Sampling and Chemistry of Size Segregated Aerosols

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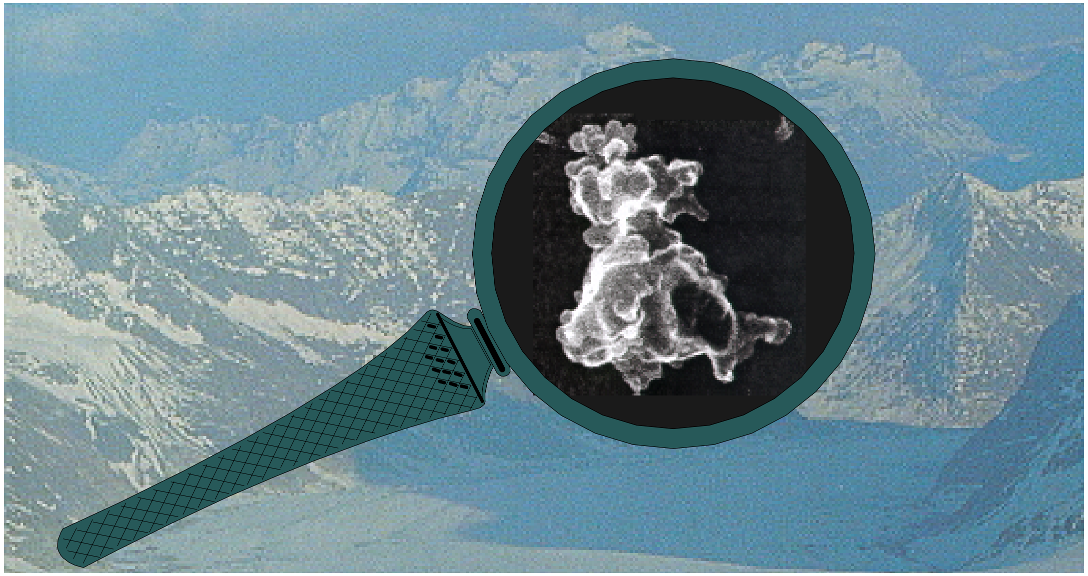


TFMM workshop

Oslo, 22–24 November 2004

Aerosol parameters relevant to climate forcing

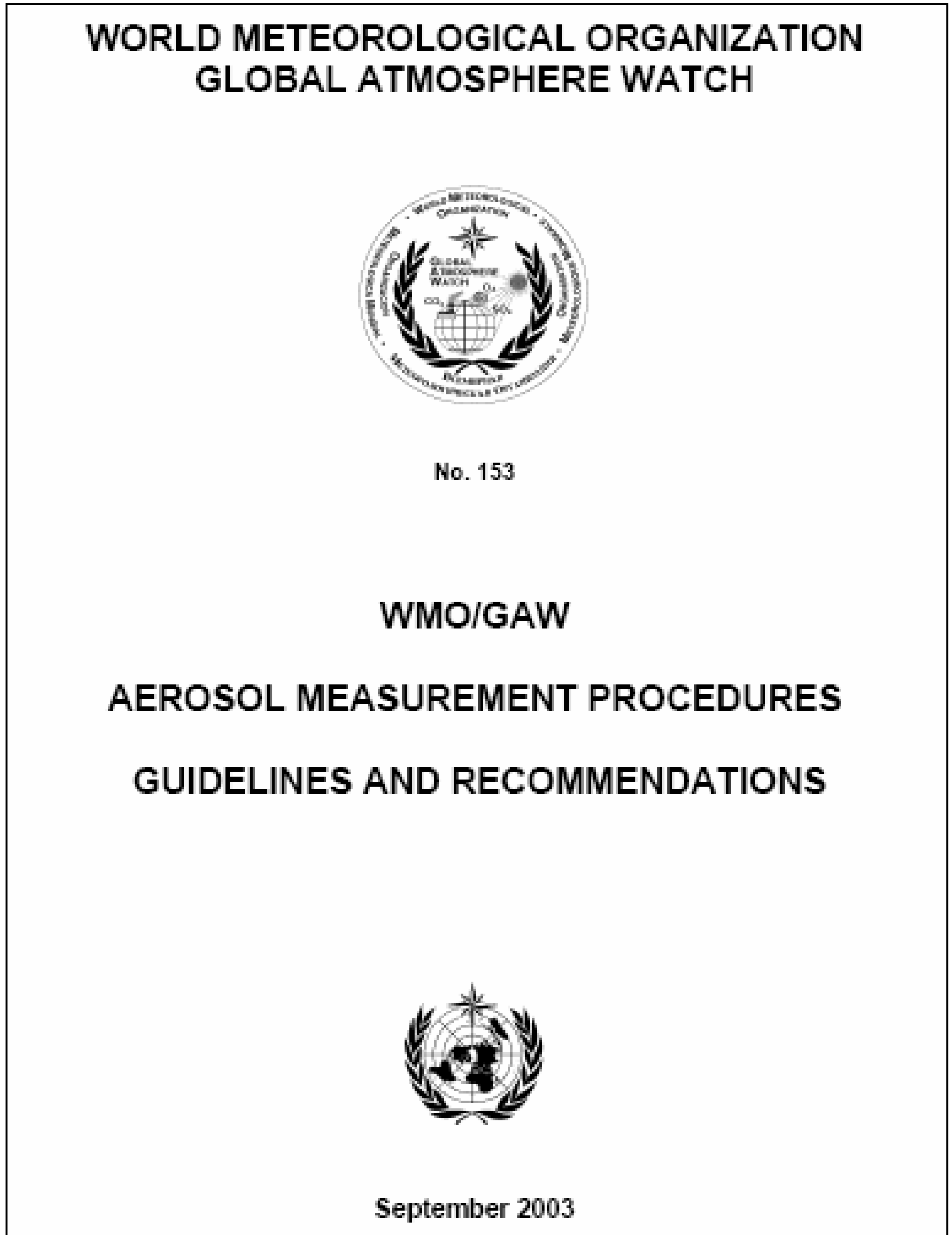
(suggestions by the GAW Scientific Advisory Group for Aerosols)

•Continuously:
- Multiwavelength optical depth
- Mass in two size fractions
- Major chemical components in two size fractions
- Scattering and hemispheric backscattering coefficient at various wavelengths
- Absorption coefficient
- Aerosol number concentration
- Cloud condensation nuclei at 0.5% supersaturation
- Diffuse, global and direct solar radiation

• Intermittently:
- Aerosol size distribution
- Detailed size fractionated chemical composition
- Dependence on relative humidity
- CCN spectra (various supersaturations)
- Vertical distribution of aerosol properties

Can be downloaded from WMO website: enter WMO GAW into Google

or from EMEP website



WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 153

WMO/GAW

AEROSOL MEASUREMENT PROCEDURES

GUIDELINES AND RECOMMENDATIONS

September 2003

The GAW recommendations

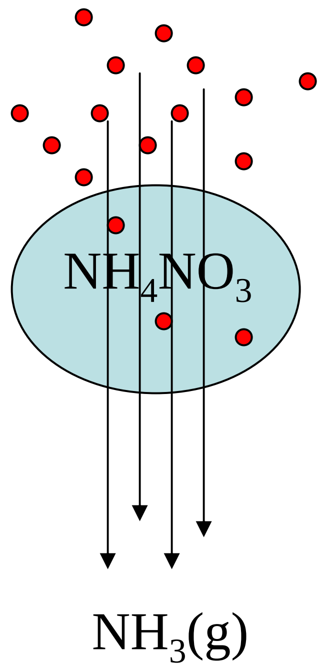
- ‚Standard ions': Sulfate, nitrate, chloride, sodium, ammonium, potassium, magnesium, calcium: teflon filter
- Special care for nitrate and ammonium:
  Nitrate: teflon/nylon filterpack behind a denuder to remove HNO_3
  Ammonium: correct for NH_4NO_3 loss from teflon filter
- Elements: teflon filter
- Carbon: quartz filter

Sampling and extraction issues from nylon filters (ION SPECIAL STUDIES in the IMPROVE program)

- Does water efficiently extract nitrate from nylon filters?
  - HNO_3 not efficiently recovered with water extraction?
  - use H_2O or $NaHCO_3/Na_2CO_3$?
- What happens to NH_4NO_3 volatilized from nylon filters?
  - HNO_3 trapped? Decrease in water extraction efficiency?
  - NH_3 lost? Bias in measured $PM_{2.5}$ ammonium?

Courtesy: Bill Malm, IMPROVE

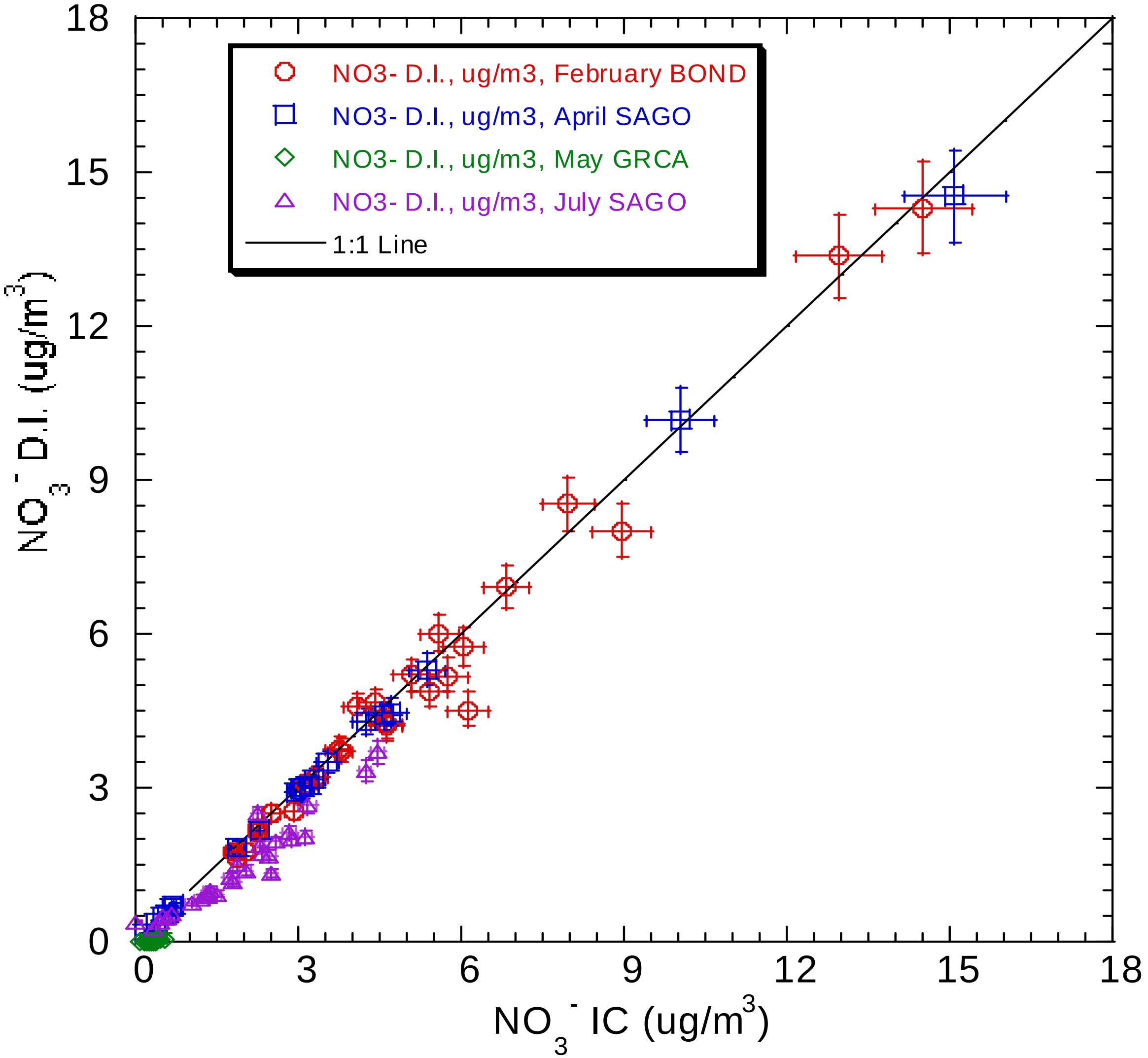
$$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(p)$$



NO_3^- extraction on nylon

- Nylon filter extraction by water showed no bias in first three studies
- San Gorgonio July experiment will be repeated this summer

Courtesy:
Bill Malm,
IMPROVE

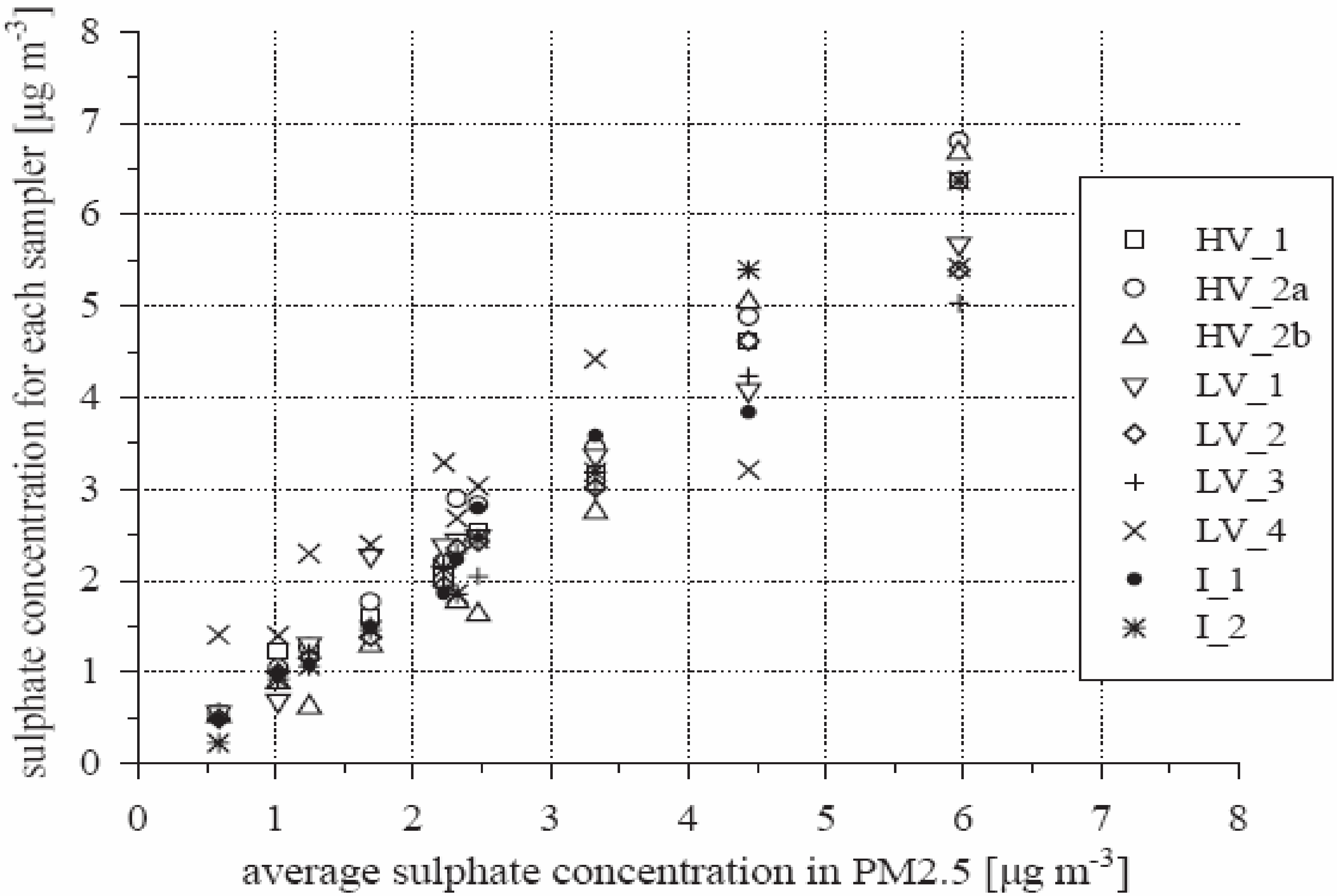


Filter materials used in the Melpitz intercomparison

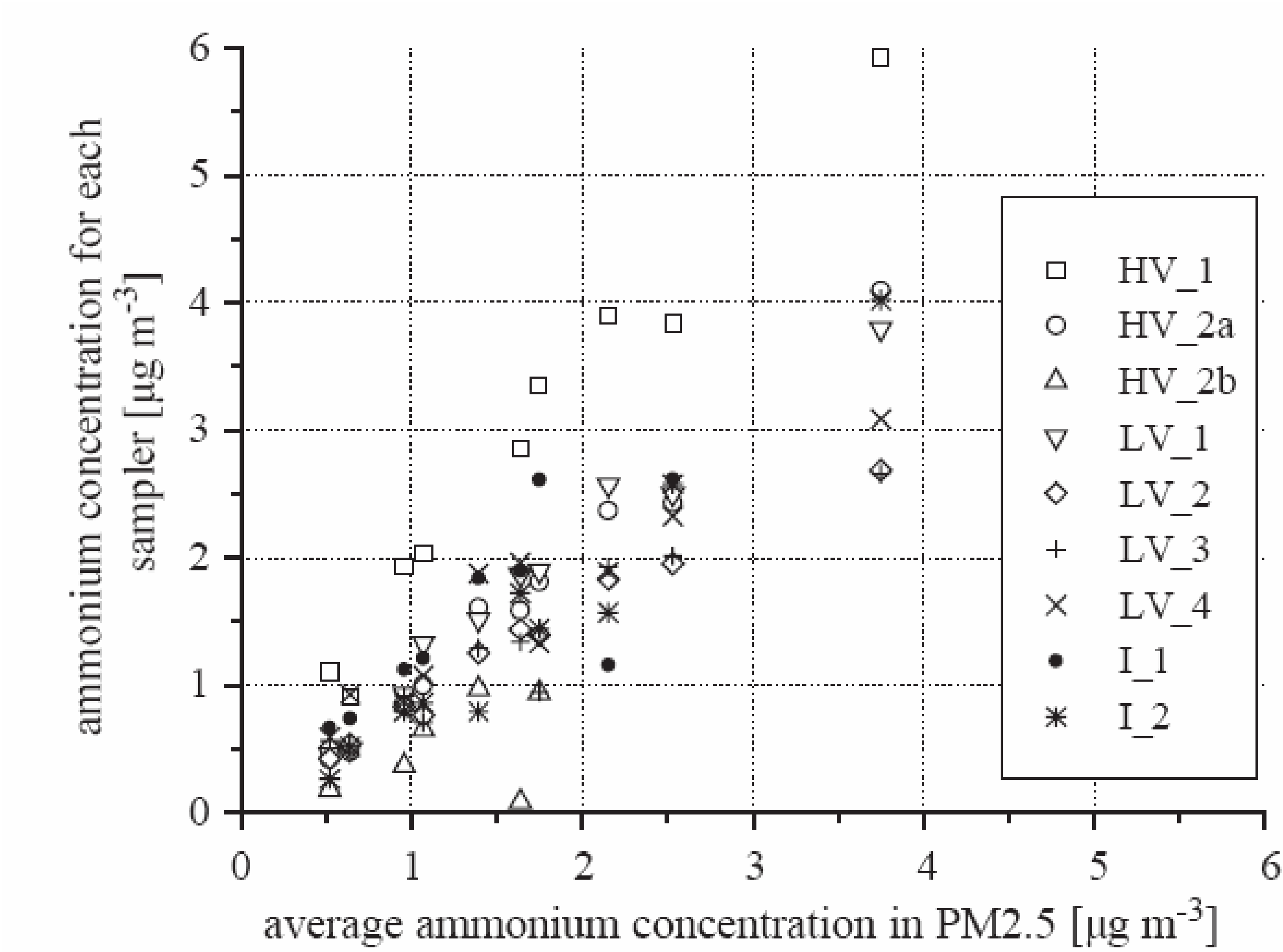
Sampler type	Upper cut size	Filter material (pore size)	Weighing protocol	Operated by
SFU	PM10	Nuclepore, 8 µm	20 °C, 50% rel. hum.	UGent
SFU	PM2	Nuclepore, 0.4 µm	id.	UGent
SFU	PM2	Teflon, 2 µm	id.	UGent
SFU	PM2	Millipore mixed cellulose ester, 3 µm	id.	UGent
Gent	PM2.5	Quartz fibre Whatman QM-A	id.	UGent
Gent	PM10	id.	id.	UGent
TSP	n.a.	id.	id.	UGent
TEOM 1400A	PM2.5	n.a.	n.a.	UGent
Digitel DHA-80	PM2.5	Quartz fibre, Munktell MK360	20 °C, 50%	Leibnitz Institute for Tropospheric Research Leipzig (IfT)
Sierra–Anderson	PM10	Quartz fibre Whatman QM-A	id.	IfT
Digitel DHA-80	PM2.5	Quartz fibre, Munktell MK 360	id.	BTU Cottbus, Berlin
TSP	Ca. 80 µm	Polycarbonate, 0.2 µm	20–22°, 30–40% rel. hum.	UniV

Upper cut sizes as well as substrate types are given. All stacked filter unit (SFU) samplers had the same kind of front filter (PM10) which is given only once. n.a., Non applicable. id., Same as above.

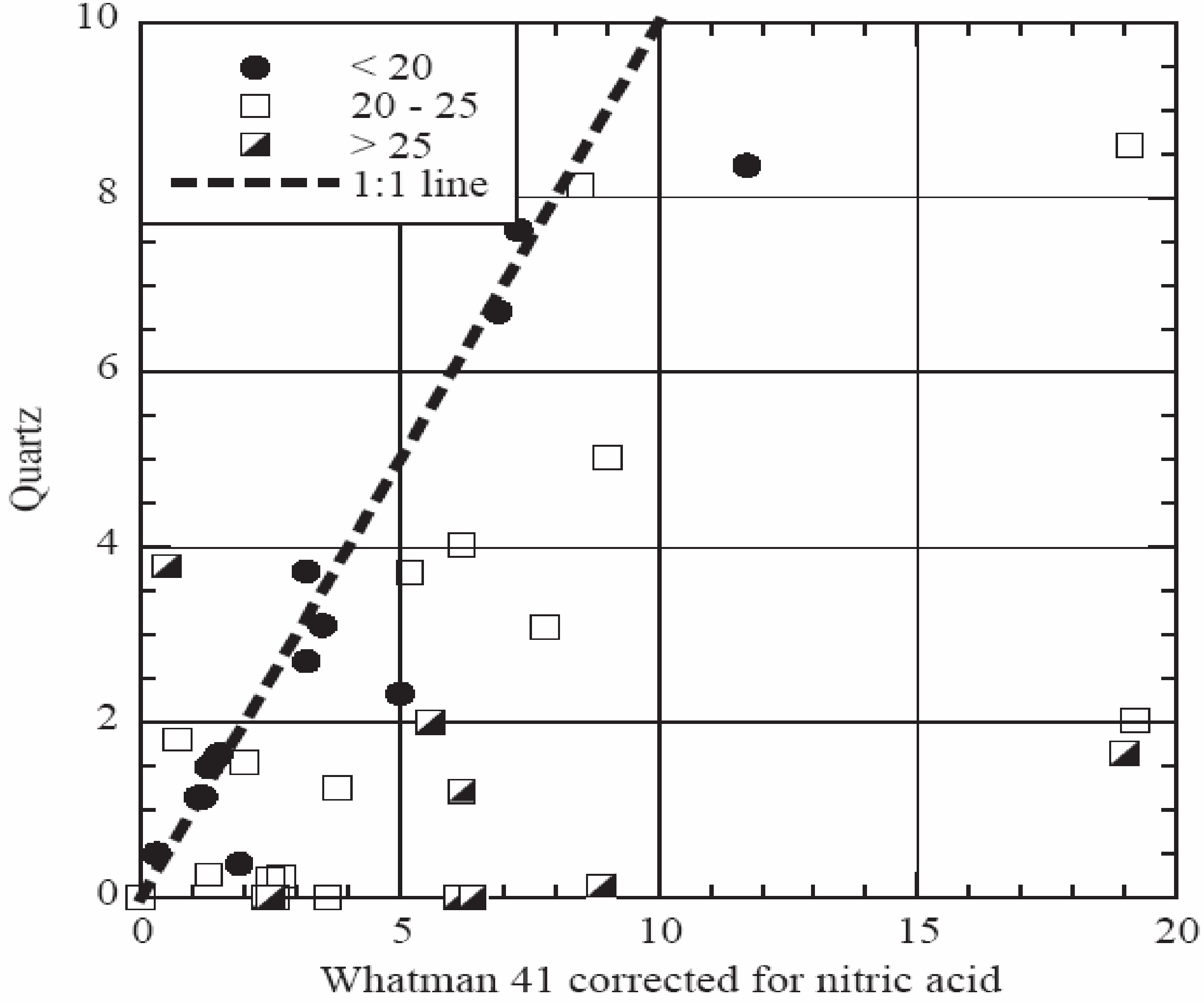
Sulfate intercomparison Melpitz



Ammonium intercomparison Melpitz

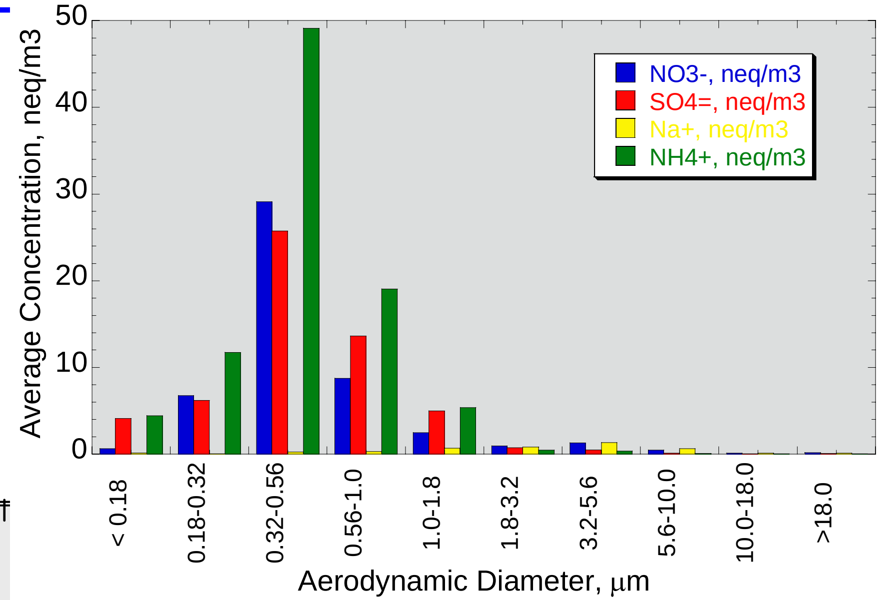


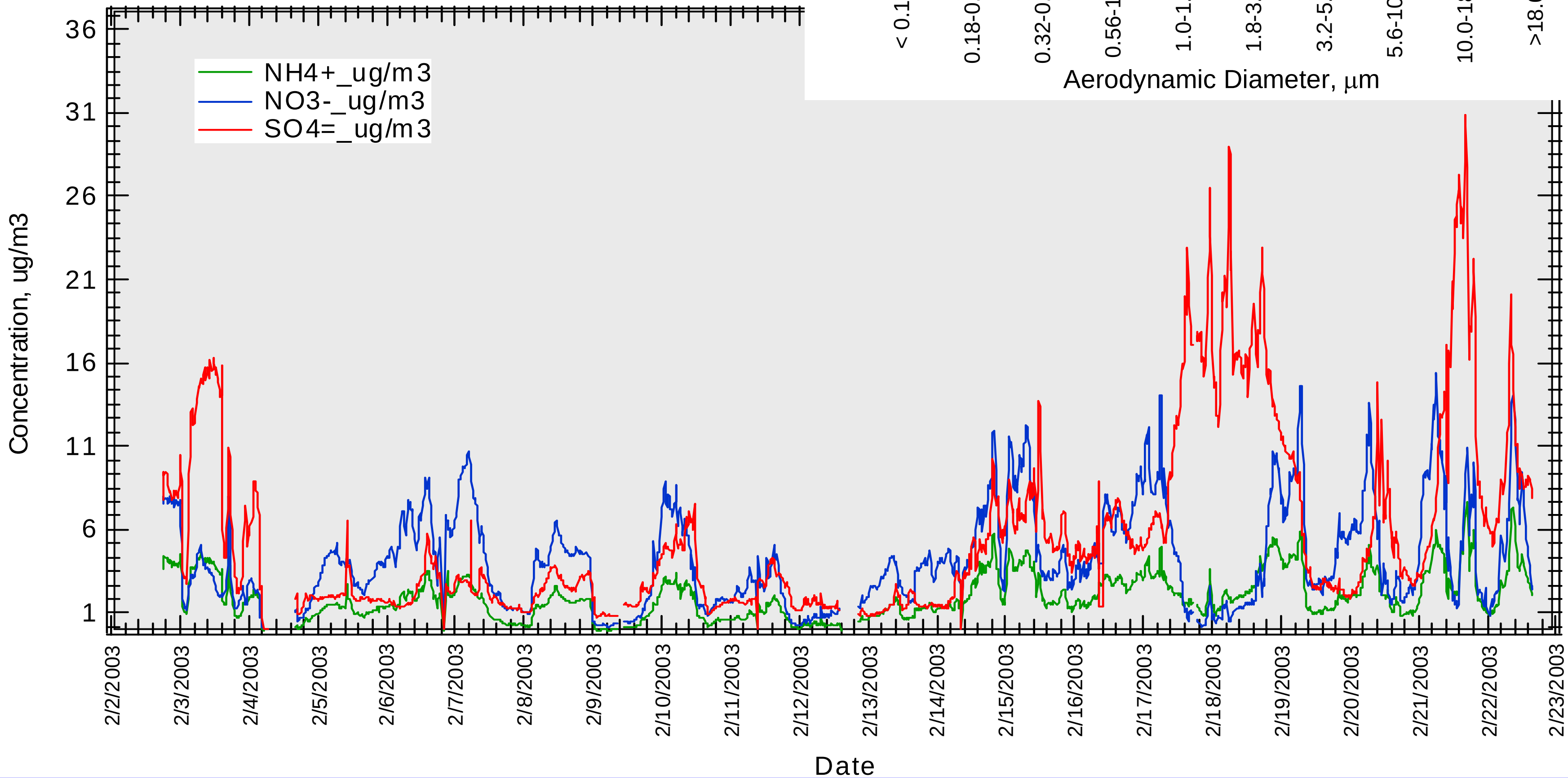
Nitrate volatilisation from quartz fiber filters



Bondville 2/03

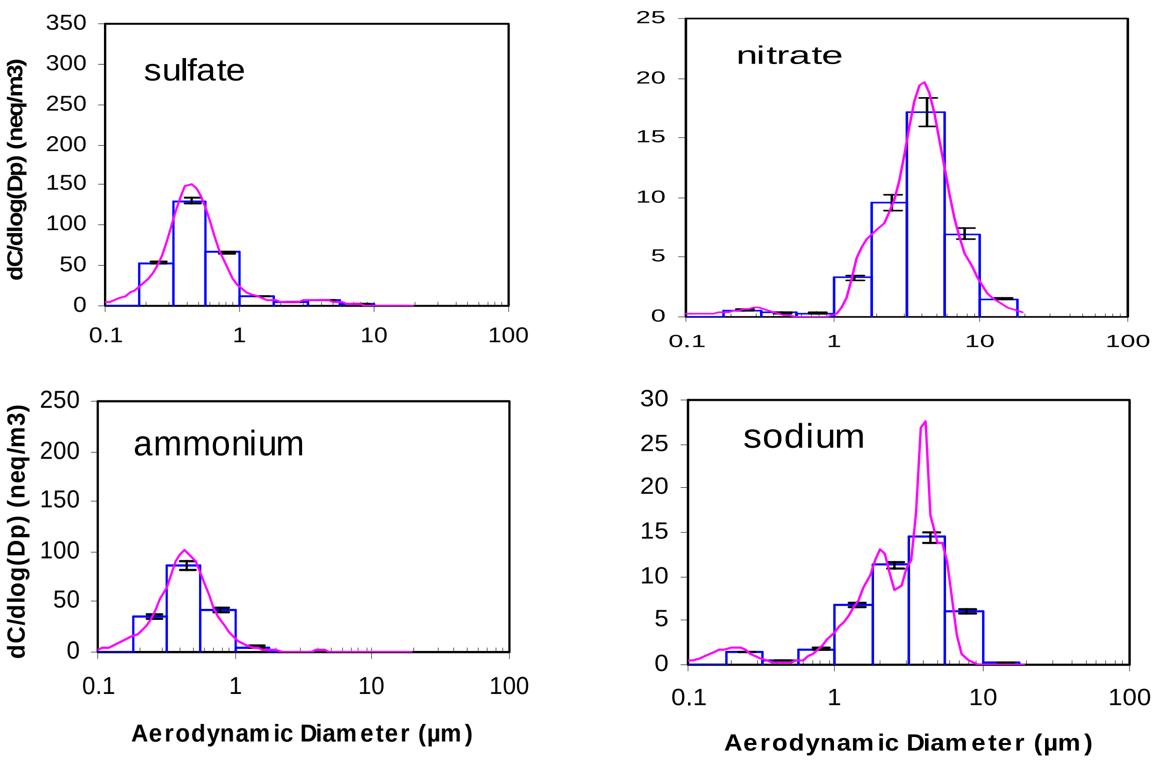
- NO_3^- and SO_4^{2-} both important
- NH_4NO_3 in submicron mode



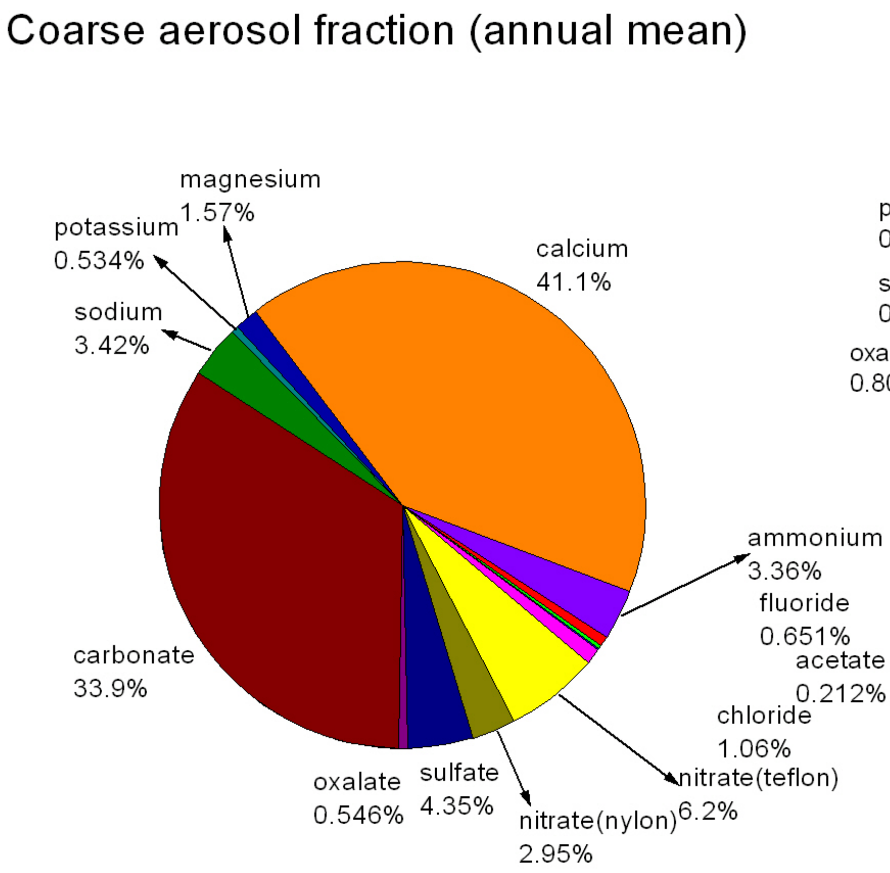


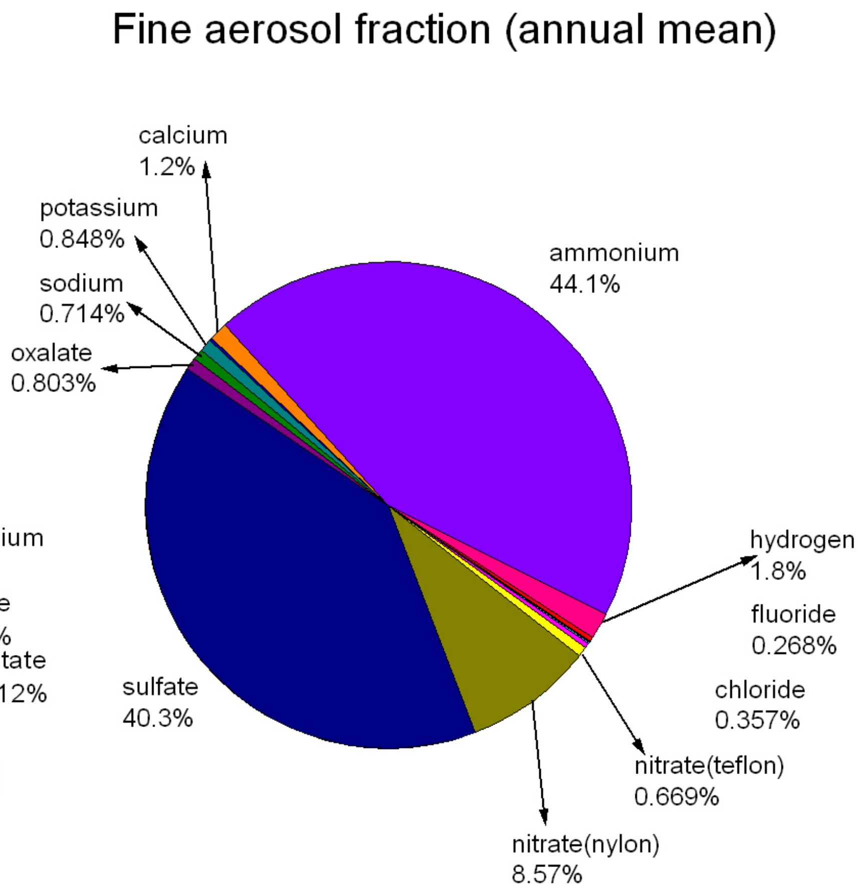
Nitrate in Big Bend

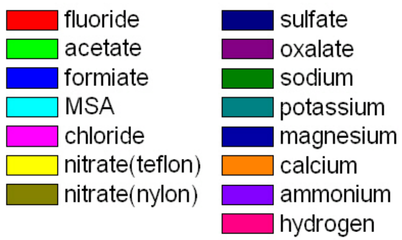
- Nitrate found in coarse mode particles
  - Mode size ~4-5 µm
  - Size distribution similar to Na^+
- $PM_{2.5}$ includes tail of coarse mode



Chemical composition of the Jungfraujoch aerosol

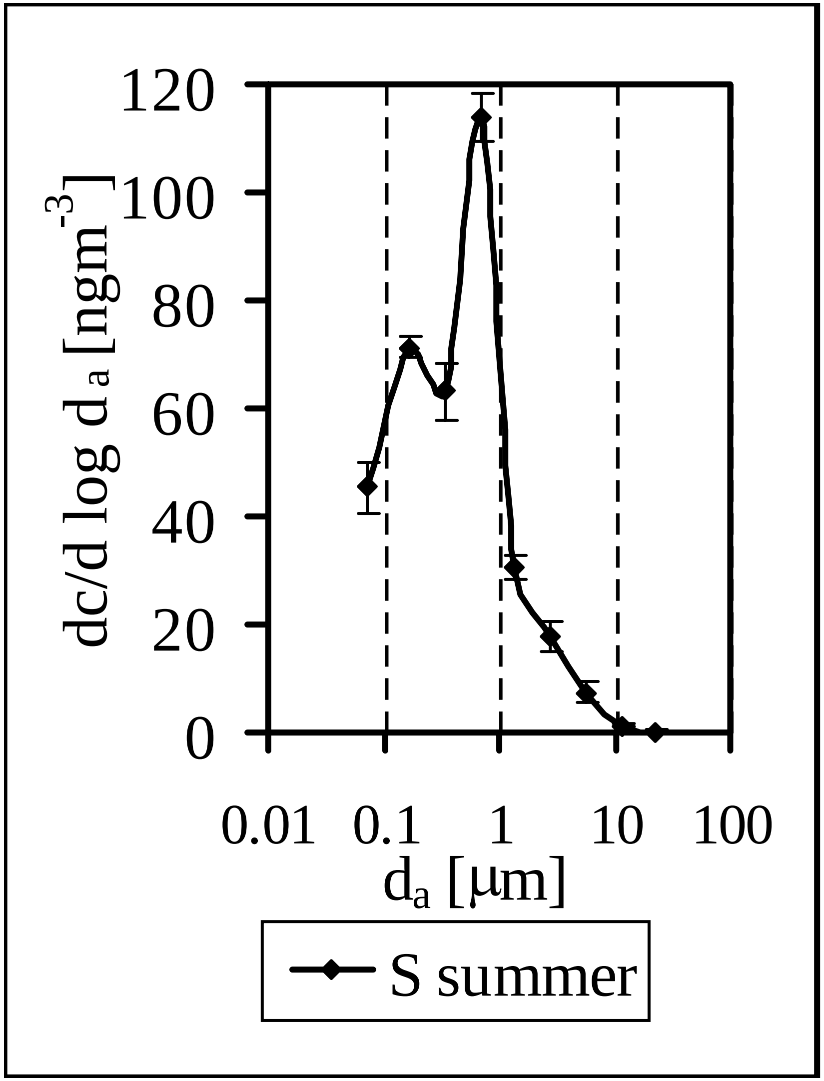


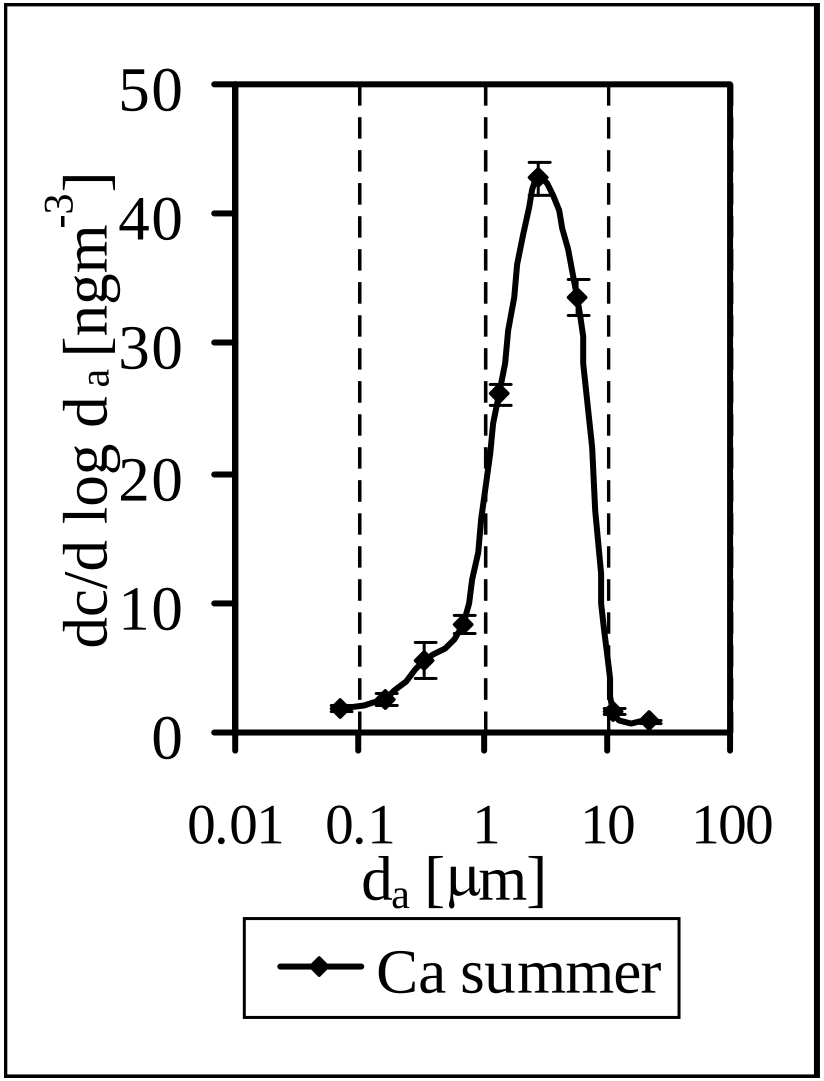




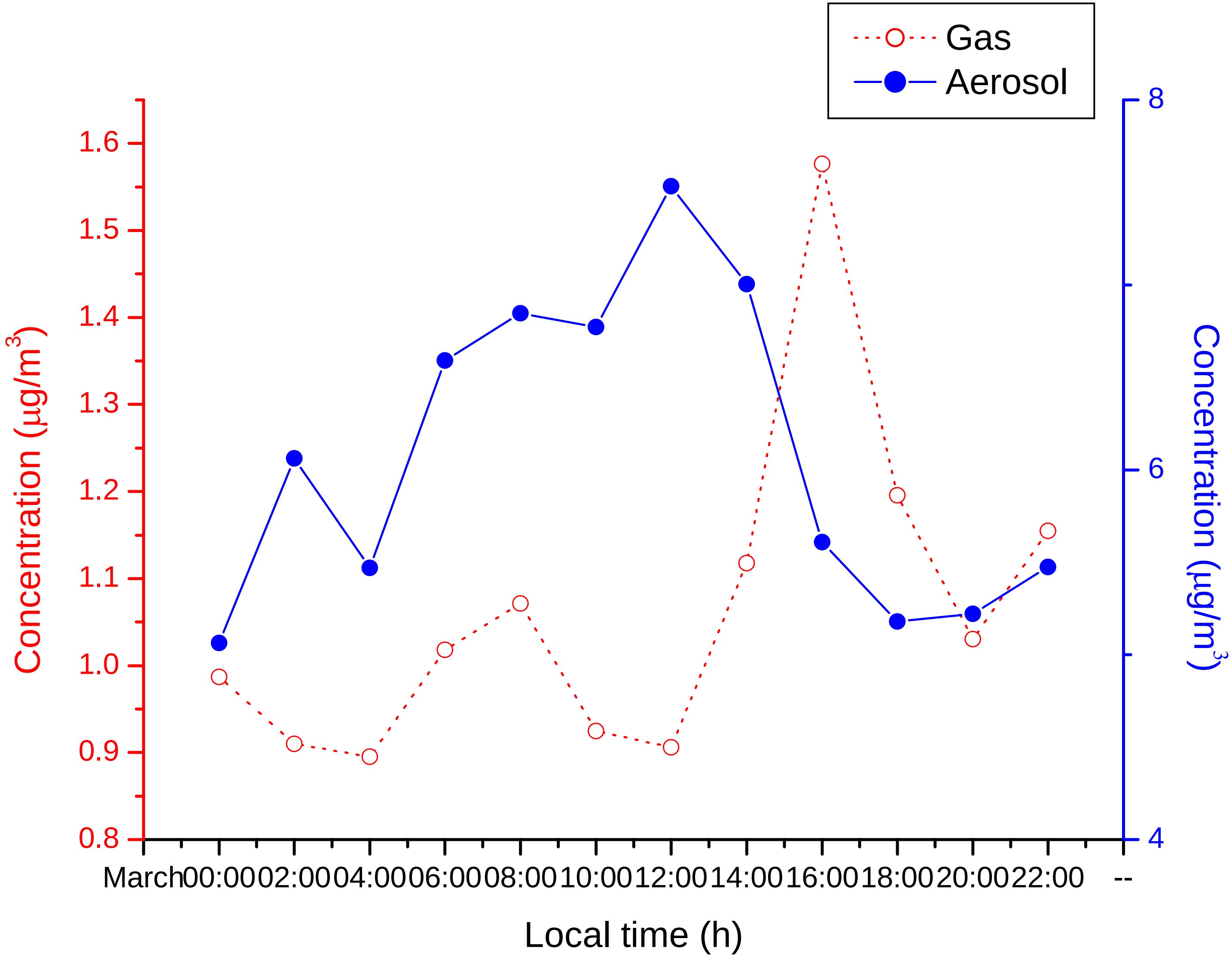
Henning et al., J. Geophys. Res. (2003)

Size distributions of sulfate and calcium at the Jungfraujoch



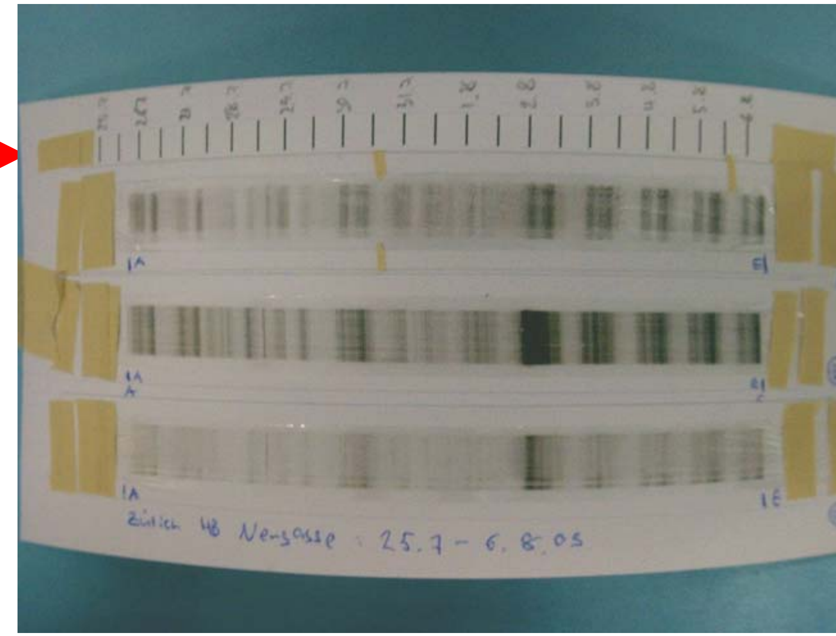


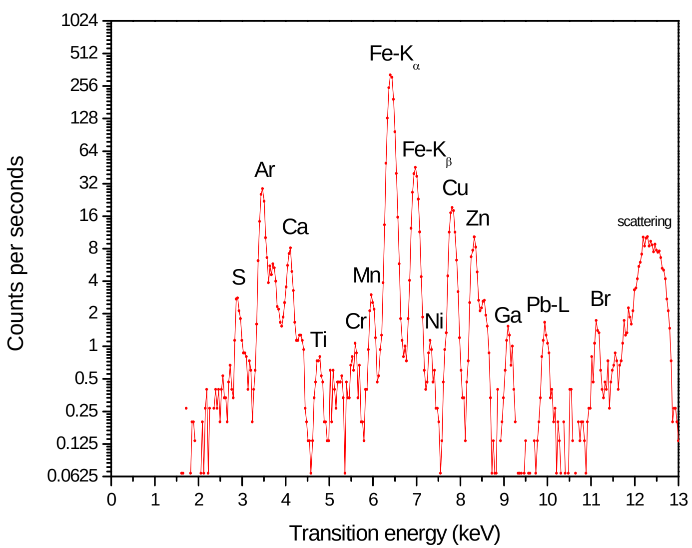
Diurnal variation of nitrate in the gas and aerosol phase in March 2003



Size resolved measurements of elemental ambient concentrations with RDI/SXRF

Rotating Drum Impactor (RDI) collects aerosol in **3 size classes** with **1-hour resolution**

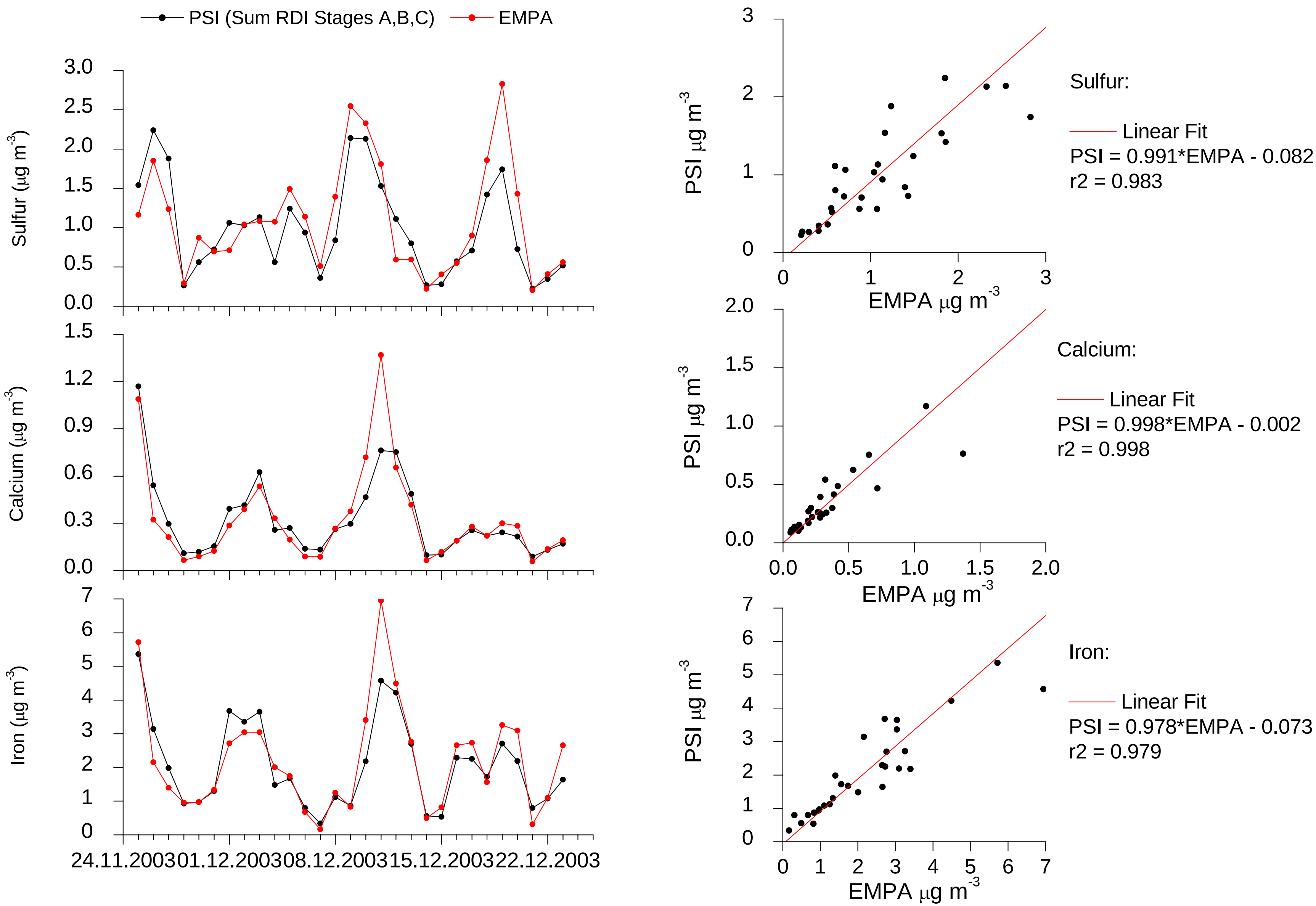




- SXRF allows for quantitative analysis of 1-hour samples
- High relevance for source apportionment of elemental air pollutants

Element	Mass concentration RDI Stage A (2.5-10 µm) (ng m^{-3})			Mass concentration RDI Stage B (1-2.5 µm) (ng m^{-3})			Mass concentration RDI Stage C (0.1-1 µm) (ng m^{-3})			Minimal detect-ion limit (MDL) (ng m^{-3})	Relative methodo-logical error (%)
	0.25 perc	Aver-age	0.75 perc	0.25 perc	Aver-age	0.75 perc	0.25 perc	Aver-age	0.75 perc		
S	164	388	516	90.2	216	269	32.6	253	346	0.310	34
Cl	37.0	297	328	9.71	37.6	39.6	2.40	4.86	5.68	0.091	24
Ca	79.7	220	282	27.5	51.5	60.1	7.12	11.3	13.5	0.038	10
Cr	3.58	10.2	14.1	1.52	3.91	5.11	0.252	0.672	0.878	0.029	14
Mn	6.42	16.8	22.6	2.25	5.37	7.45	0.420	1.08	1.43	0.027	13
Fe	544	1371	1847	167	409	576	24.7	68.3	89.3	0.042	10
Cu	22.6	57.6	72.5	7.90	21.2	27.1	1.34	3.64	4.46	0.019	10
Zn	10.3	25.0	33.0	5.00	12.1	15.8	1.38	4.07	5.48	0.014	11
Br	0.092	0.252	0.311	0.027	0.118	0.162	0.021	0.227	0.343	0.016	25
Pb	1.42	3.89	4.78	0.727	1.77	2.22	0.238	0.827	1.22	0.088	11

Comparison of RDI/SXRF and HiVol/XRF



Conclusions

- Teflon/nylon filterpacks behind denuder is safest option
- 1 μm size cut is better suited for source apportionment, but we also accept a 2.5 μm (dry) cut
- Cascade impactor measurements are a research topic and not suitable for monitoring (work load!)
- RDI/SXRF has the potential for routine applications (as done in IMPROVE program), with high sensitivity
- 24-averages are not suited for process studies