

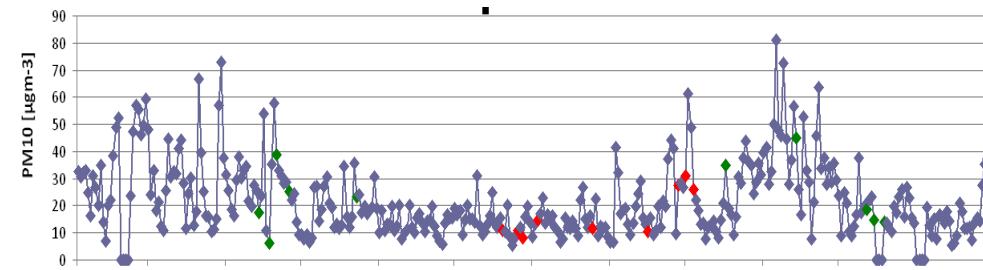
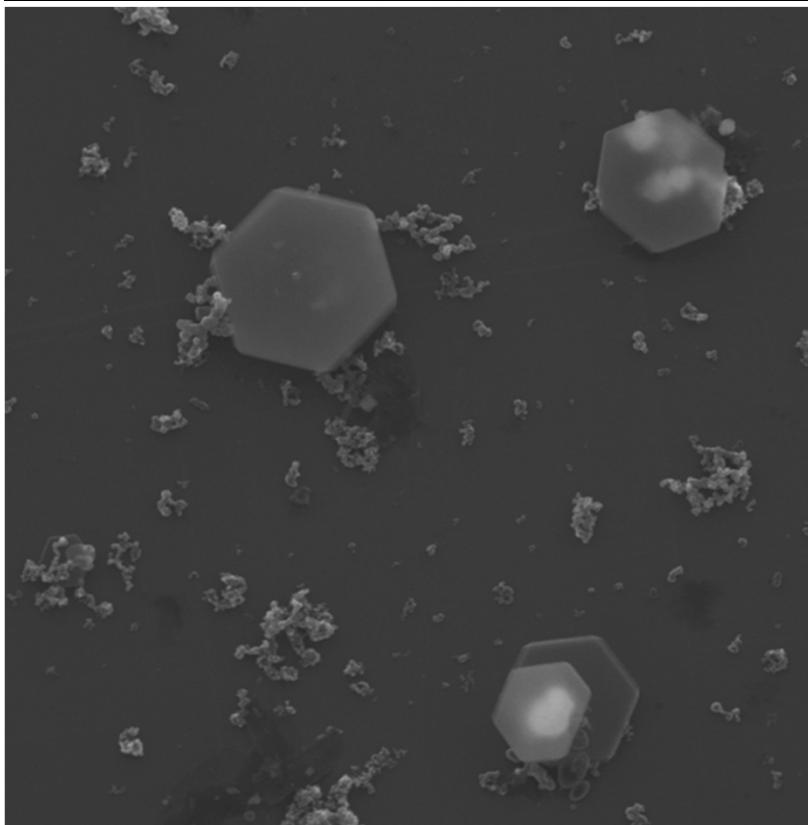
Chemical characterization of PM₁₀ at four German background monitoring stations by individual electronmicroscopic particle analysis

Apl. Prof. Dr. Martin Ebert & Dörthe Müller-Ebert

Institute for Applied Geoscience, Environmental Mineralogy



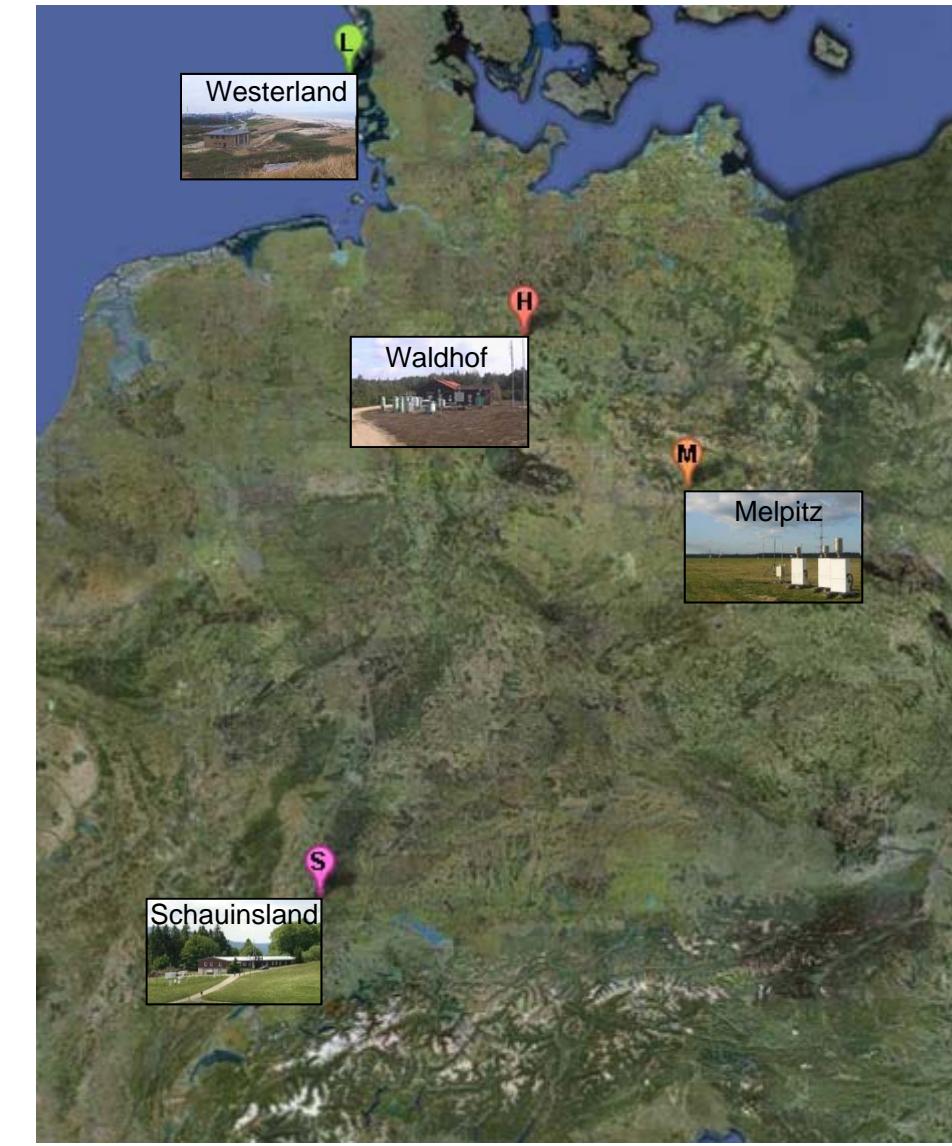
TECHNISCHE
UNIVERSITÄT
DARMSTADT



Project FKZ35101078 – Conception

Electronmicroscopic individual particle analysis (EM-IPA)

- Routinely particle sampling at monitoring stations **Melpitz**, **Schauinsland**, **Waldhof** and **Westerland** in 2012.
- Electronmicroscopic Individual particle analysis of 10 selected samples at each spot
(41.000 particle analysis)



Main questions:

- **refractory** aerosols
- **anthropogenic** contribution
- **carbonaceous** aerosol
- **artefacts** at monitoring stations

Electronmicroscopic individual particle analysis

EM-IPA



FEI Quanta 200 FEG ESEM
equipped with Ametek Genesis
EDX microanalysis system,

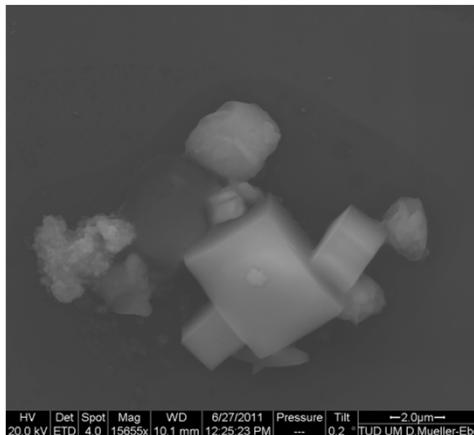
- For significant results some 100 particles in each sample must be analyzed, what makes this kind of **analysis very time-intensive**.
- Method yields **size, morphology, elemental composition** ($Z > 4$) and **mixing state** of individual particles.
- Method yields **number concentrations**, not mass concentrations as most other chemical methods.

Particle groups

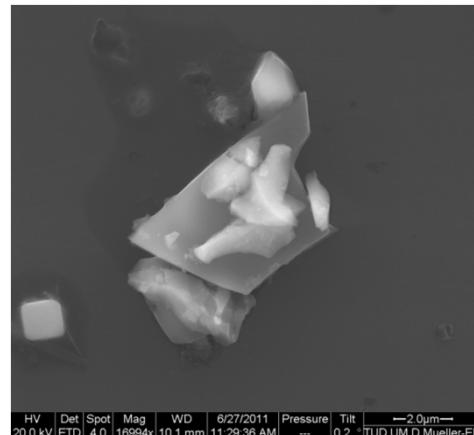
Main groups



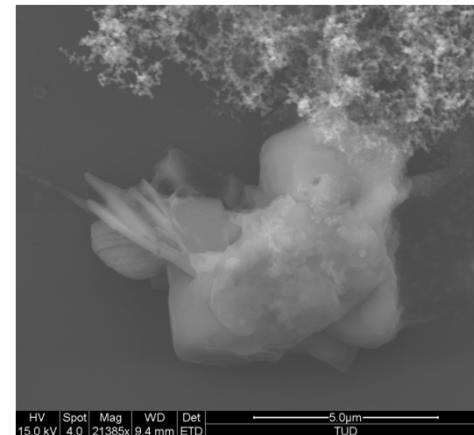
TECHNISCHE
UNIVERSITÄT
DARMSTADT



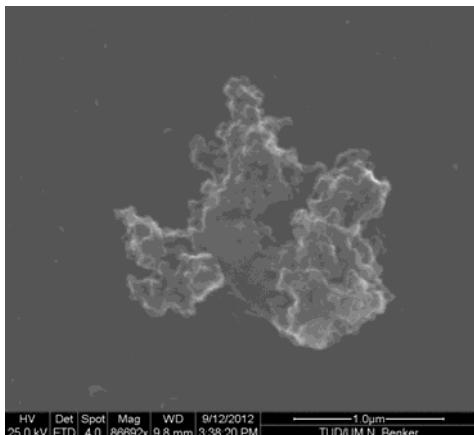
Sea-salt



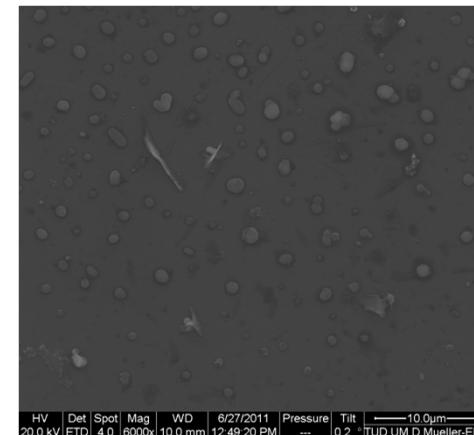
Alumosilicates



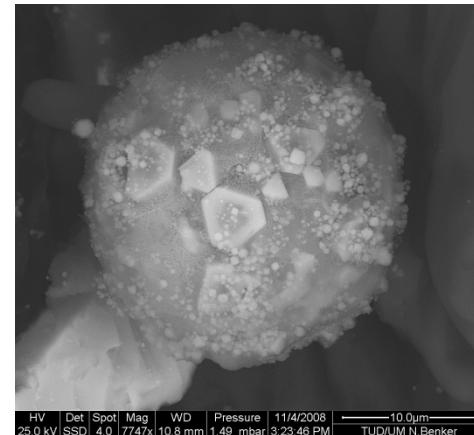
Ca-rich



C – rich



secondary



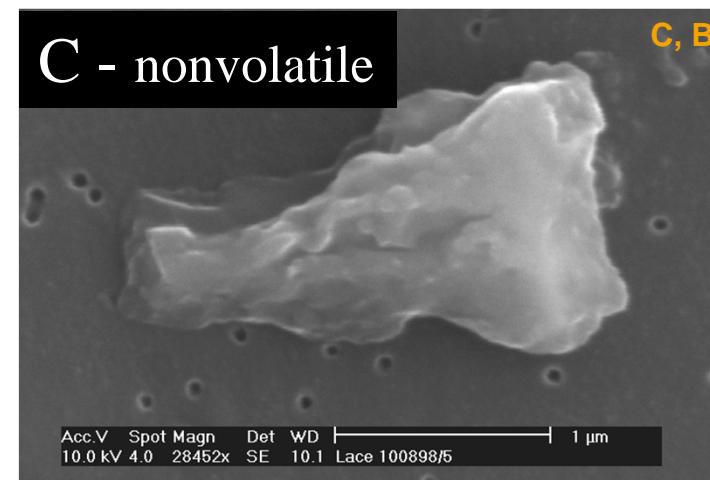
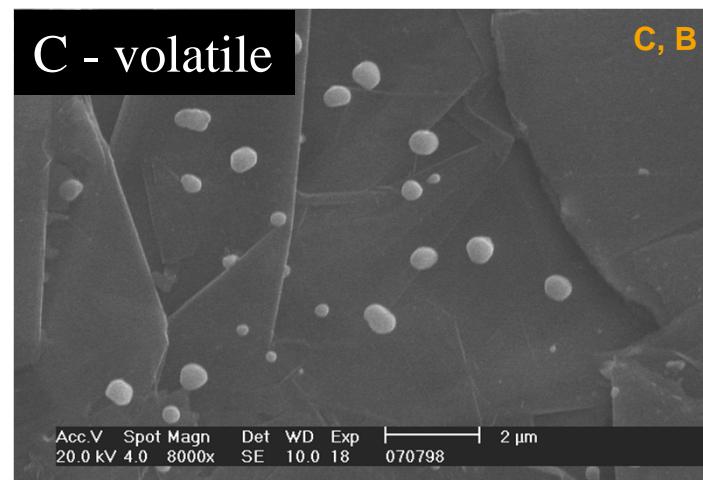
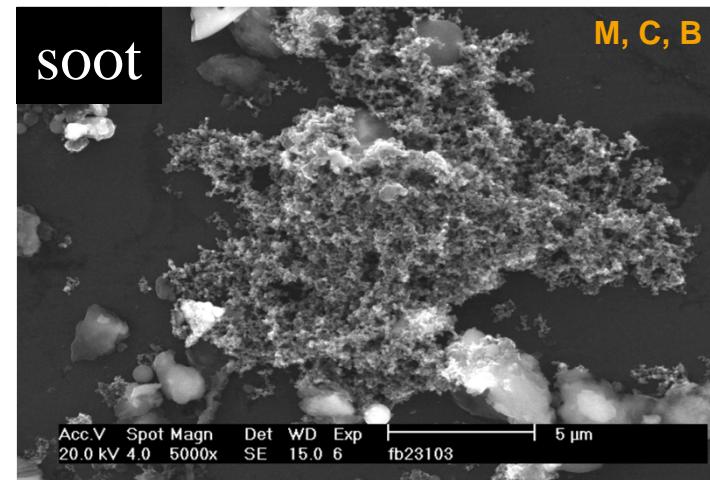
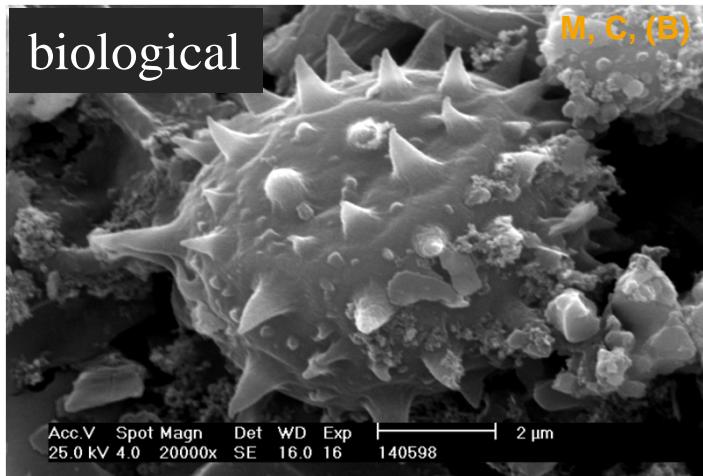
Metal/oxide

Classification of carbonaceous material

Identification of soot and biological particles



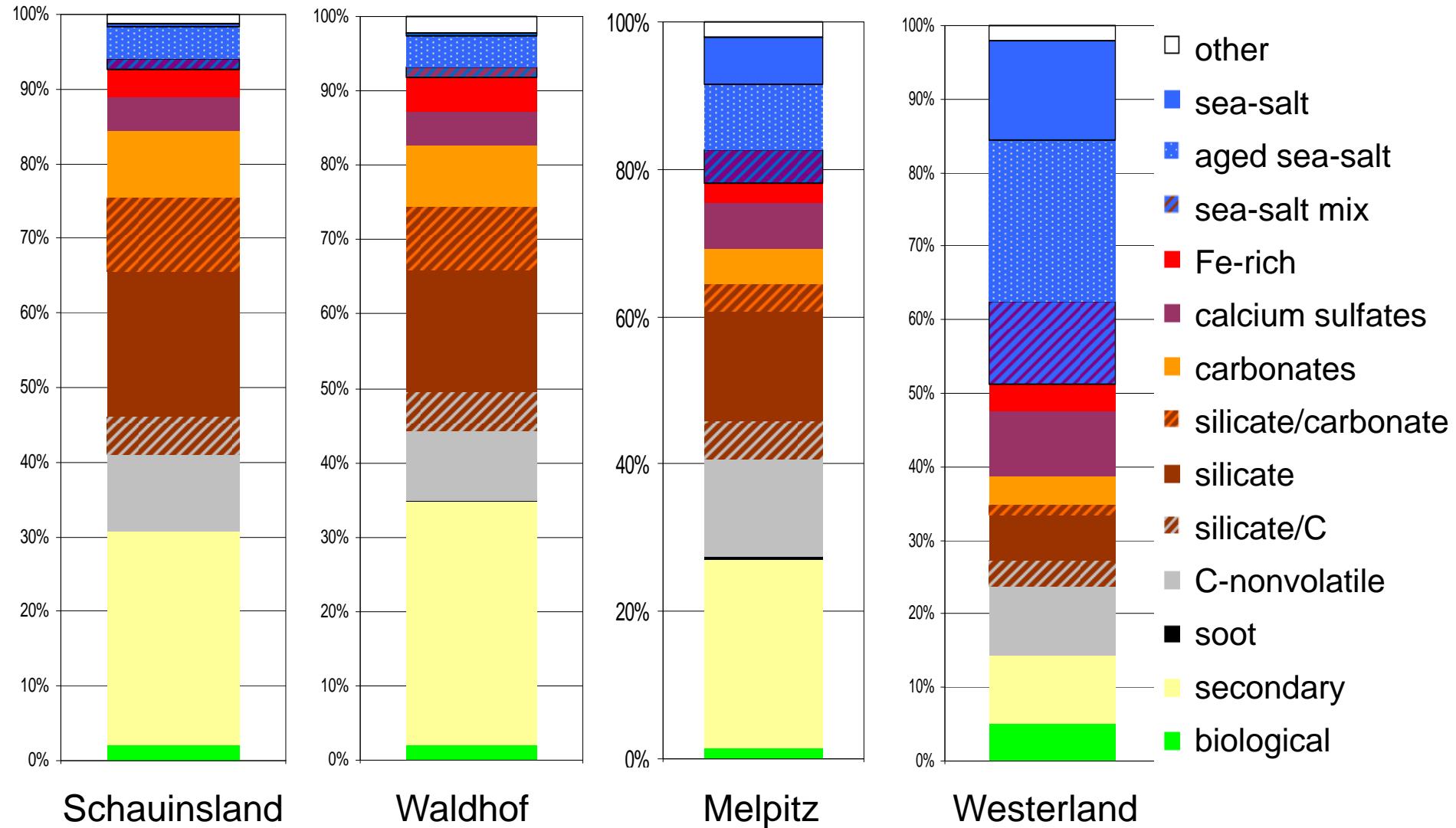
TECHNISCHE
UNIVERSITÄT
DARMSTADT



Classification criteria: M-morphology C- chemistry B- beam stability

Average particle group number abundance

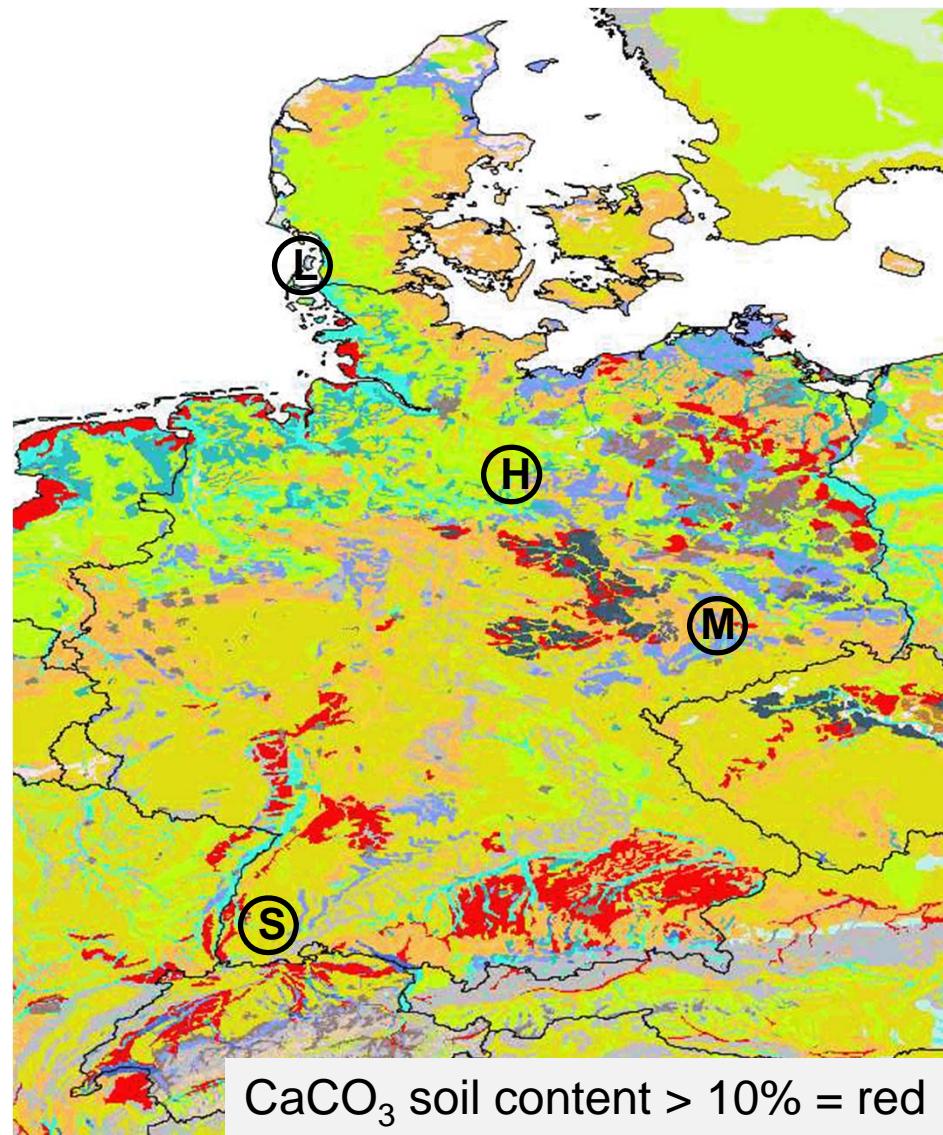
(for coarse fraction: 1 – 10 μm)



High contents of Carbonates and Carbonate/silicate mixtures in Waldhof and Schauinsland



TECHNISCHE
UNIVERSITÄT
DARMSTADT



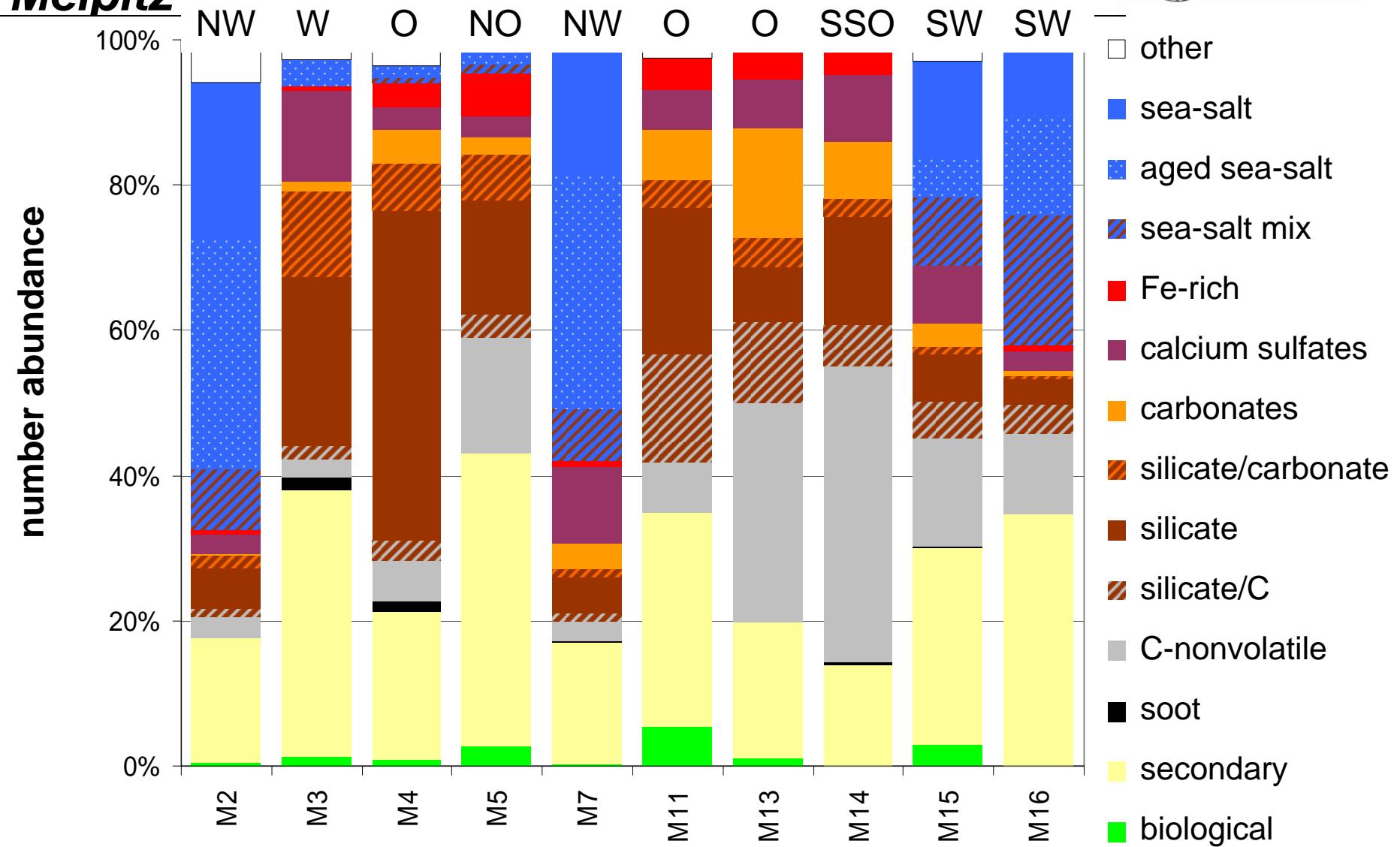
Carbonate content in aerosol samples seems explainable from the regional soil carbonate content.

Particle group number abundance (1- 10 µm)

Melpitz

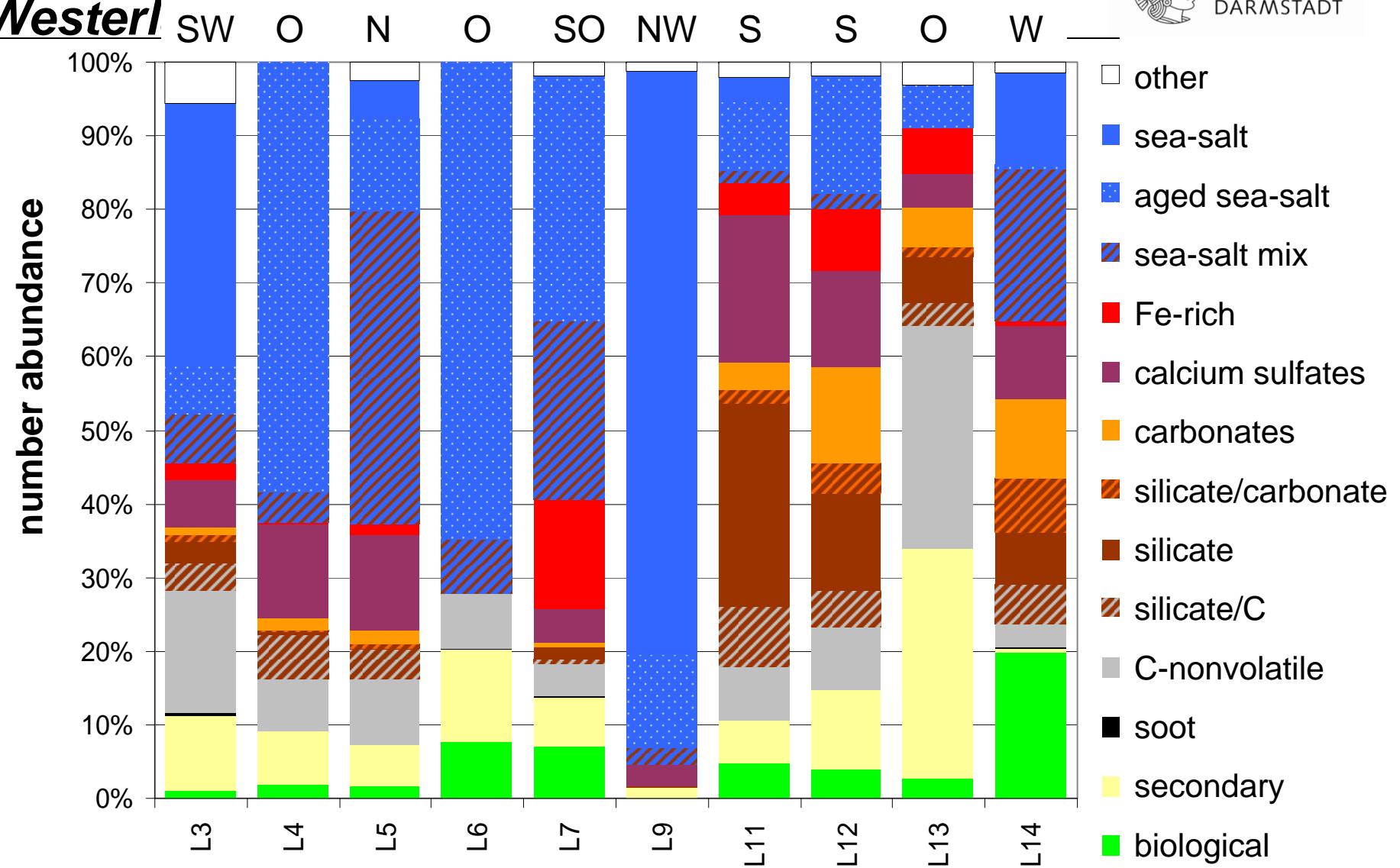


TECHNISCHE
UNIVERSITÄT
DARMSTADT



Particle group number abundance (1- 10 µm)

Westerl



TECHNISCHE
UNIVERSITÄT
DARMSTADT

Subdivision of the carbonaceous fraction

PM₁₀-abundance of carbonates, biology, soot, volatile and nonvolatile organic particles



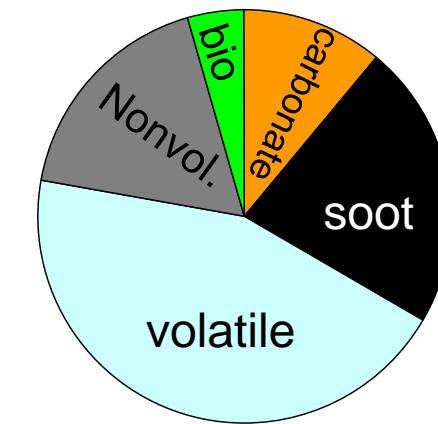
TECHNISCHE
UNIVERSITÄT
DARMSTADT

Measured number abundance of carbonaceous particles in the size-range **1 – 10 µm**

	Schauinsland	Waldhof	Melpitz	Westerland
carbonates	12	11	6	4
Soot (EC+OC)	3	3	3	1
volatile C	10	11	9	3
nonvolatile C	12	12	17	14
biological	2	2	1	5

Derived mass abundance of carbonaceous particles within **PM₁₀-fraction**

	Schauinsland	Waldhof	Melpitz	Westerland
carbonates	7	6	4	2
soot (EC+OC)	8	11	13	7
volatile C	20	20	20	18
nonvolatile C	6	7	10	8
biological	2	2	2	7



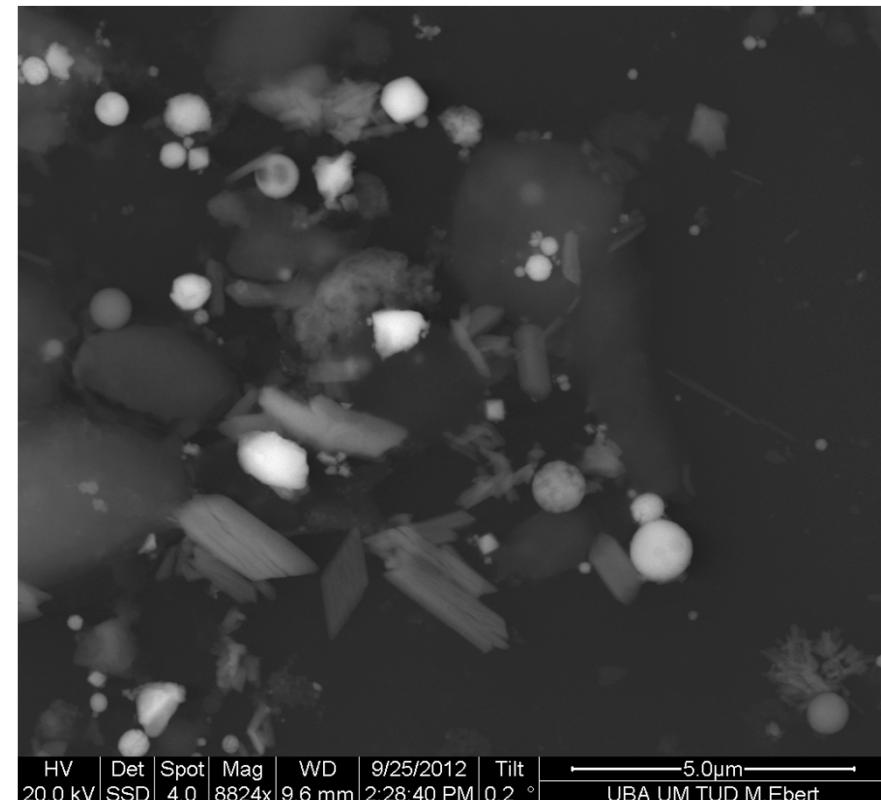
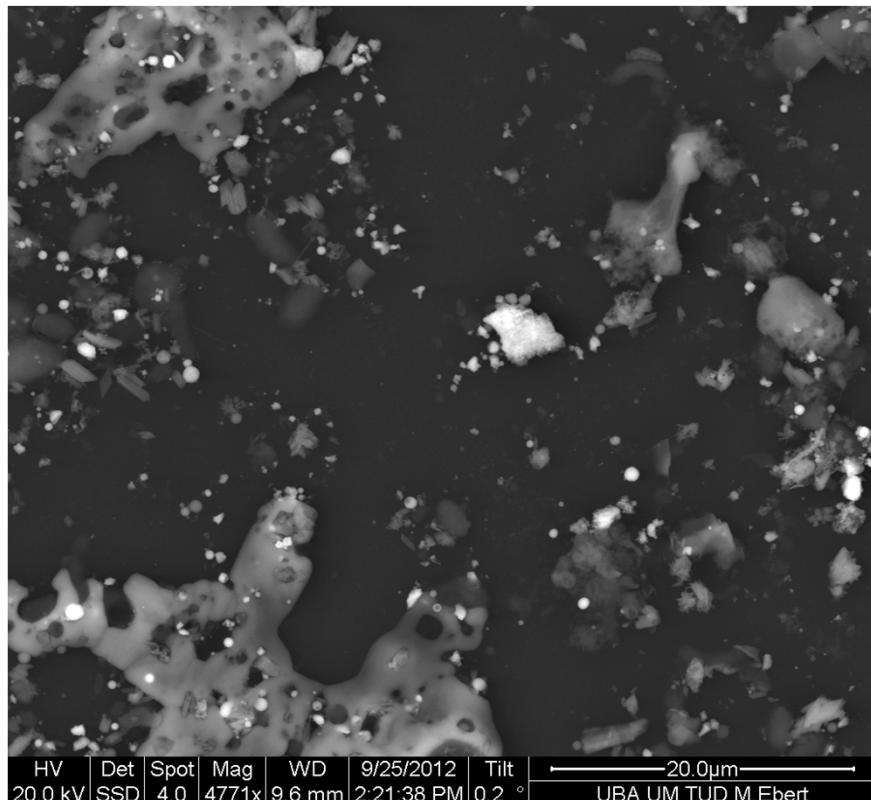
In average ~ 45% of PM₁₀

Anthropogenic Tracer

1. fly-ashes (Fe/Cr/Zn and silicatic) in Waldhof and Melpitz



TECHNISCHE
UNIVERSITÄT
DARMSTADT



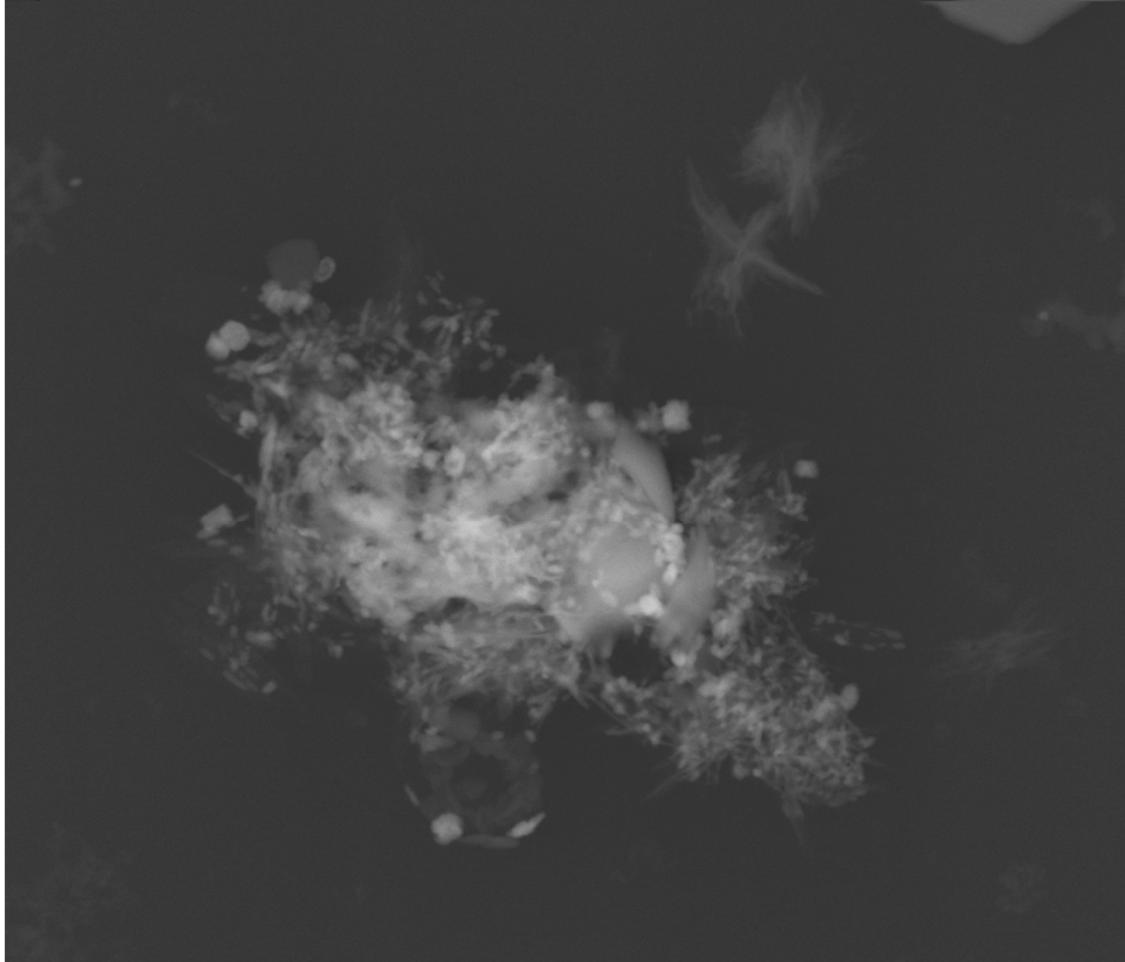
- Increased number abundance of **metal (oxides)** and **silicatic fly-ashes** in Waldhof (Southwest) and Melpitz (East).
- Hint for contribution of **Industry** respectively **burning of fossil fuels**.

Anthropogenic Tracer

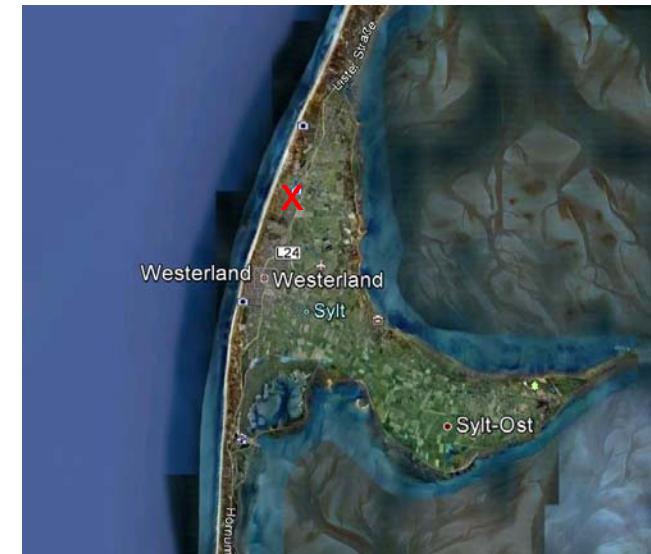
2. Lead halogenides in Westerland



TECHNISCHE
UNIVERSITÄT
DARMSTADT



HV 20.0 kV	Det SSD	Spot 4.0	Mag 17419x	WD 9.5 mm	9/25/2012 1:14:52 PM	Tilt 0.2 °	2.0µm
---------------	------------	-------------	---------------	--------------	-------------------------	---------------	-------



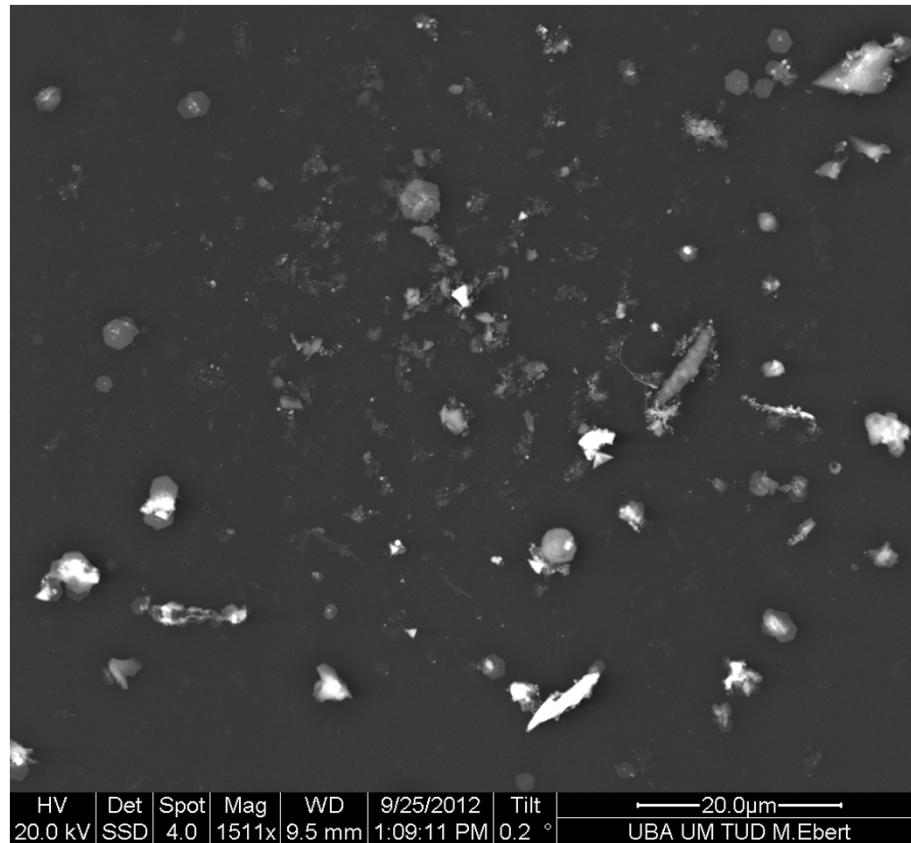
- Most probable source for lead are small planes/helicopter

Local Artefacts at monitoring stations

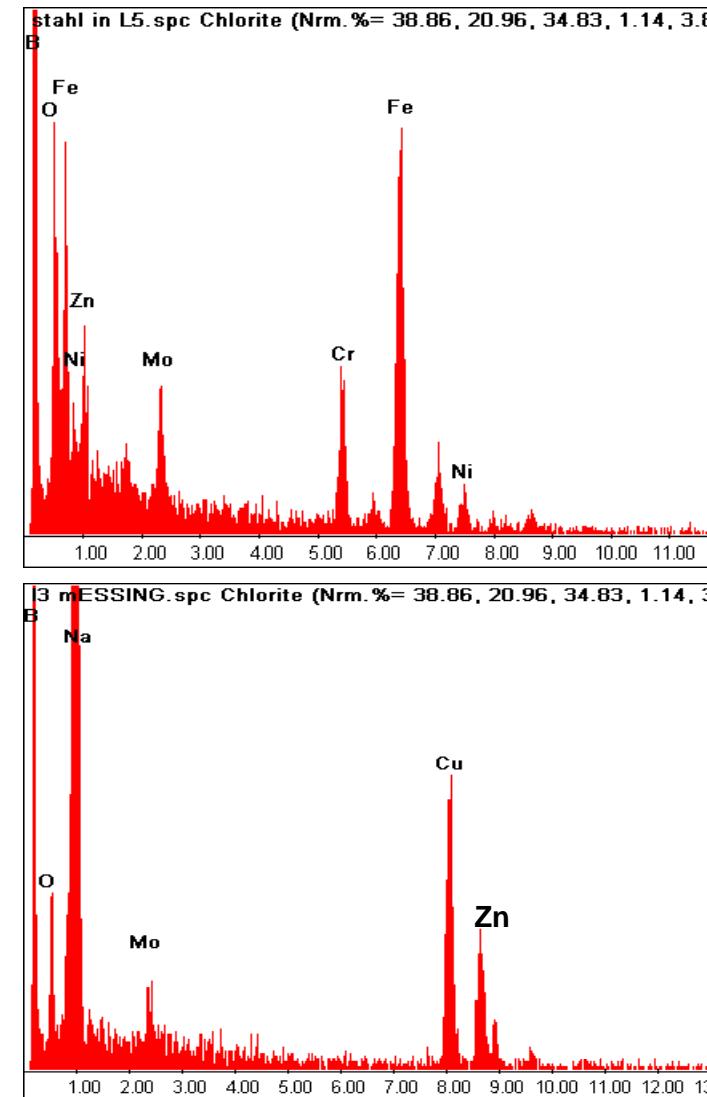
1. Steel, Zn and brass in Westerland



TECHNISCHE
UNIVERSITÄT
DARMSTADT



Large **abrasion particles** clearly points to a **local source** (South).

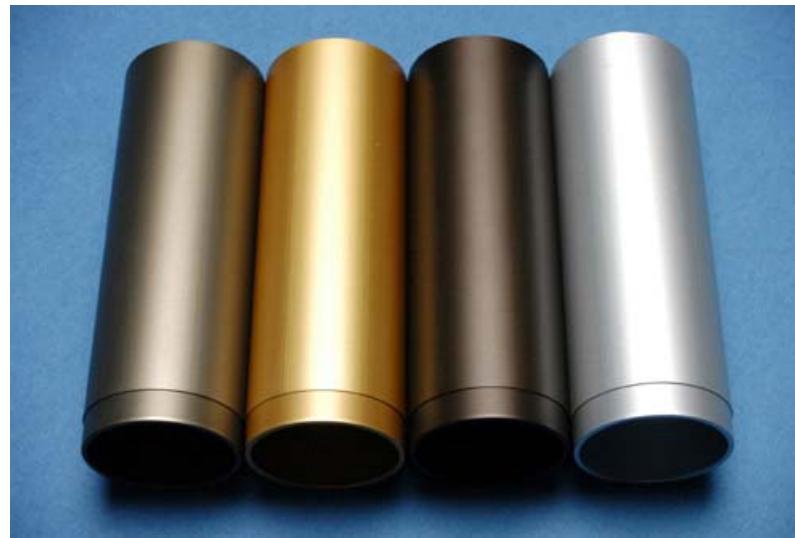
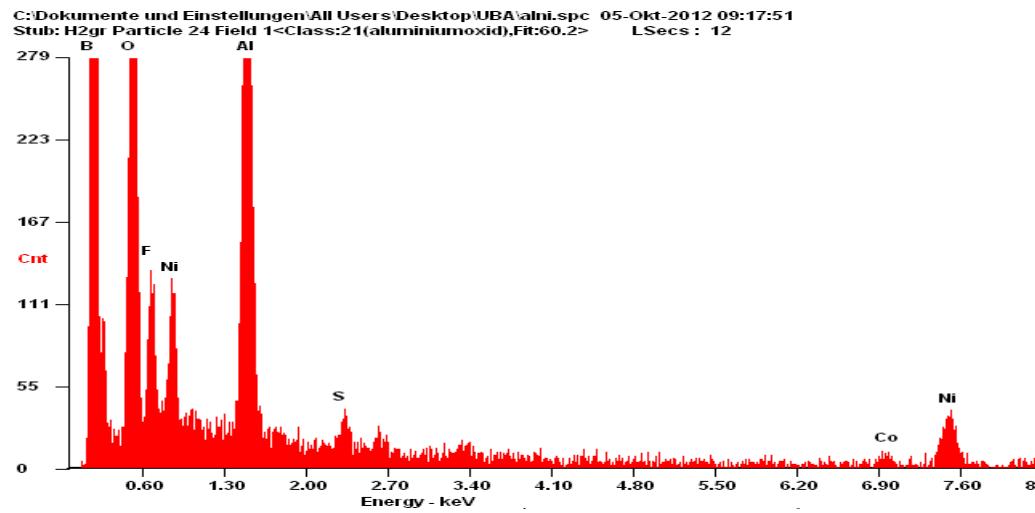
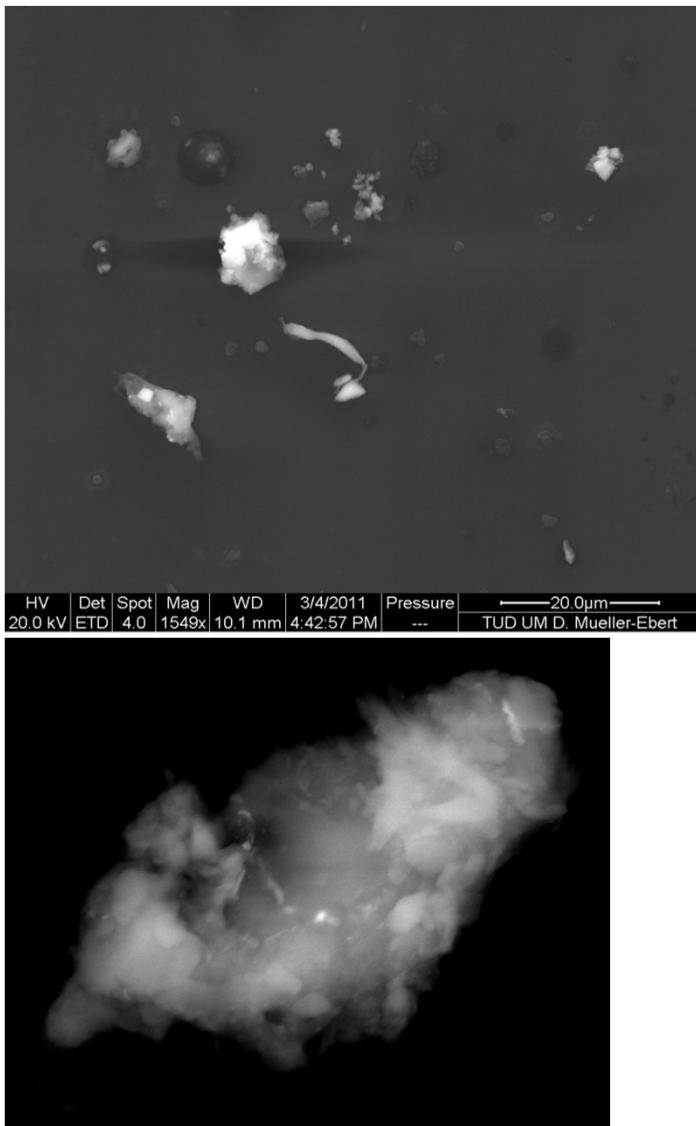


Local Artefacts at monitoring stations

2. Al/Ni/Co/F- particles in Waldhof



TECHNISCHE
UNIVERSITÄT
DARMSTADT



local artefact of *anodization layers*

Summary and Conclusion

- Similar particle group abundances (1-10 µm) at all 4 monitoring stations

silicate	20 – 35 %	Ca-rich	5 – 15 %
secondary	25 – 30 %	C-rich (nonvol.)	10 – 15 %
sea-salt	5 – 20 %	Fe-rich	3 – 5 %

- **Stronger compositional variability** (in dependence of air mass origin) in **Westerland** and **Melpitz**, less in Schauinsland and Waldhof.
- **Carbonaceous material** contributes to ~ **45% of PM₁₀** (20% volatile, 10% soot, 8% nonvolatile, 5% carbonate, 2% biological).
- In **Waldhof** and **Westerland** local particulate **artefacts** (Zn, Fe, Ni) were found, which should be considered in discussion of determined metal concentrations..
- An **increased** abundance of **fly-ashes** (Fe/Si) were determined in the sub-µm fraction in **Waldhof** (SW) and **Melpitz** (O). This is a clear tracer for **industrial sources** respectively **burning of fossil fuels**.