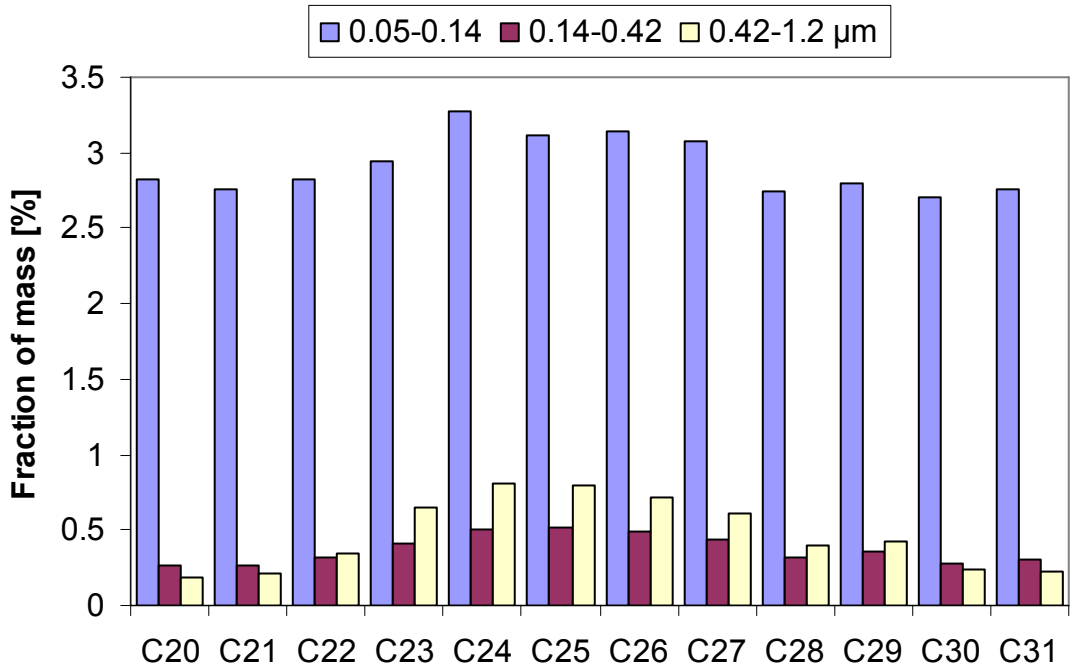
Averages of ∑alkanes (all samples): [ng/mg]

Stage 1 (0.0.-0.14): **10** > Stage 2 (0.14-0.42): **3.2** > Stage 3 (0.42-1.2 µm): **2.1**

MINT campaign maximum alkane sample (W-group):

Maximum concentrations from C_{24} to C_{26} indicate fossil fuel burning (esp. in winter time)

Alkanes are concentrated on smaller particles due to their higher surface per mass ratio



In summer time alkanes are emitted mainly by plant wax abrasion and are found in the coarse particle fraction not considered here.

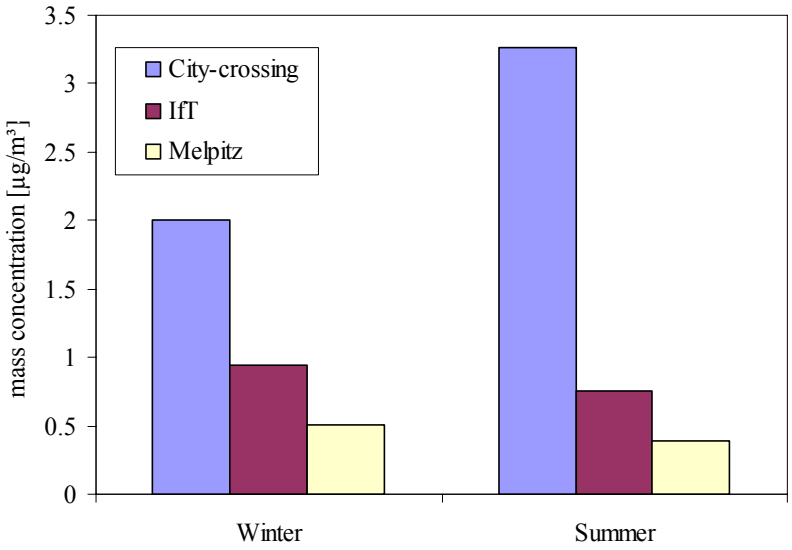
MINT: Distribution of alkanes $C_{20} - C_{31}$

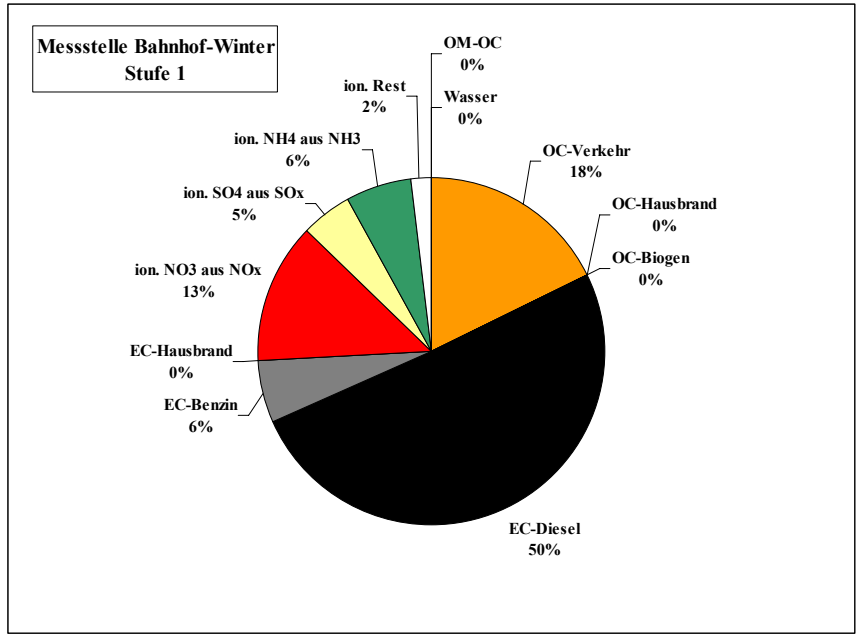
LfUG I - Leipzig

At three sites in a summer and a winter campaign PM collection by BERNER impactors was carried out in parallel at a city-crossing (near the Leipzig main station), at the IfT (urban background) and in Melpitz (rural background) to identify sources of PM.

IfT – roof sampling site

View from the sampling site to the Leipzig city-crossing at Hallesches Tor.

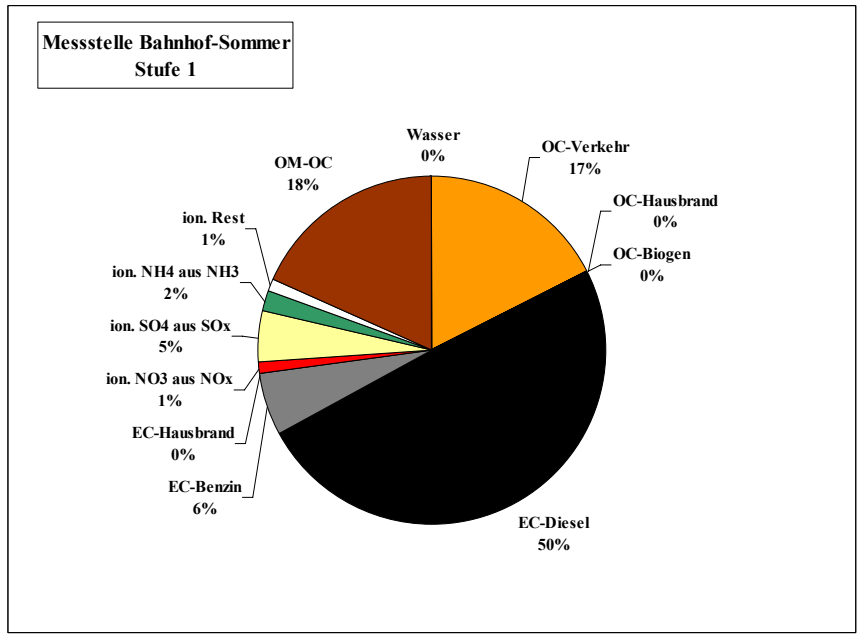




Mean mass of nano particles during the experiment time

Nano particle compositions at the city crossing: EC > OC > ionic PM

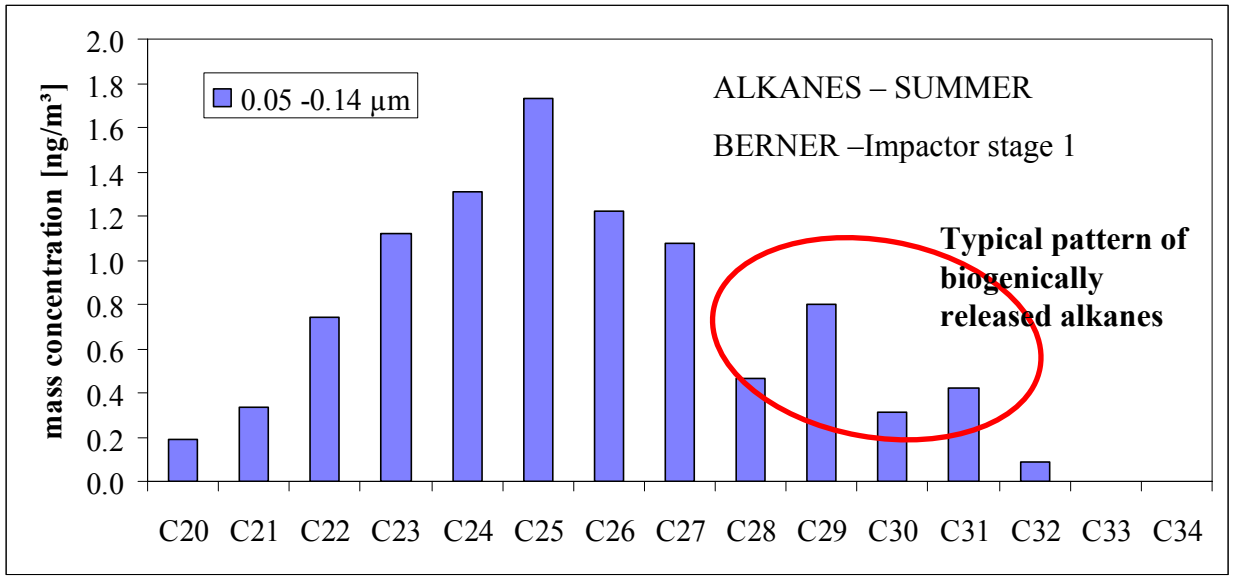
Volatile nitrates were found only during winter in high concentrations.



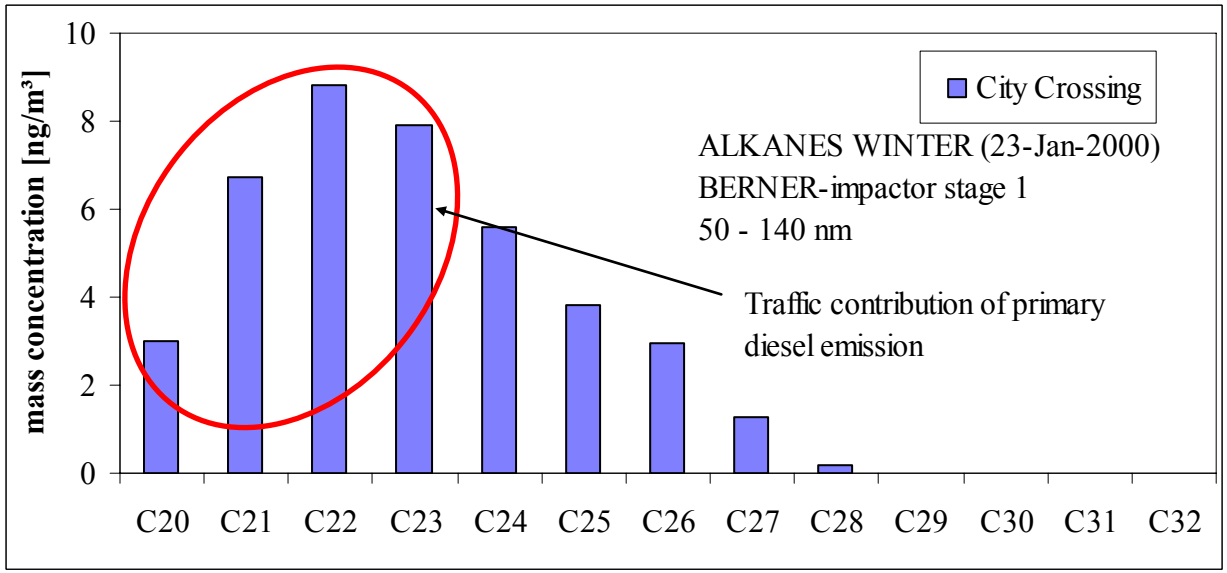
BI stage 1 composition (seasonally)

Organics

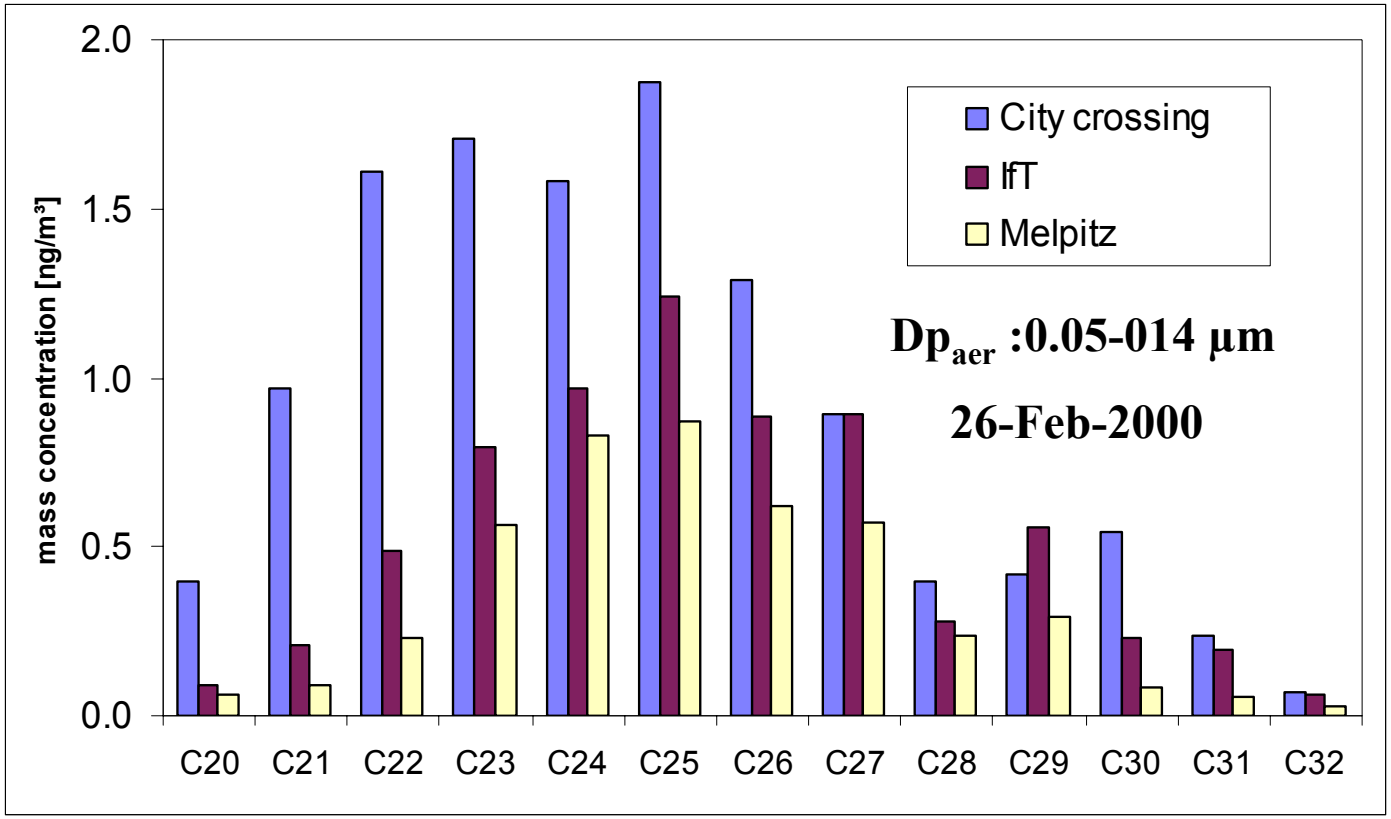
Summer concentrations of alkanes at the traffic site are biogenically influenced (higher concentration of C_{29} and C_{31} vs. C_{28} and C_{30}).



High concentration of alkanes on nano particles are caused by direct traffic emissions, mainly from diesel trucks.



The Leipzig LfUG I project (1999-2000) – mean alkanes pattern at city



Concentrations of traffic related alkanes are significantly higher at the urban city crossing than at the other sites (wind direction: WSW; Temp. 6-9 °C).

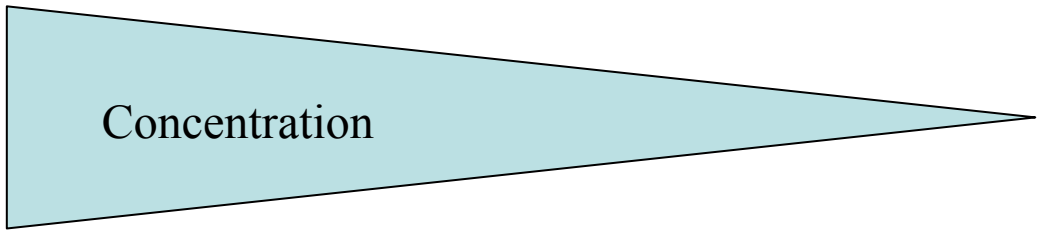
Comparison of the alkanes concentration at all sampling sites

Summer	Size-Class	City-Crossing	Urban Background	Rural Background
	AeD [nm]	ng/m³	ng/m³	ng/m³
alkanes	0.05-0.14	9.75	4.34	1.3
PAH	0.05-0.14	0.56	0.09	0.02
o-PAH	0.05-0.14	0.092	0.03	0

Winter	size-class	City-crossing	urban Background	Rural Background
	AeD [nm]	ng/m³	ng/m³	ng/m³
alkanes	0.05-0.14	20.86	9.03	5.78
PAH	0.05-0.14	1.24	0.8	0.27
o-PAH	0.05-0.14	0.11	0.08	0.04

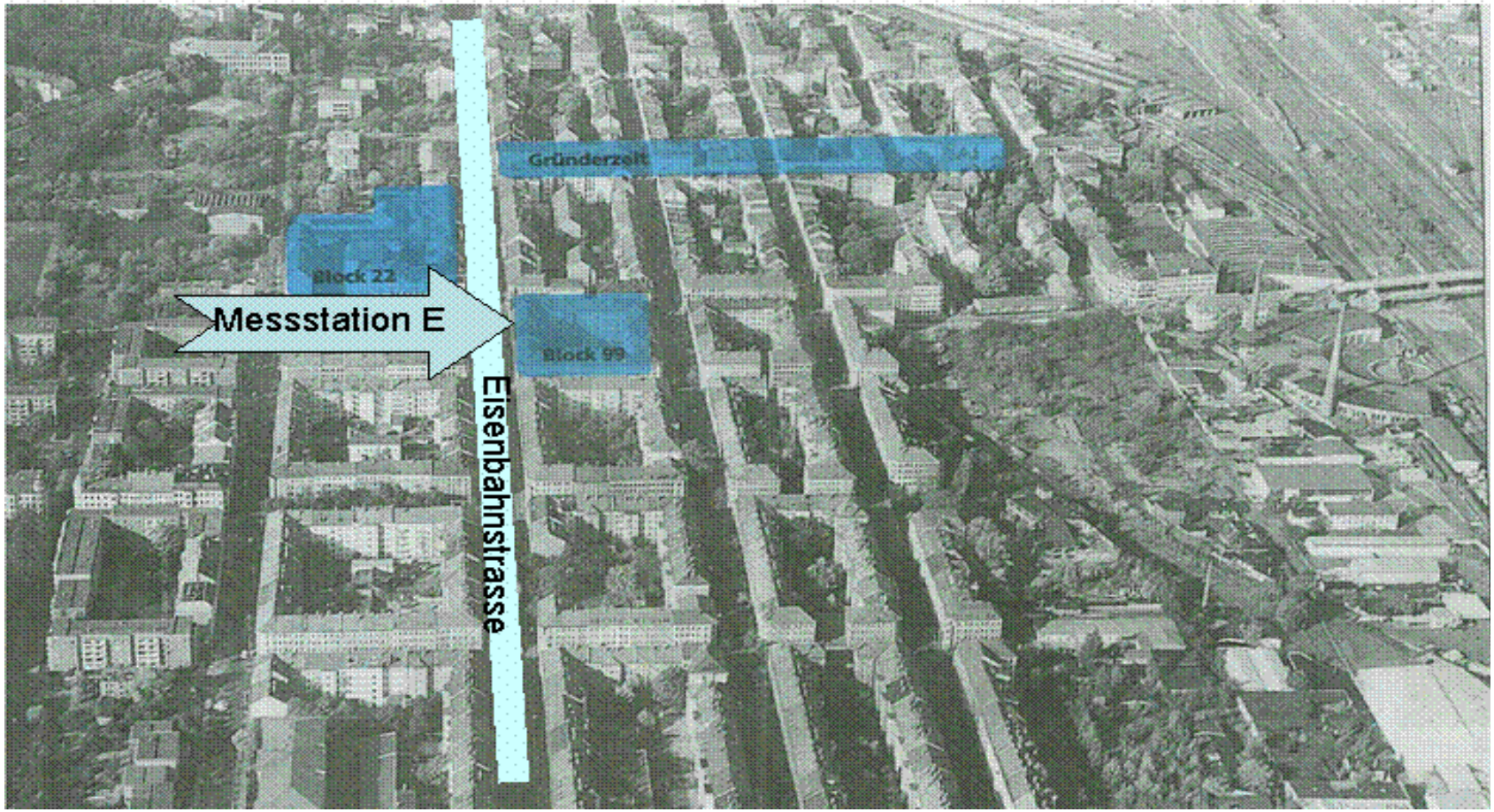
Decrease of all concentrations in dependence of traffic volume

Differences between seasons



FAT-Project - Leipzig

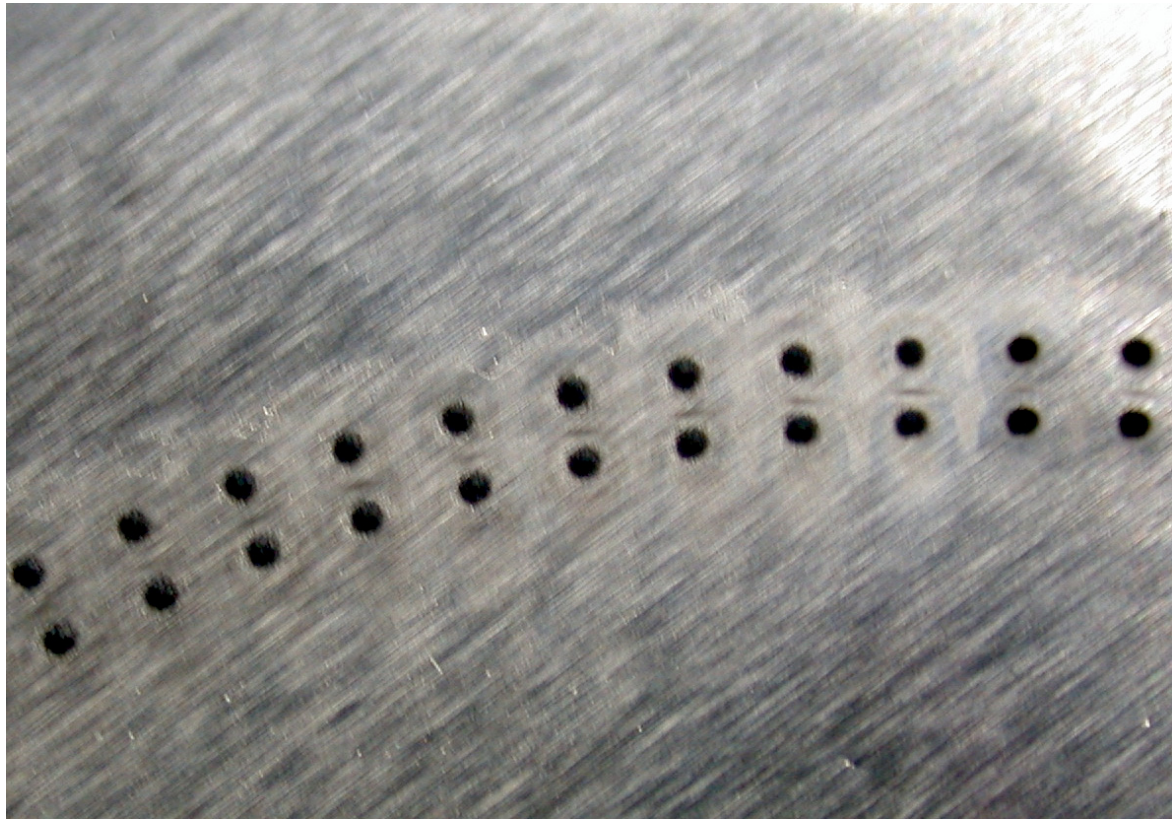
Lage der Messstation in der Eisenbahnstrasse (Einlasshöhe über Grund: 7m)



Measurement station Eisenbahnstraße („Block 99“)

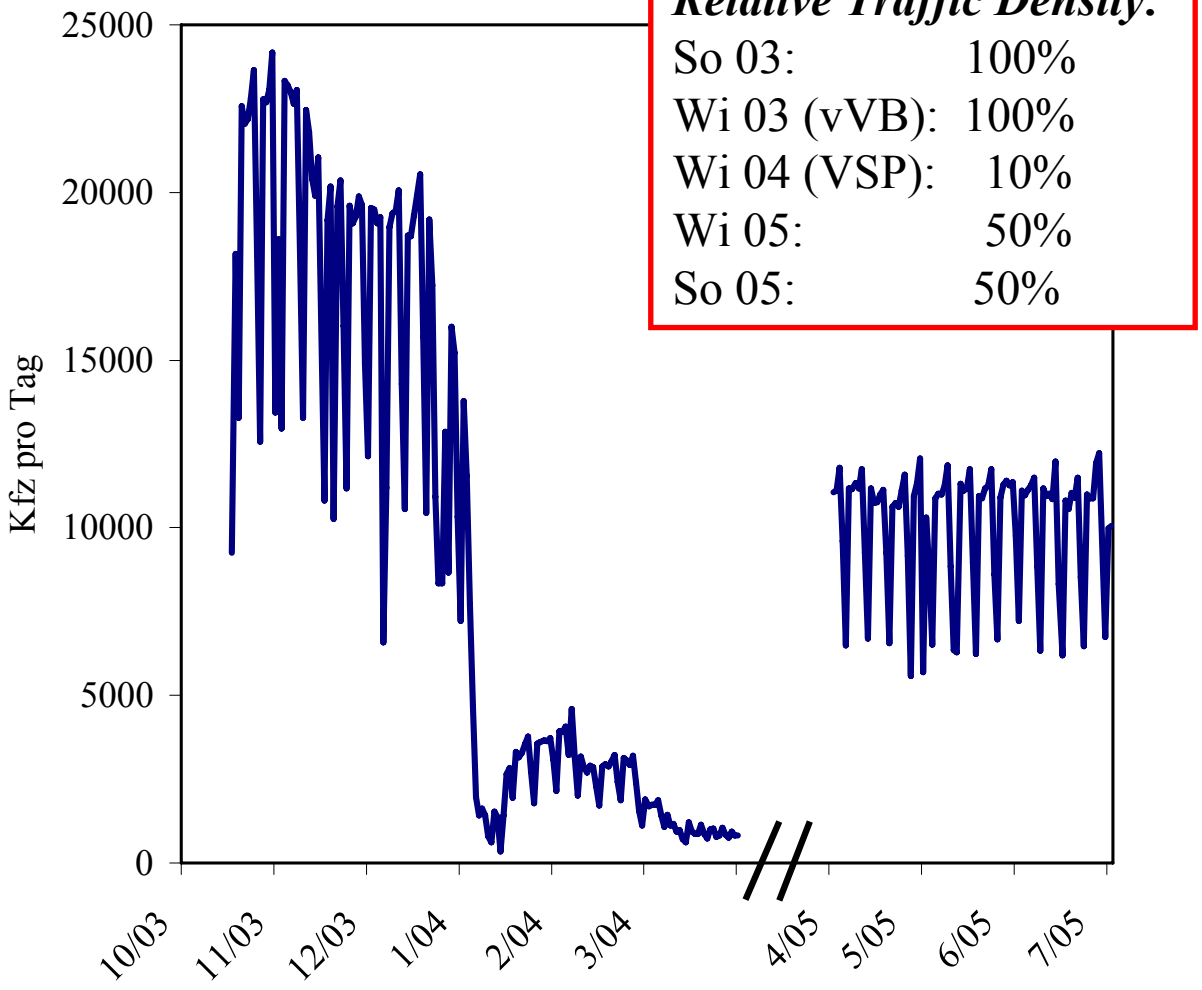
Block 99 in Leipzig: Das Gründerzeit-Karree liegt an der Eisenbahnstraße (rechts). Umschlossen wird es von der Hermann-Liebmann- (links), Ludwig- und Hildegardstraße. Foto: André Kempner

Measurement station Eisenbahnstraße (‘Block 99‘)



Impaction of nano particles (dp_{aer}: 50-140 nm) on an Al-foil

⇨ high content of soot is visible



Relative Traffic Density:

So 03:	100%
Wi 03 (vVB):	100%
Wi 04 (VSP):	10%
Wi 05:	50%
So 05:	50%

Sommer 2003
Full traffic with about 20.000 cars per day

Winter 2003 (vVB)
Full traffic with about 20.000 cars per day.

Winter 2003 (VB)
Partial closure of street, street construction going on: transition state

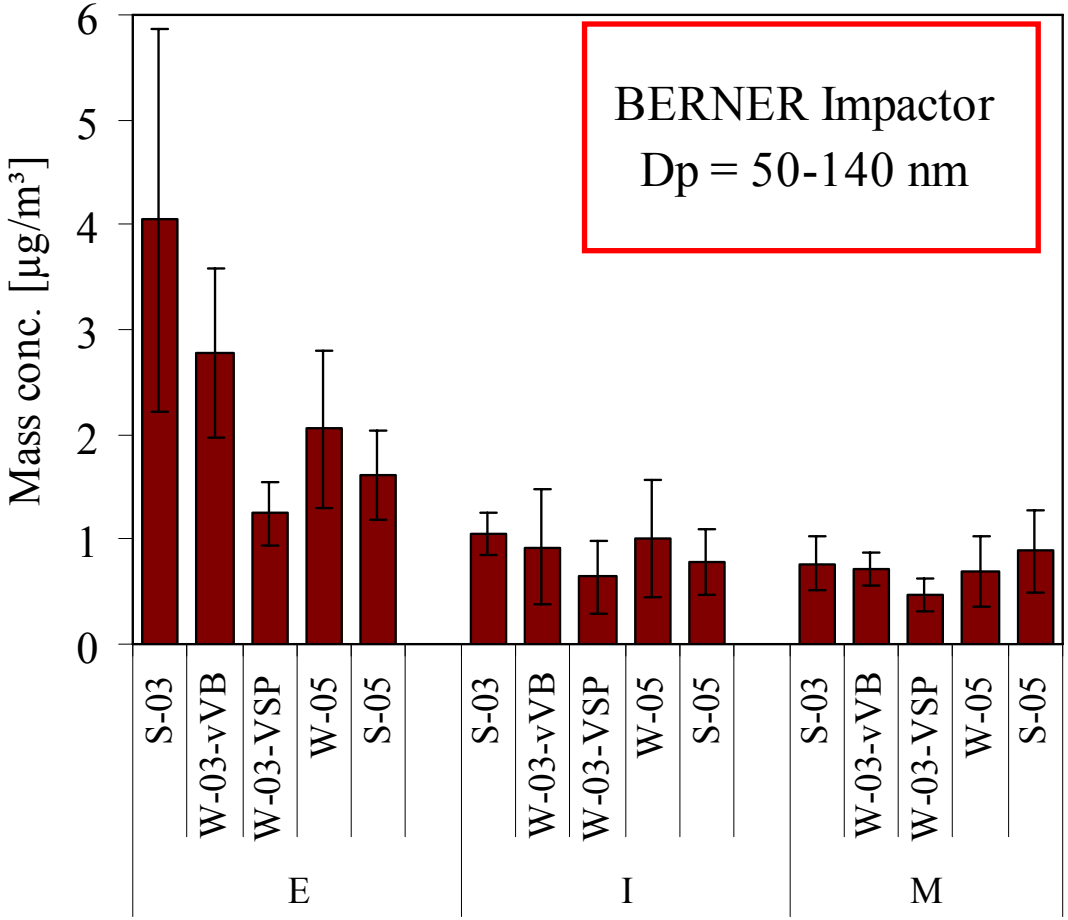
Winter 2004 (VSP)
Total close of street, only 2000 cars per day

Winter 2005
New normal state of street after renovation: 10 000 cars per day

Sommer 2005
New normal state of street after renovation: 10 000 cars per day

Traffic count: Courtesy W. Birmili, IfT

Traffic count: Number of cars per day at station E



- PM at sites I and M is similar

- PM at site E is higher caused by **TRAFFIC**

-Strong decrease from summer 03 to summer 05 as well as winter 03 (vVB) to winter 03 (VSP) and winter 05

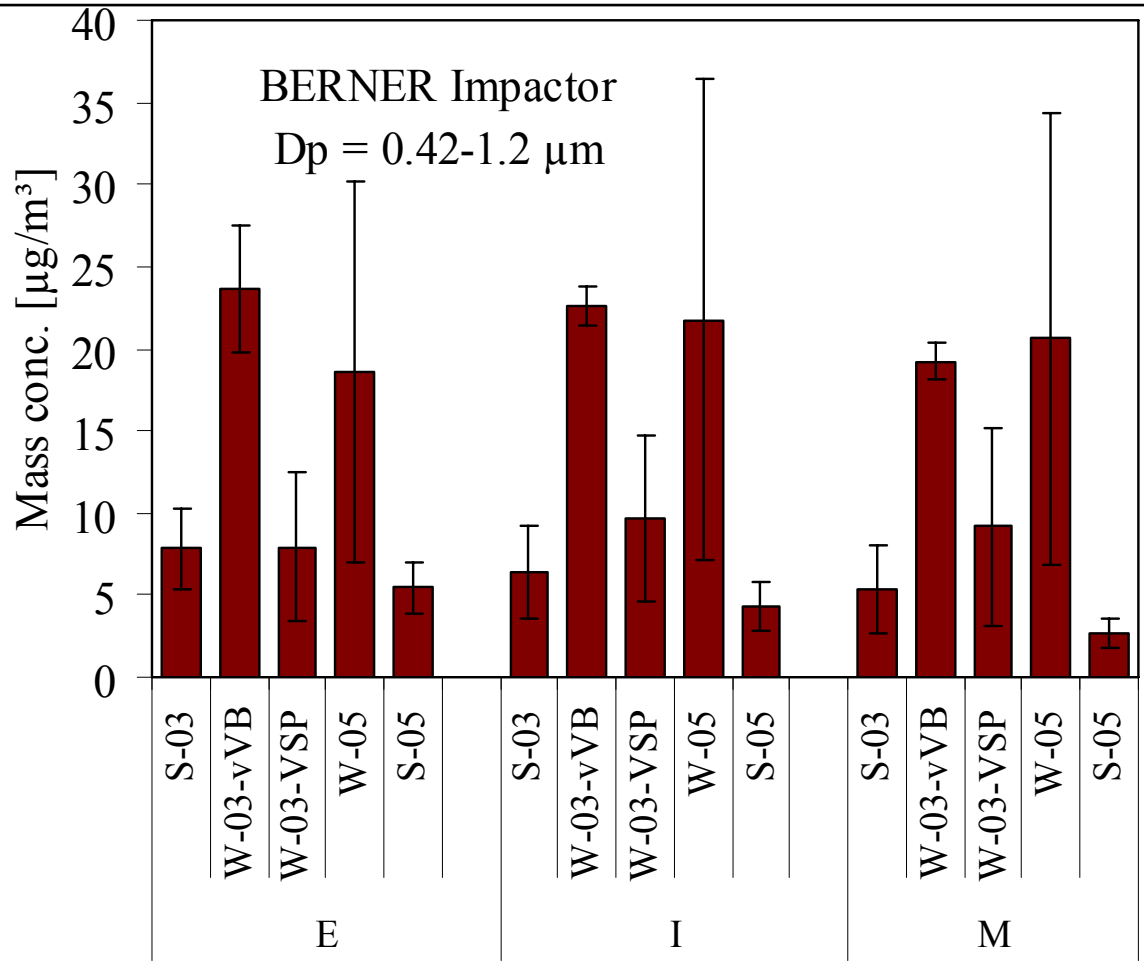
↓

TRAFFIC

REDUCTION

Mean PM concentration of the several measurement periods at the sites E, I und M (BERNER Impactor)

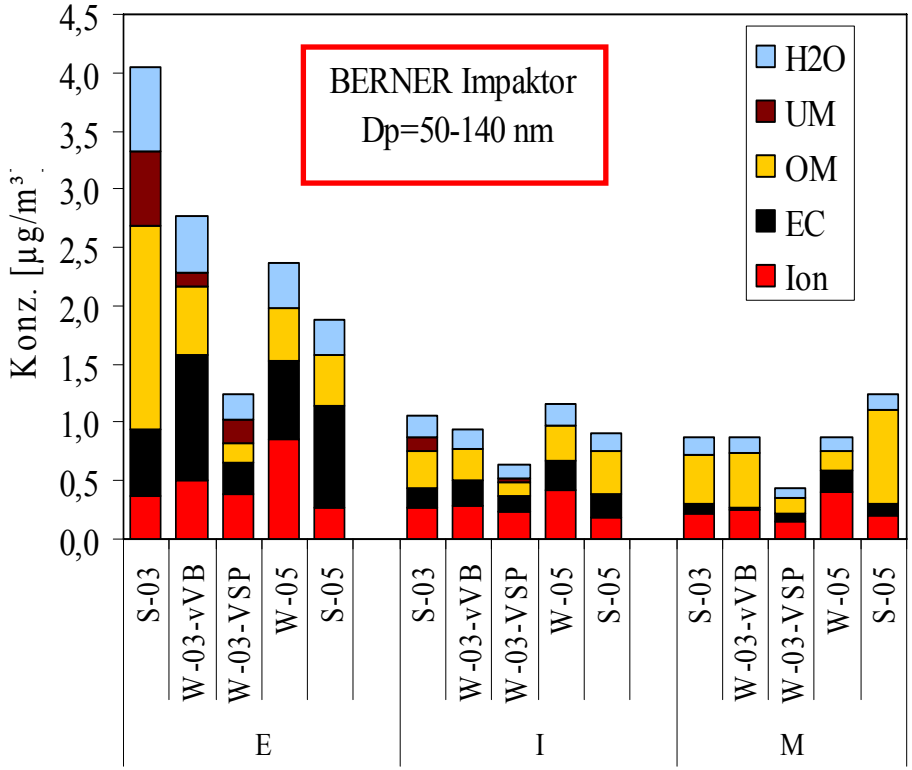
- FOR COMPARISON with BI stage 1 -

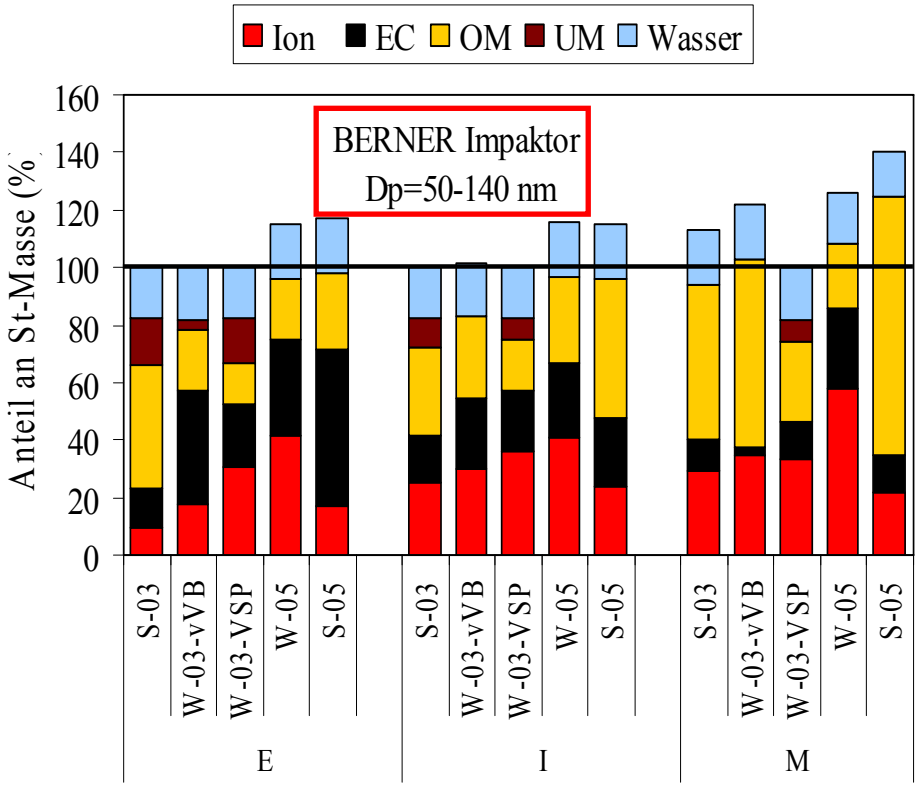


The mean PM concentration of the several measurement periods is similar at the three sites

Particles of this size class originate mainly from long-range transport and domestic heating

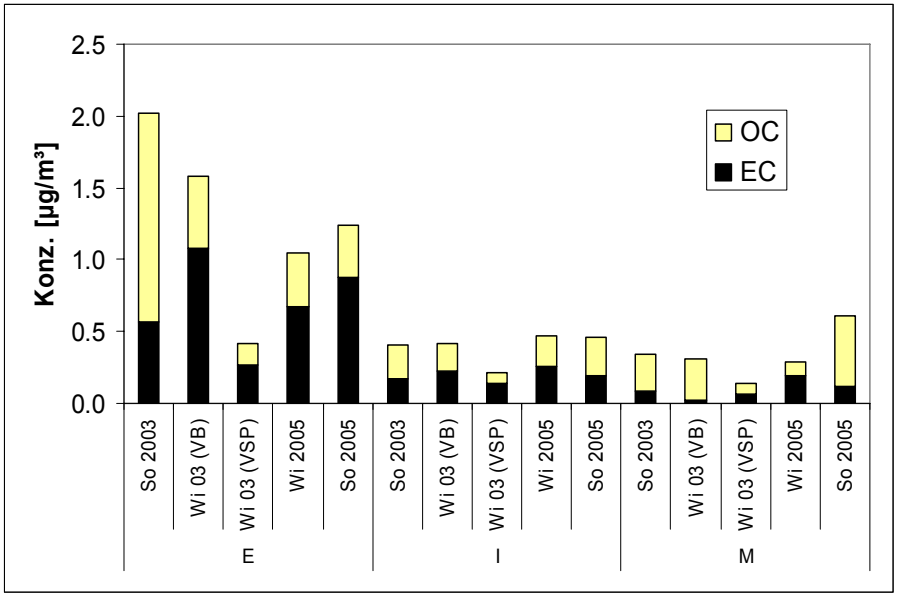
Mean PM concentration of the several measurement periods at the sites E, I und M (BERNER Impactor)





Particles in this size range have the highest EC-fraction at station E (Traffic) and the highest OM-Fraction (organic material) at Melpitz (station M)

Particle composiotn and chemical mass closure Dp=50-140 nm (BI Stage 1)

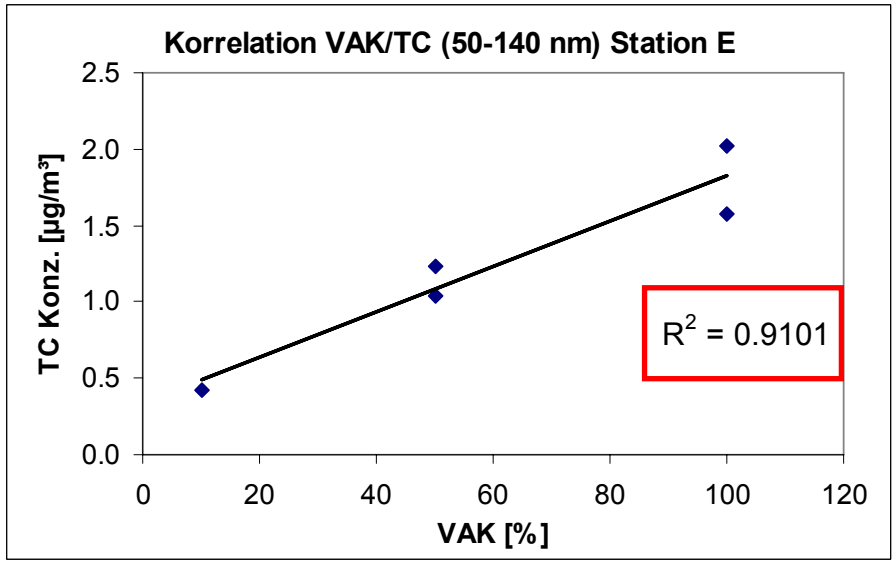


The OC/EC-concentration at station E was clearly higher (by a bout a factor of 2.5) than at stations I and M in all measurement periods.

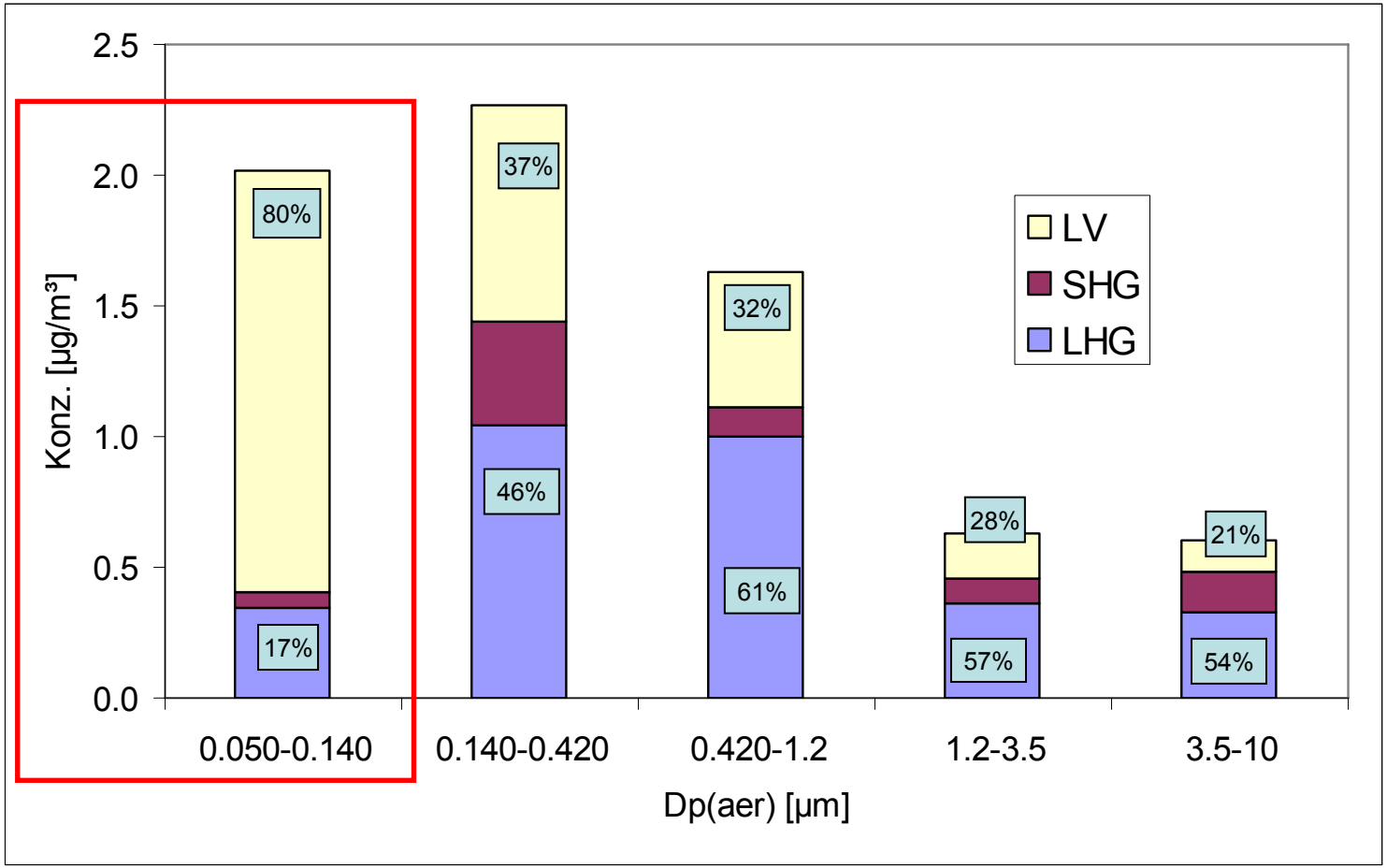
At station E the OC/EC-concentration was clearly dependent on the traffic volume. Traffic reduction by (a) 50 % and (b) 90 % made BI stage 1 TC decrease **to** (a) 40 % and (b) 20 % .

A traffic-independent basic level of 0,34 µg/m³ TC was found as an urban background

For BI stage 1 particles there is a very good correlation between TC particle concentration and traffic volume.



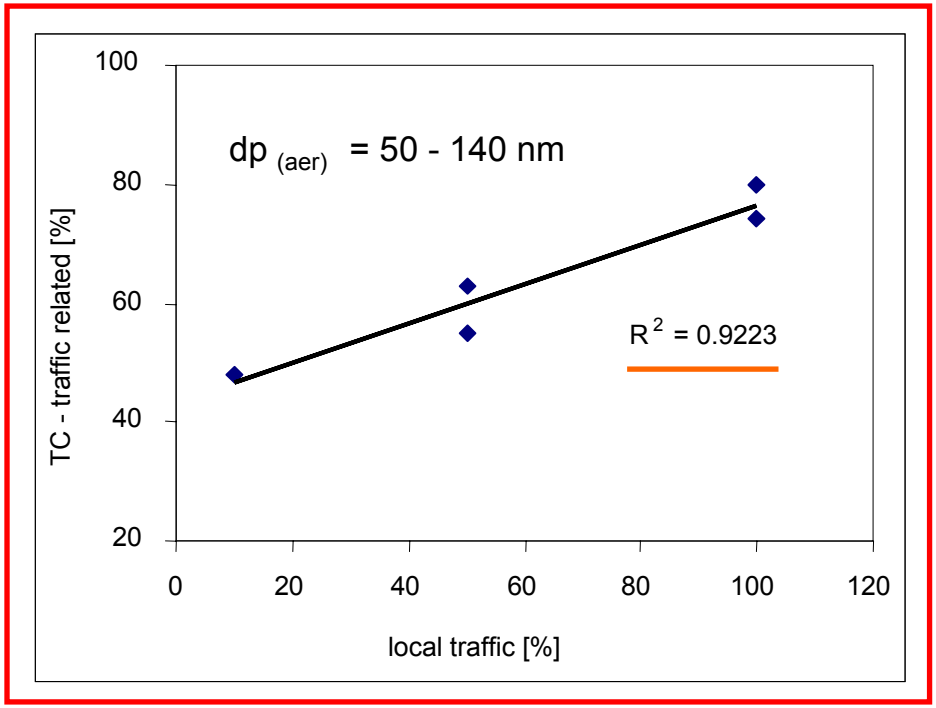
OC/EC-concentration in BI stage 1 particles (Dp(aer) = 50-140 nm)

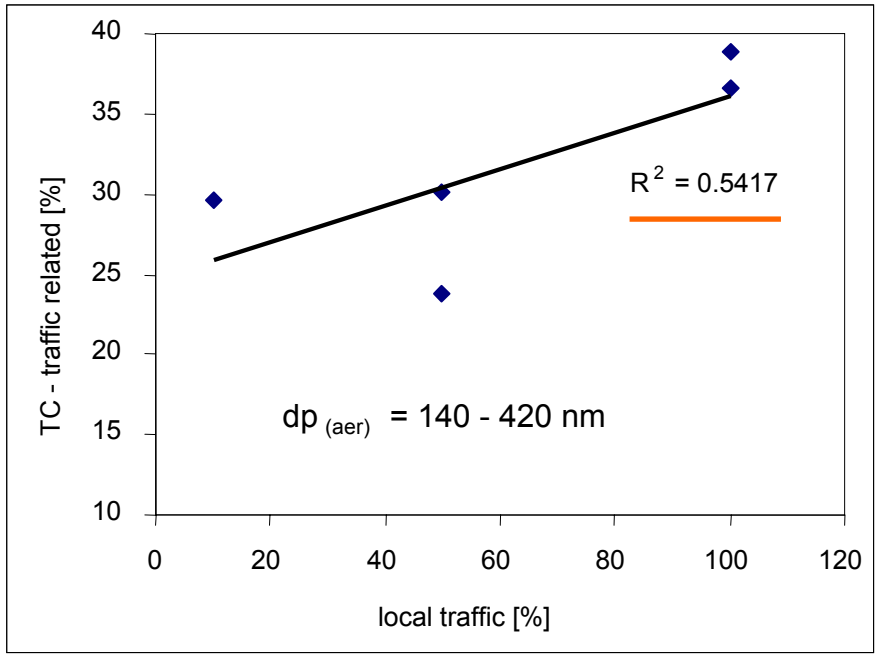


TC from local traffic emissions dominate the finest particle fraction.

Traffic related mass fraction decrease with increasing particle size.

Sources of TC in all size fractions at 100 % traffic volume in summer 2003





Highest correlations between TC content in particles were observed for the BI stage 1 particles:

Much UFP TOC can be ascribed to traffic in urban street canyons with high traffic load.

TC versus traffic volume in the Eisenbahnstraße (mean values of all periods)

LfUG II - Dresden

A - urban traffic: 55 000 vehicles per day

PM every second week 8/2003 – 08/2004

Berner (11 * Th + 2 * Su)

MOUDI (11 * Mo – Th + 1* (2*Sa-Su)):

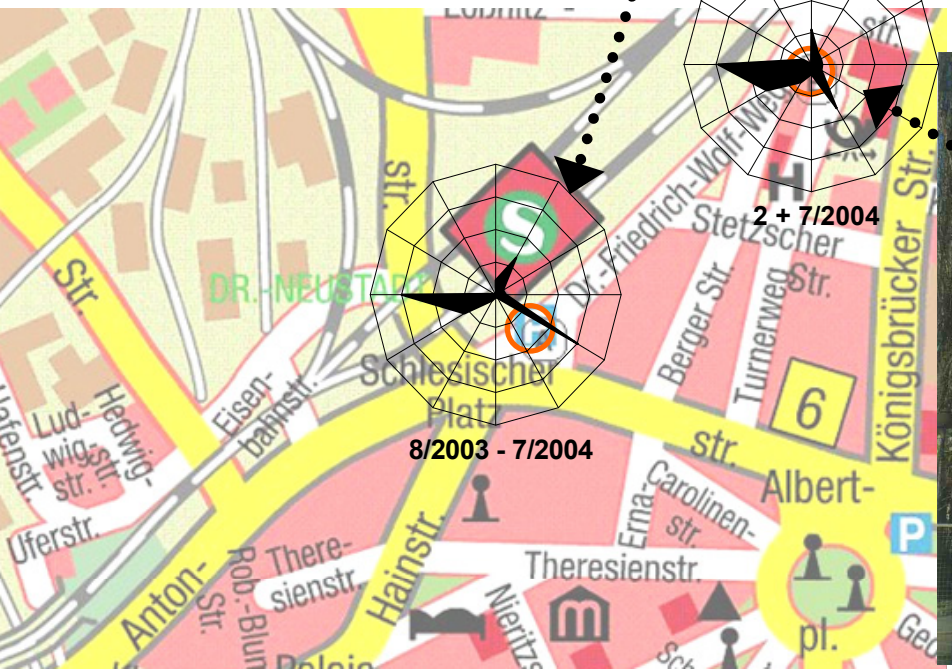
B - urban background (400 m Northeast):

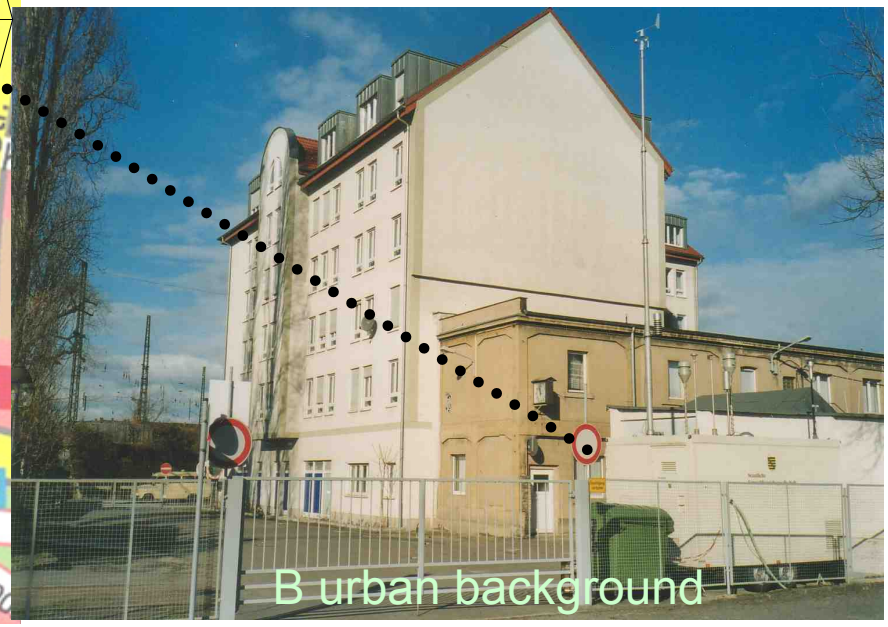
< 5 000 vehicles per day

PM winter (2 weeks) summer (3 weeks)

Berner winter (1 Th) summer (1 Th)

MOUDI winter(1 Mo–Th) summer (1 Mo-Th)



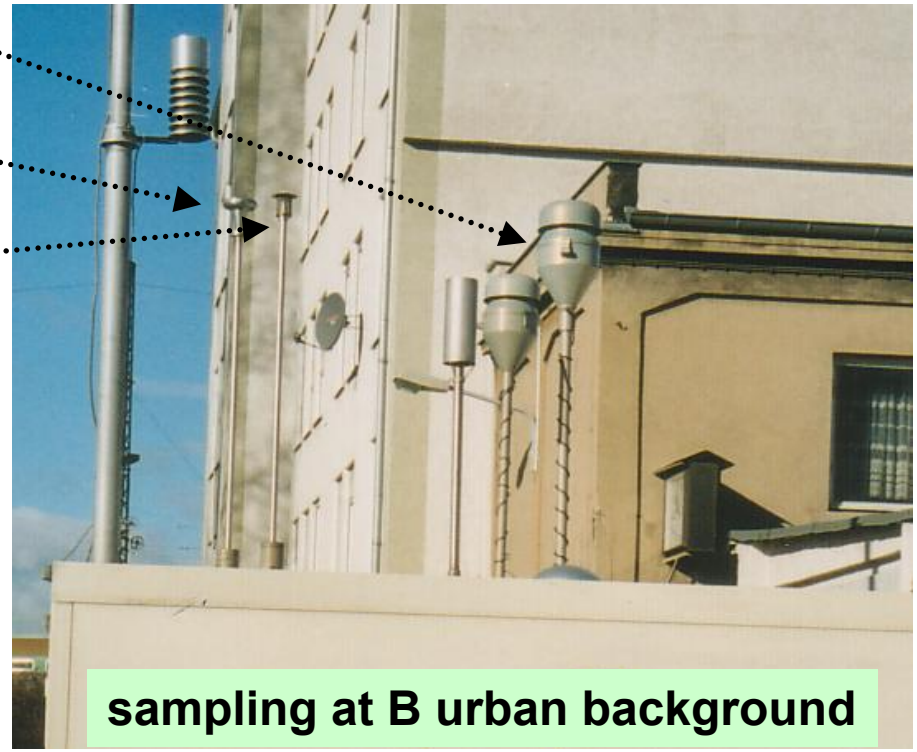


Measurement stations in the Dresden SLUG II project

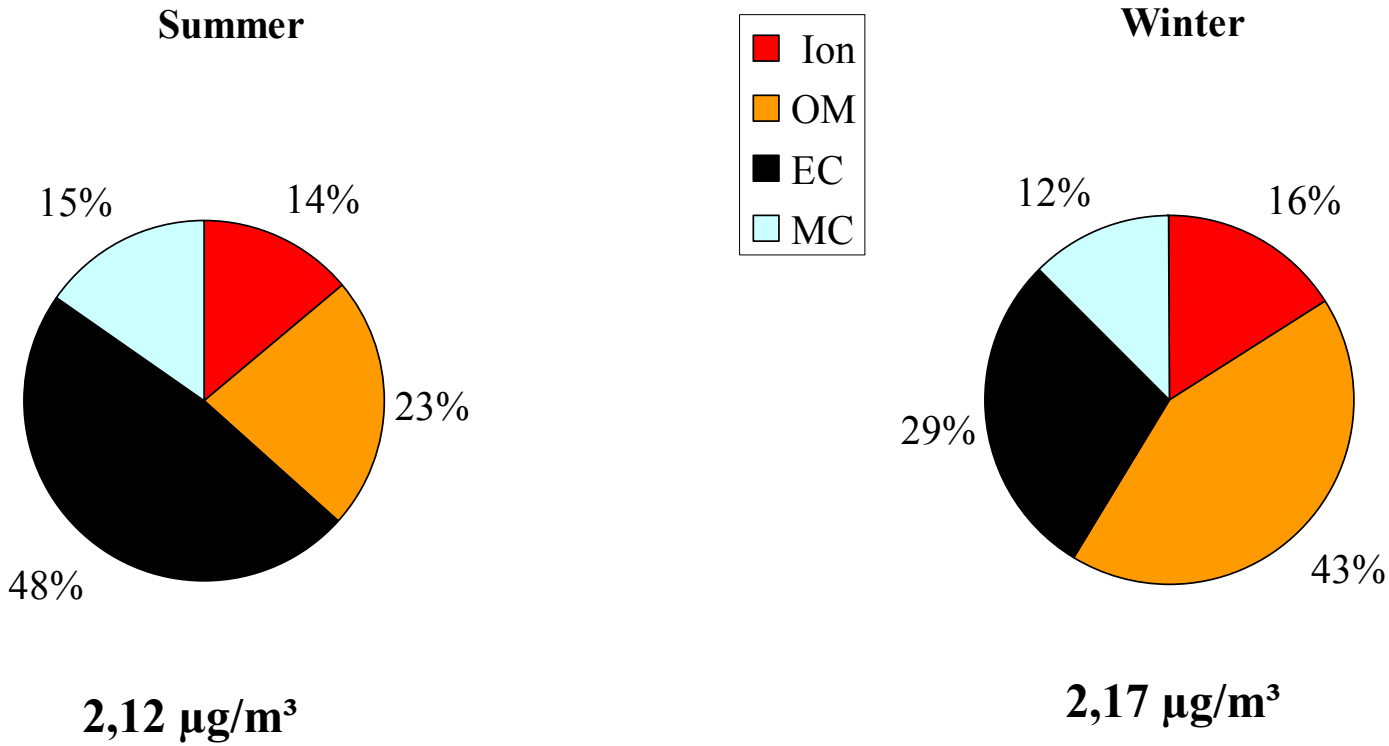
- **PM_{10} und $PM_{2,5}$:** 24h 720m³

- **BERNER-Impactor**
  5 stages:
  0.05 - 10 µm / 24-h 108 m³ / 75 L/min

- **MOUDI**
  13 stages
  „Micro Orifice Uniform Deposit Impactor“
  0.01 - 18 µm / 96-h 172,8 m³ / 30 L/min
  NanoMOUDI:
  0.001 – 0.056 µm / 96-h 57,6 m³ / 10 L/min



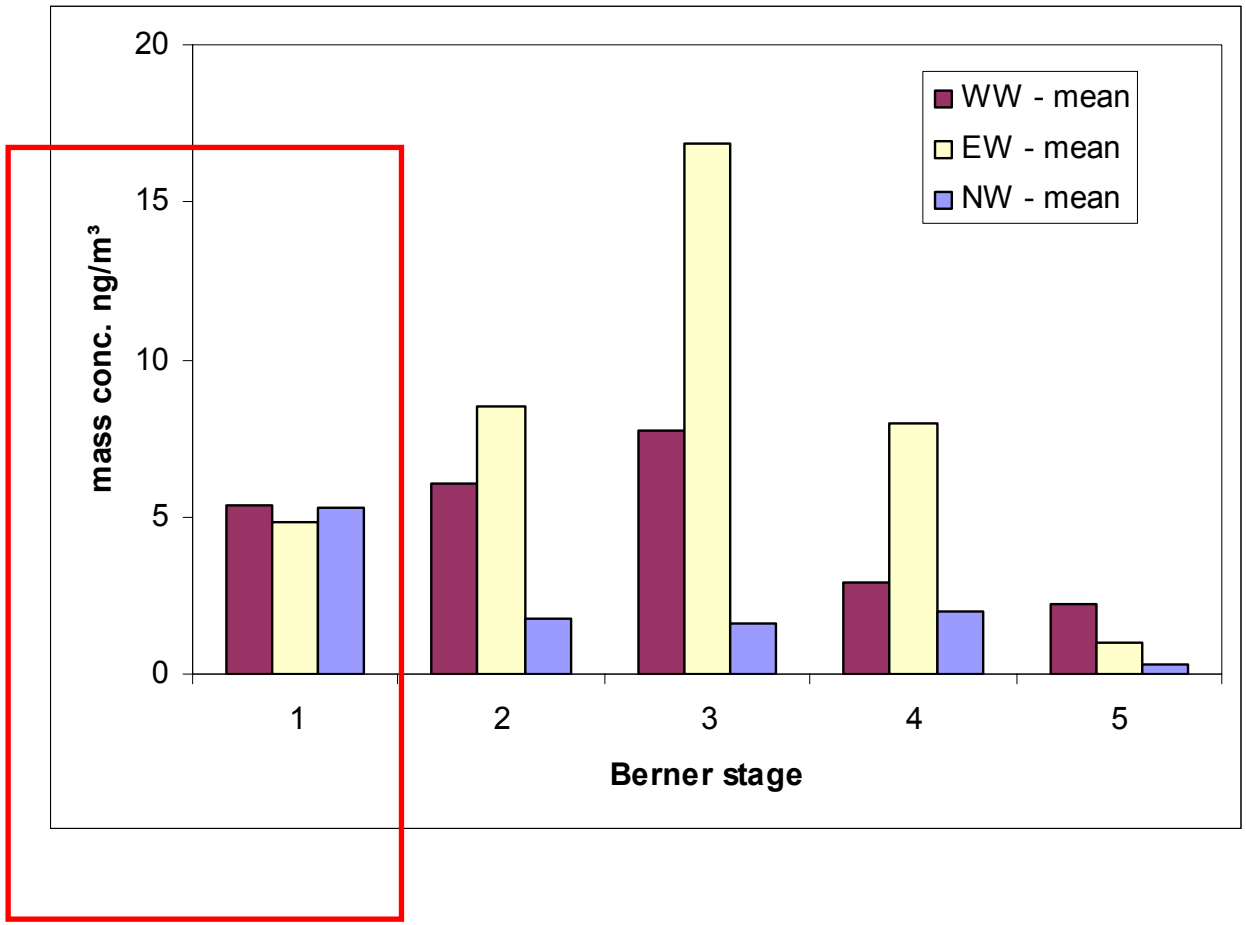
- **Ions:** IC and capillary electrophoresis
- **EC/OC:** Impactor: thermographic two step model ;PM: Coulometry
- **Elements:** Impactor: PIXE; PM: GF-AAS
- **meteorology + gaseous components**

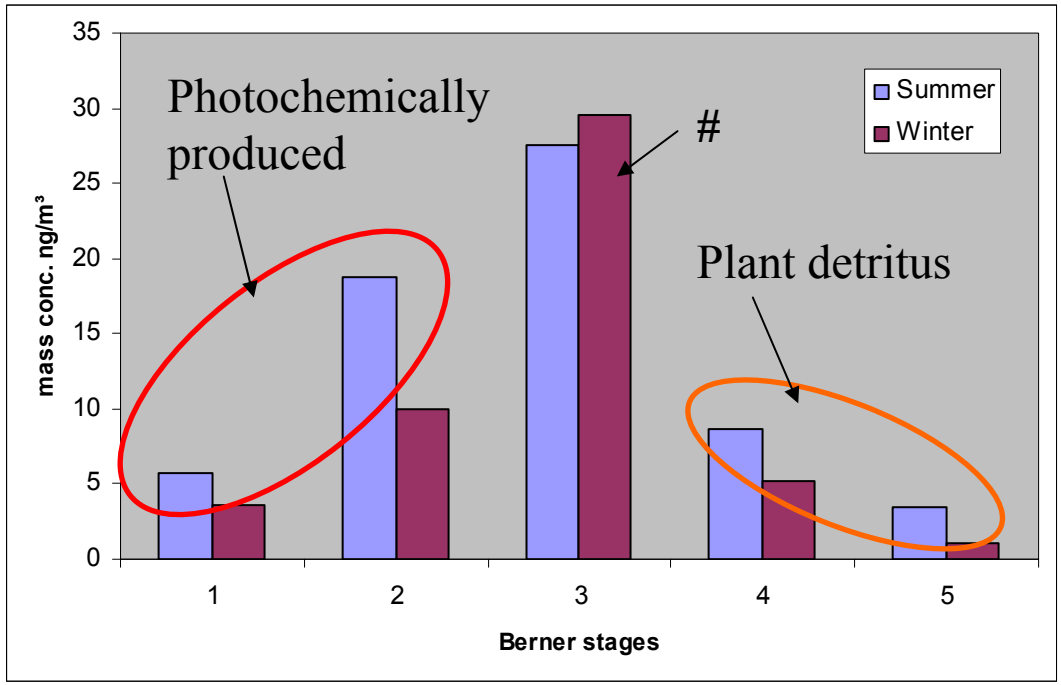


The particle mass of UFPs consists of about 70% total carbon at a urban street station in Dresden (Summer: 50% EC, 20% OM, Winter: 30% EC, 40% OM). The OM/EC ratio accounts to 0.5 in summer and 1.4 in winter. (MC: metal compounds)

Organics

During winter measurements the total mass concentration in Dresden was strongly influenced by wind direction but not for the nano particles – they come from the urban environment and not from long range transports.





- primary emission from biomass burning processes

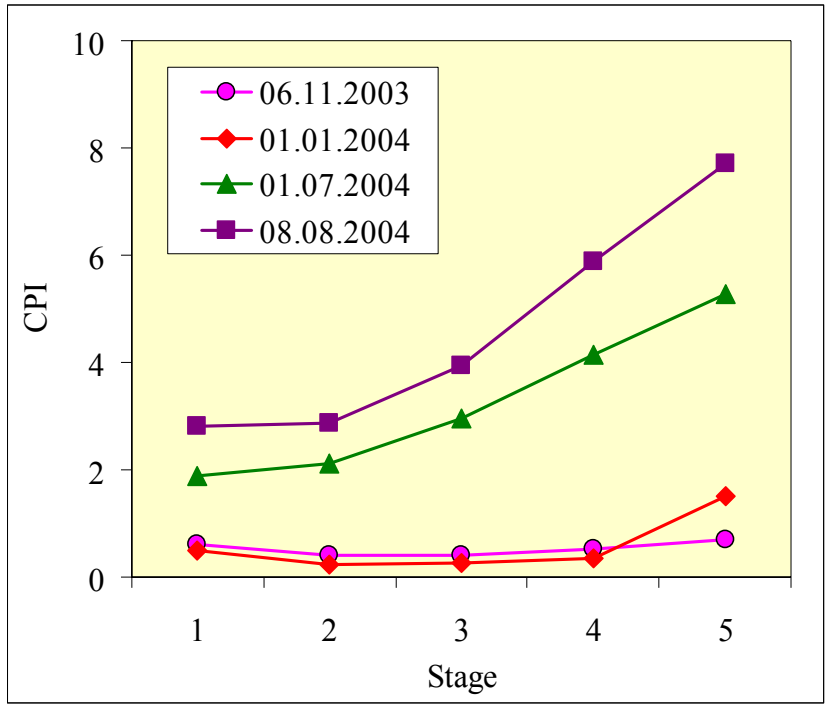
Oxalic acid typically was produced by photochemical oxidation of organic compounds but primary emissions from exhausts and biomass burning are known as well.

Gas to particle conversion and adsorption on existing particles occurs mainly on smallest particles.

In leaves and other plant material oxalic acid was produced, too. Plant detritus is found on coarse aerosol fraction.

Odd carbon numbered alkanes (C-27, C-29, C-31 and C-33) are typical compounds from biogenic sources (plant waxes).

They were found in summer coarse mode aerosols but only in much smaller concentration in ultrafine PM, which were dominated by traffic emissions.



Also biogenic contributions to BI stage 1 particles !

The Carbon Preference Index is a measure for the biogenic contribution to the OC content of PM:

Anthropogenic: CPI: 1

Biogenic: CPI: 4-10

• UFP quantitative sampling is far from trivial. Only some of the available samplers work as specified

• In principle analytical methods currently working for the BI stage 1 can be employed for UFP chemical analysis – 10 µg mass at least required for combinations of offline analytics including organics. Even for 10 µg sampling times could be 100 h

• Online analysis with the AMS is an alternative but only to some extend, as it lacks the information from the detailed chemical analysis, especially for organics

• Traffic-dominated UFPs contain a lot of TOC, i.e. elemental carbon and a wide variety of organics, partly usable as tracers, and, macromolecules

• At rural sites traces for biomass burning and SOA are found

• Other main chemical constituents: Ions, metal compound, also unresolved material still found

• UFPs are close to primary and secondary sources both in time and space

Measurements Part I – Session 3 today:

Session 3	Measurements of Ultrafine Particles in Urban air Part I	Chair: H. Horn, Aachen/D / G. Sem, St.Paul/USA
13:15	Measurements of ultra-fine particles in Europe: differences and similarities	R. van Dingenen*, J.P. Putaud, D. Mira-Salama, N.R. Jensen, F. Raes, IJRC Ispra/I
13:45	Origin and features of ultrafine particles in Barcelona	S. Rodríguez1,2, J. Pey2, N. Perez2, X. Querol2, A. Alastuey2, R. Van Dingenen3 and J.P. Putaud3; 1University of Huelva, Santa Cruz de Tenerife/E; 2 CSIC, Barcelona/E; 3 Inst. Env. Sust., EC – DG JRC, Ispra/I
14:05	Ultrafine particles in the UK	A. Jones*, R M Harrison Univ. Birmingham/GB
14:25	Ultrafine particles in Stockholm	C. Johansson*, M. Norman, H. Karlsson, Univ. Stockholm/S
14:45	Ultrafine particles in Prague	J. Novak, CHMU, Prague/CZ

Measurements Part II - Session 6 tomorrow with more physical and some chemical measurements:

Session 6	Measurements of Ultrafine Particles in Urban air Part II	Chair:H. Herrmann, IfT,Leipzig/D /R. Caldow, TSI,St.Paul/USA
10:30	Five years ultrafine and fine ambient particles number concentrations measurements at a traffic-orientated site in Dresden	G. Löschau*, LfUG, Dresden/D; B. Wehner, IfT, Leipzig/D; A. Wiedensohler, IfT, Leipzig/D
10:50	Ultrafine particles in NRW - case studies in the urban background and at an "Autobahn"	T. Kuhlbusch, A. John, U. Quass*, IUTA/D
11:10	Ultrafine and fine particle measurements in Switzerland at various stations and on different roads	A.S.H. Prévôt*, E. Weingartner, S. Weimer, J. Sandradewi, M.R. Alfarra, V. Lanz, C. Hueglin, S. Szidat, U. Baltensperger
11:30	Temporal and spatial variability of sub-µm aerosol concentrations in the urban atmosphere of Leipzig	Wolfram Birmili[1], Susan Klose[1], Maik Merkel[1], Birgit Wehner[1], Korinna König[1], André Sonntag[1], Alfred Wiedensohler1, Oswald Knoth1, Detlef Hinneburg1, Thomas Tuch1,2, and Ulrich Franck2; 1 IfT, Leipzig/D; 2 UfZ, Leipzig/D
11:50	Chemical composition of aerosol particles including UFPs in Saxony	T. Gnauk1)*, E. Brüggemann1), H. Gerwig2), H. Herrmann1), K. Müller1), G. Spindler1 1) IfT, Leipzig/D, 2) LfUG Dresden/D

More UFIPOLNET conference contributions on measurements

Acknowledgements & Thank You !

SURPLUS

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