Raman Spectroscopy as a reference method for mass absorption coefficient measurements of atmospheric soot particles.

Dr. Stephan Nordmann
Max-Planck-Institute For Chemistry
08.10.2014

MAX-PLANCK-INSTITUT
FÜR CHEMIE

TROPOS

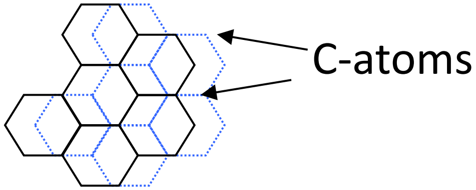
gefördert durch das Stipendienprogramm der Deutschen Bundesstiftung Umwelt
DBU
Deutsche Bundesstiftung Umwelt
www.dbu.de

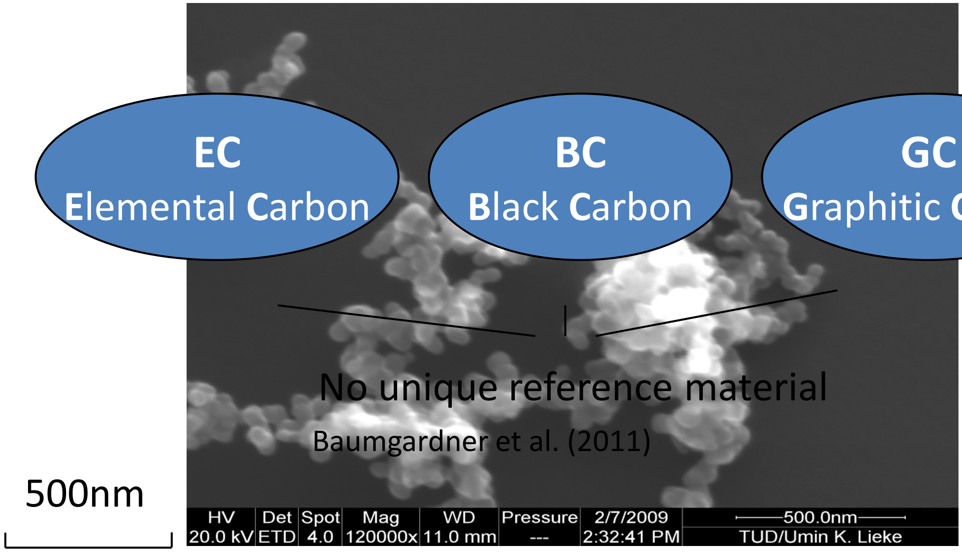
1. **Introduction**
2. **Lab measurements - Calibration**
3. **Field measurements**

1. Introduction

What is soot?

- Product of incomplete combustion
- C-atoms in graphite layers
- Onion-like arrangement in primary spherical particles
- Agglomerates and combination with other chemical compounds





EC
Elemental **C**arbon

BC
Black **C**arbon

GC
Graphitic **C**arbon

No unique reference material

Baumgardner et al. (2011)

K.Lieke / K. Kandler, TU Darmstadt

1. Introduction

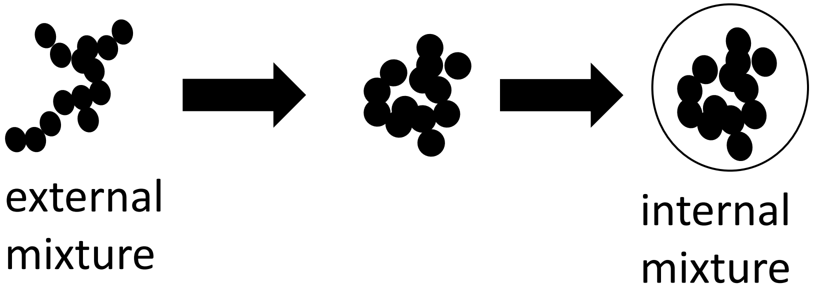
Life-cycle of soot

- **global emissions ~8 Tg/yr** (Bond et al. 2004)

Sources

natural	anthropogenic
➢ Forest- and Savannafires	➢industry ➢transport ➢Residential ➢…

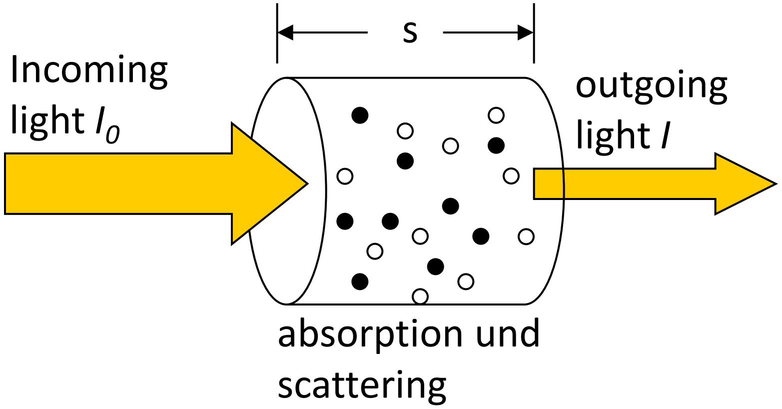
- **Atmospheric transport** – Transformation of soot



- **Removal** – dry and wet deposition

1. Introduction

Light absorption of soot particles



Lambert-Beer law

$$I = I_o e^{-(\sigma_{ap} + \sigma_{sca}) \cdot s}$$

- absorption coefficient (σ_{ap}) / (m^{-1})
- scattering coefficient (σ_{sca}) / (m^{-1})

- absorption coefficient in relation to the soot mass concentration

mass absorption coefficient: $$\delta = \frac{\sigma_{ap}}{m_{soot}}$$

- δ is used for deriving the **BC mass concentration** from absorption photometer measurements (e.g. MAAP)

Problem: Variability of δ - depends on e.g. mixing state, particle diameter

1. Introduction

Objectives

- Reference method for the direct determination of soot mass concentration by Raman spectroscopy

- Application of this method in conjunction with absorption photometry for the determination of δ for atmosheric samples

- All results published in **Nordmann et al. (2013), JGR**

JOURNAL OF GEOPHYSICAL RESEARCH: ATMOSPHERES, VOL. 118, 12,075–12,085, doi:10.1002/2013JD020021, 2013

Measurements of the mass absorption cross section of atmospheric soot particles using Raman spectroscopy

S. Nordmann,[1] W. Birmili,[1] K. Weinhold,[1] K. Müller,[1] G. Spindler,[1] and A. Wiedensohler[1]

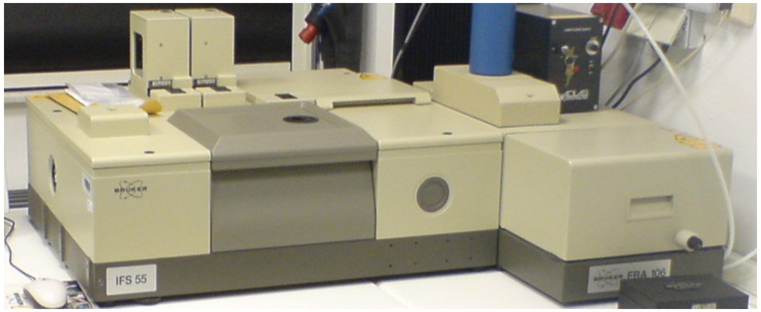
Received 12 April 2013; revised 1 October 2013; accepted 11 October 2013; published 5 November 2013.

2. **Lab measurements - calibration**

Calibration - devices

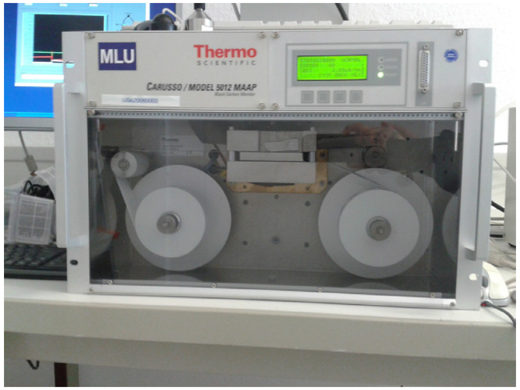
➡ Determination of **soot mass concentrations m_{soot}** with **Raman-Spectrometer**

Measurement of inelastic light scattering from graphitic lattice



➡ Particle samples from **Multi Angle Absorption Photometer (MAAP)**

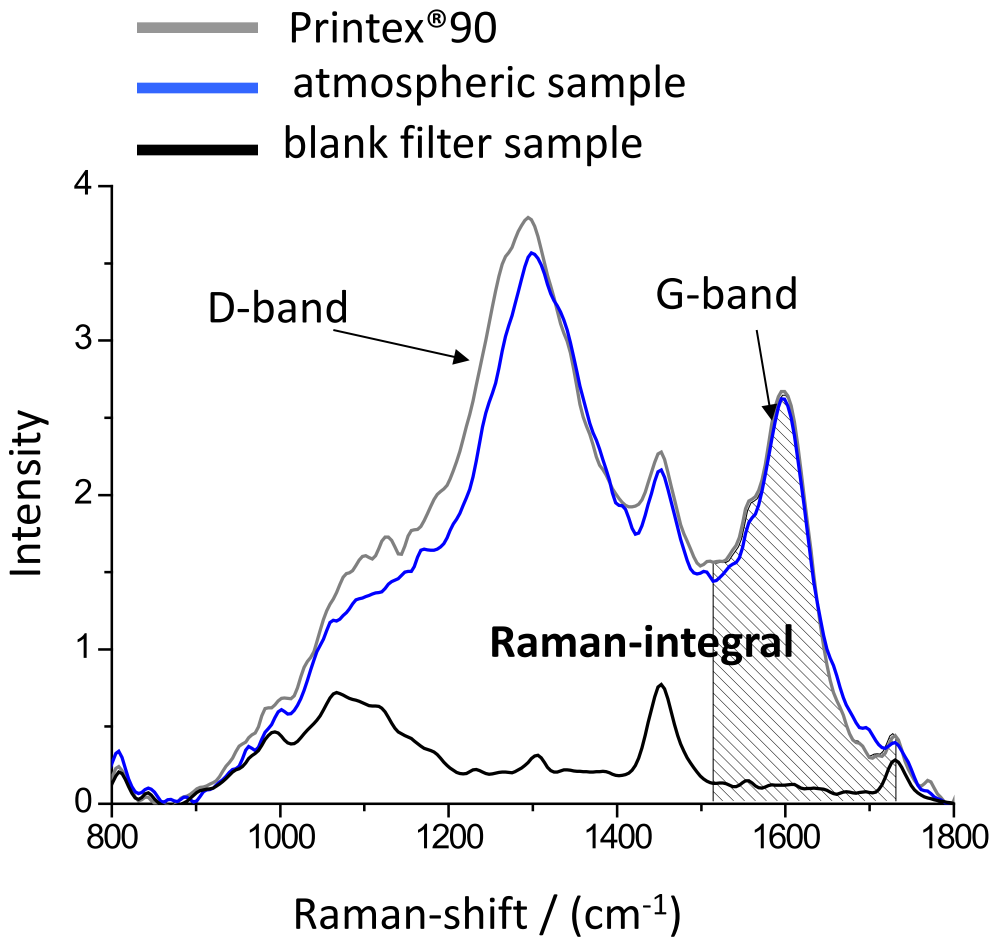
Measurement of **absorption coefficient** σ_{ap}

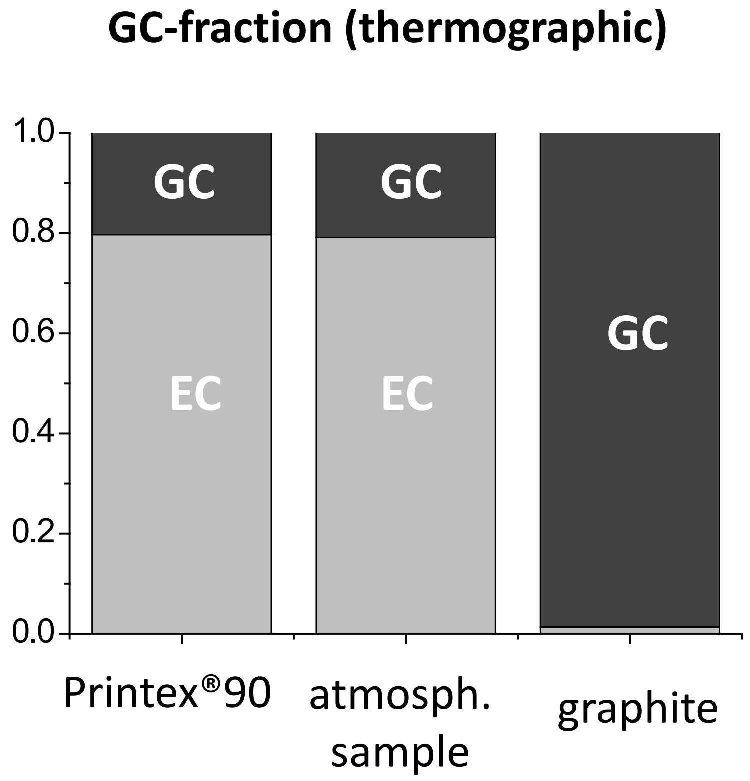


➡ $$\delta = \frac{\sigma_{ap}}{m_{soot}}$$

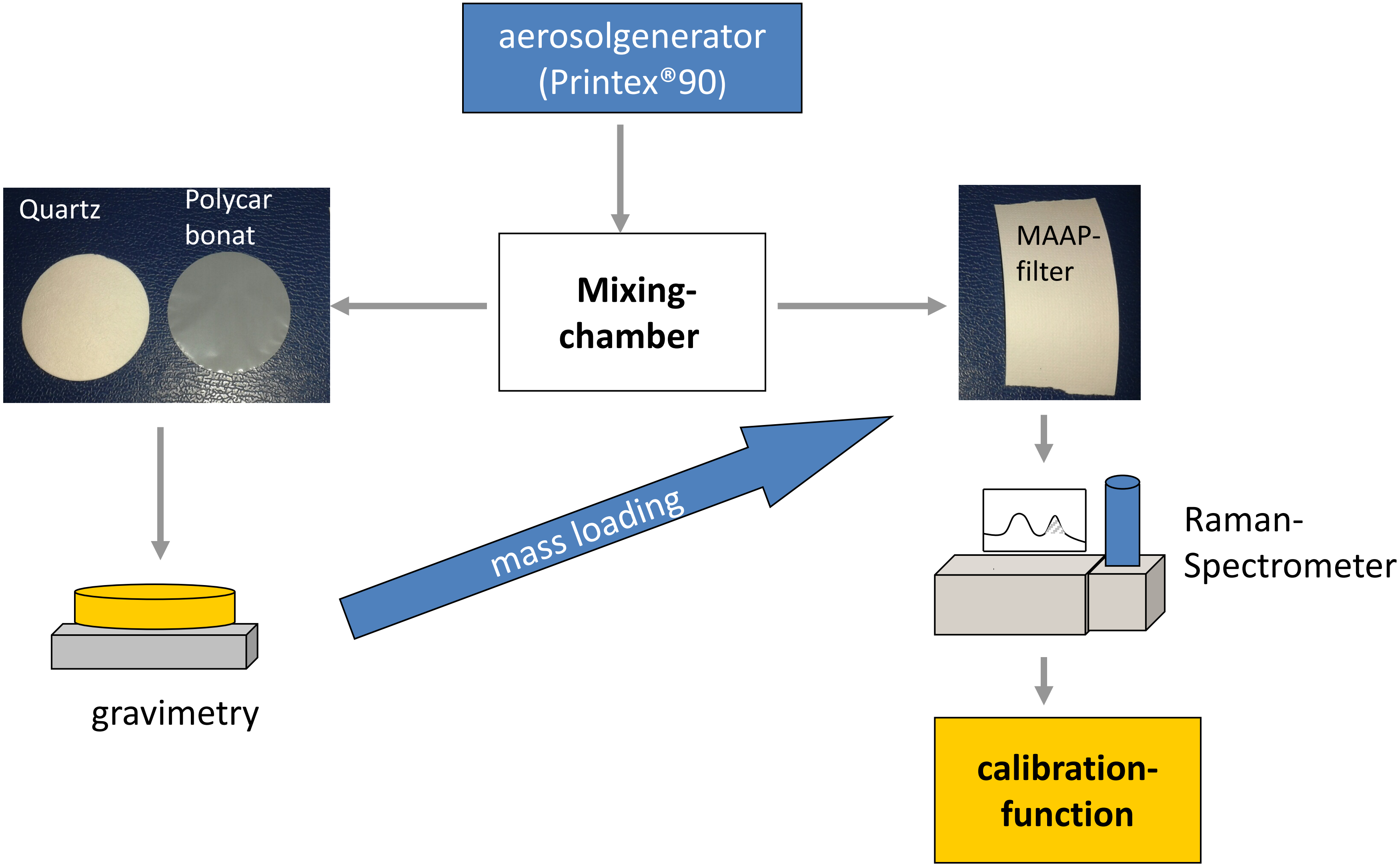
2. Lab measurements - calibration

Testparticles Printex®90





2. Lab measurements - calibration



aerosolgenerator (Printex®90)

Mixing-chamber

Quartz

Polycarbonat

MAAP-filter

gravimetry

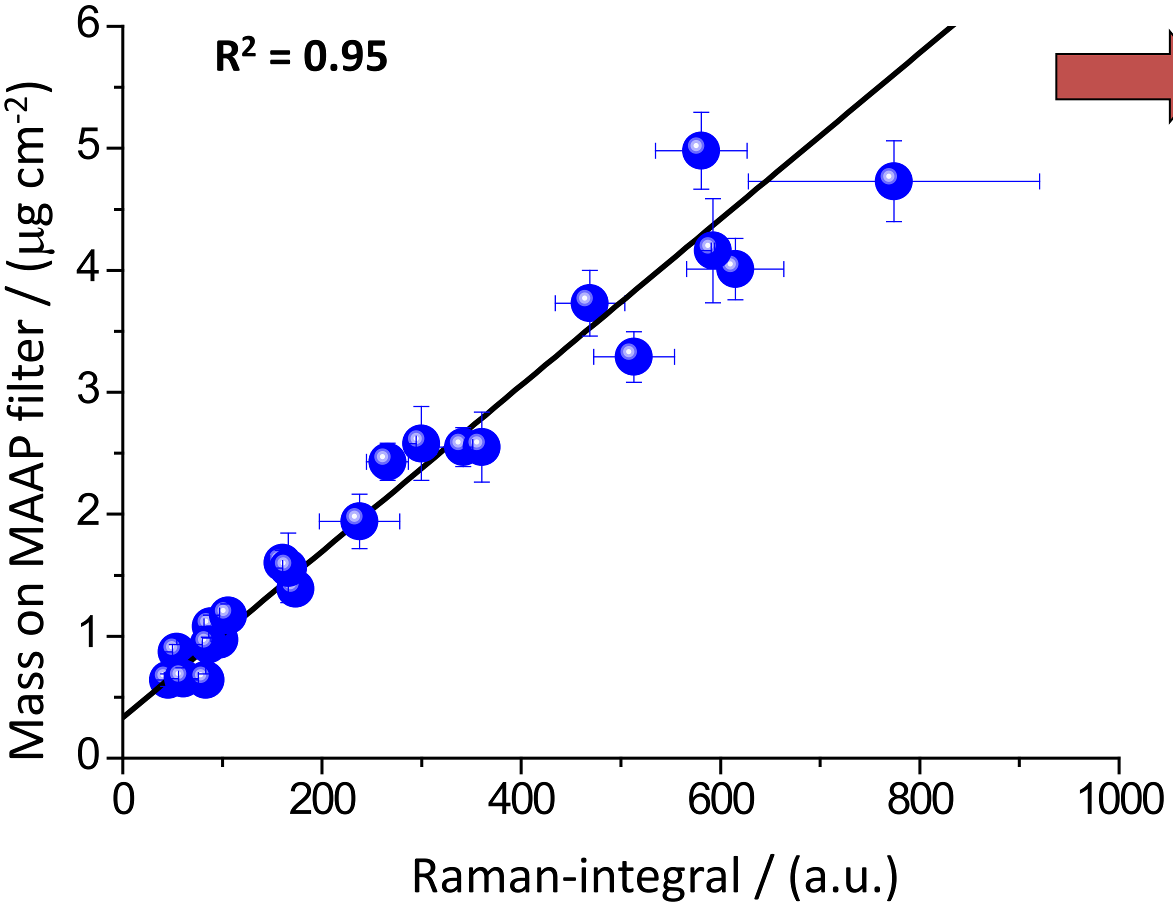
mass loading

Raman-Spectrometer

calibration-function

2. Lab measurements - calibration

Results from calibration experiment



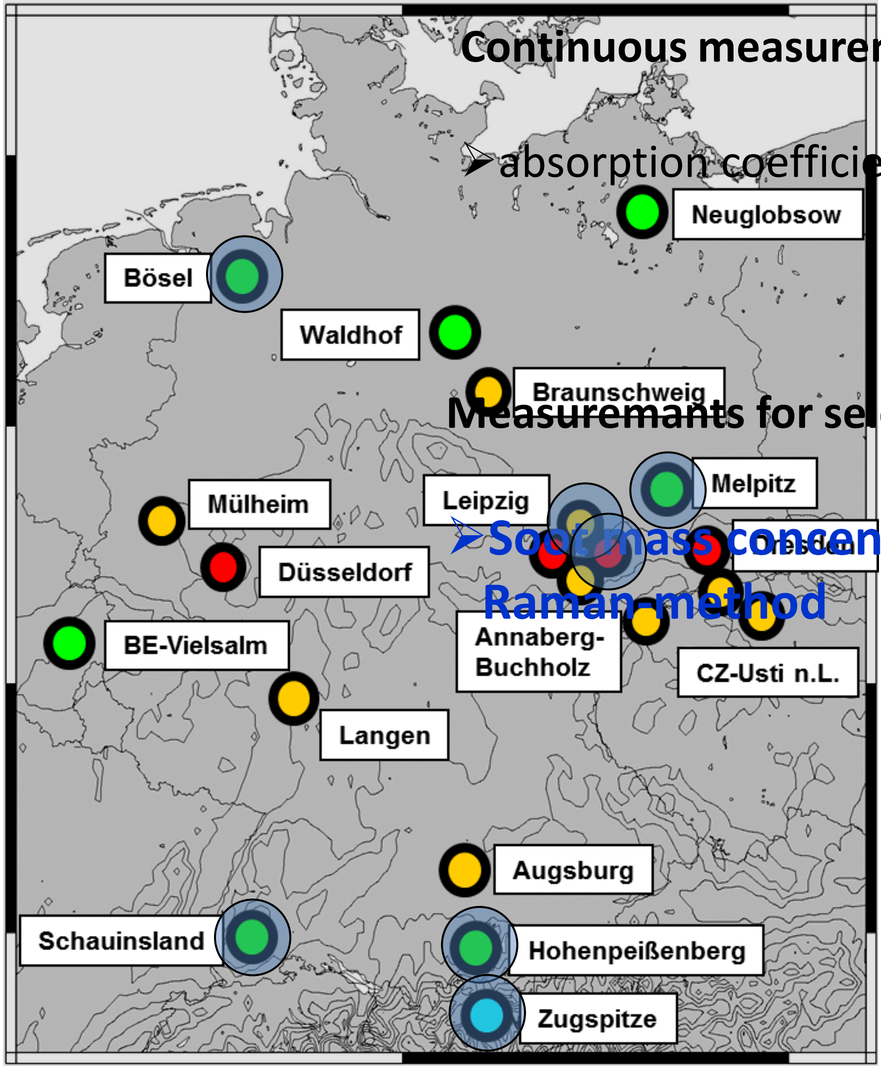
Soot mass concentration from integral

$$m_{soot} = \frac{m_{load} \cdot A_{spot}}{\dot{V} \cdot t_{samp}}$$

m_{load}	mass on MAAP-filter
A_{spot}	loaded filter area
$\dot{V}$	flow rate
t_{samp}	sampling time

3. Field measurements

German **U**ltrafine **A**erosol **N**etwork - **GUAN**



Continuous measurements:

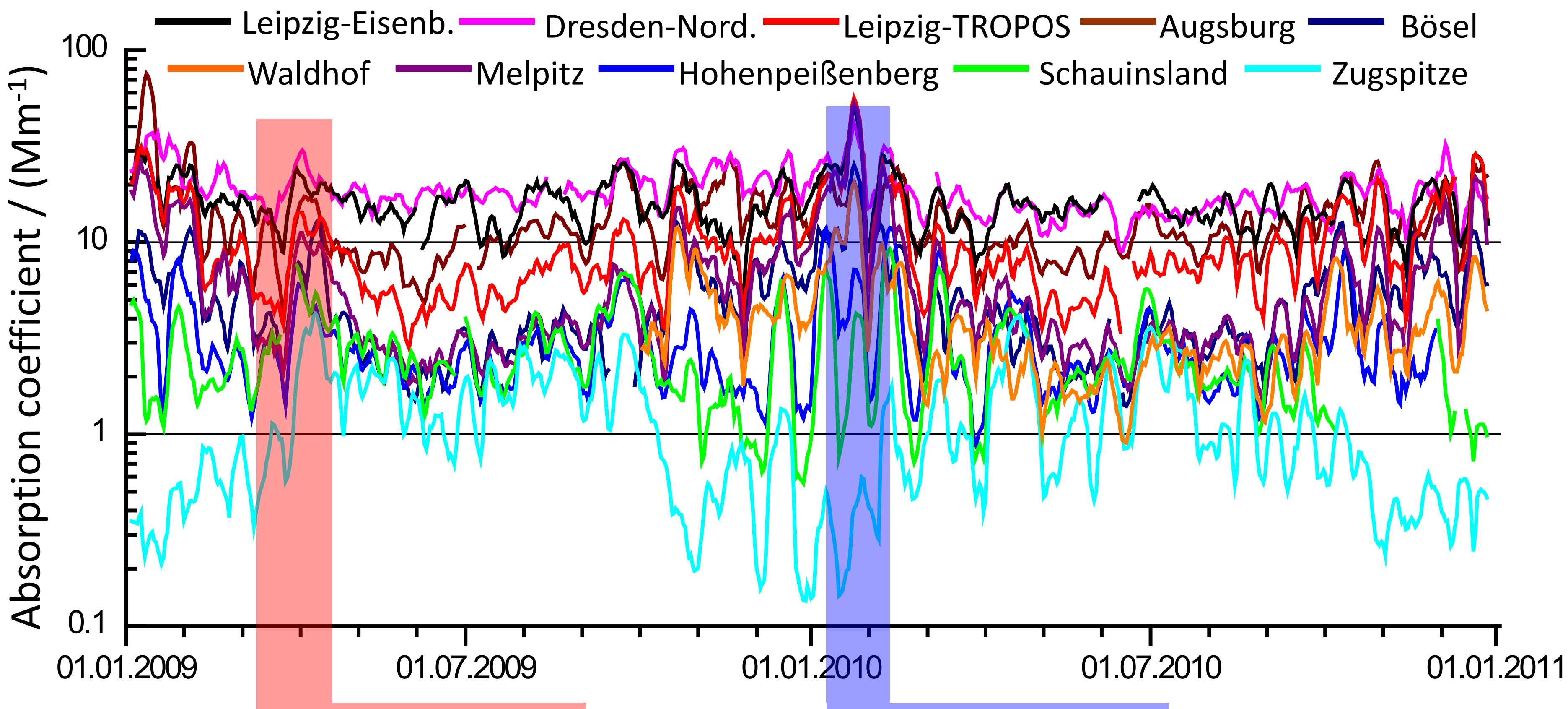
➢absorption coefficient with MAAP

Measuremants for selected time periods:

➢**Soot mass concentrations with Raman-method**

3. Field measurements

Selection of episodes



Episode I:
„continental and
maritime, summer“

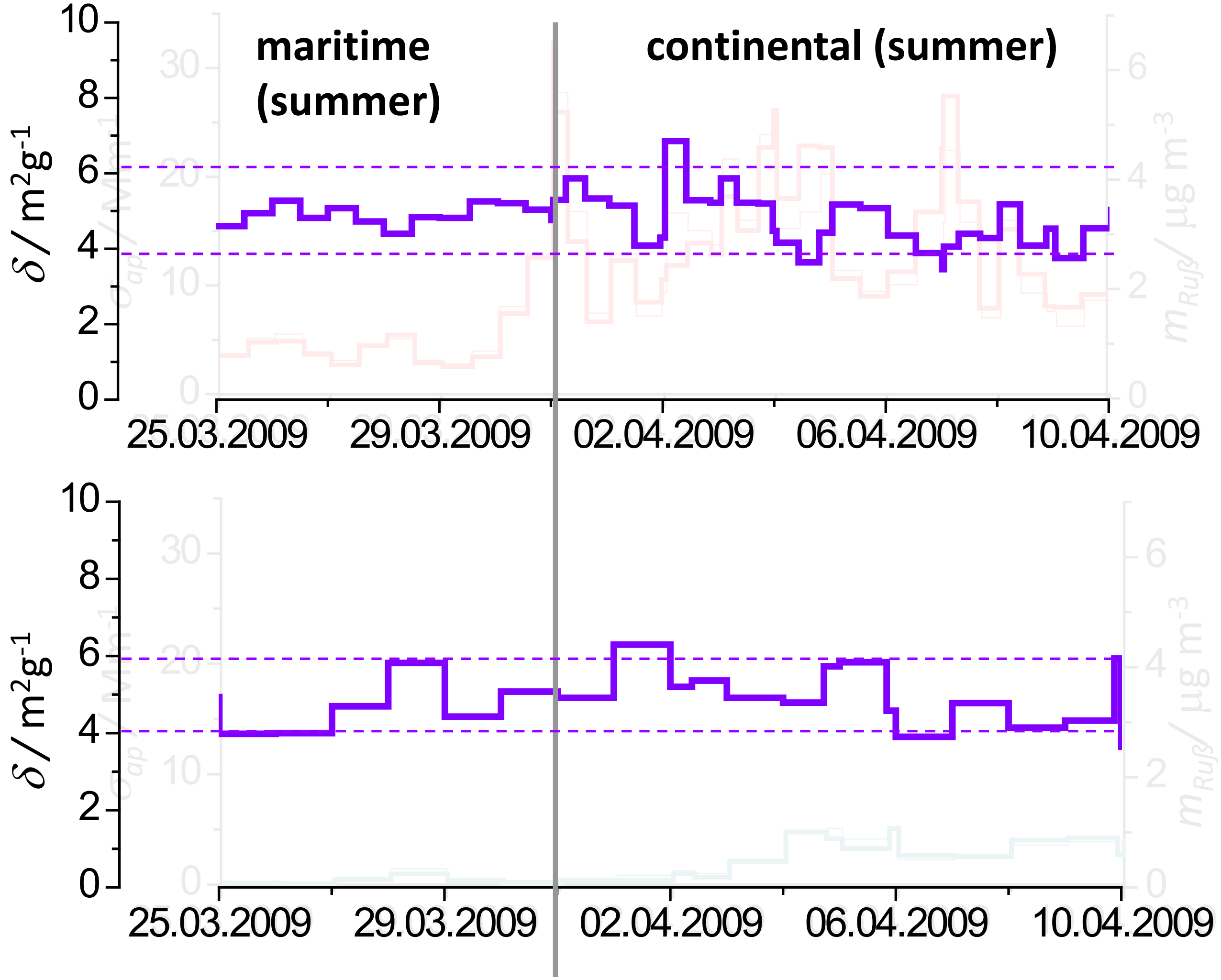
Episode II:
„continental and
maritime, winter“

3. Field measurements

Episode I

Leipzig-Tropos
(urban)

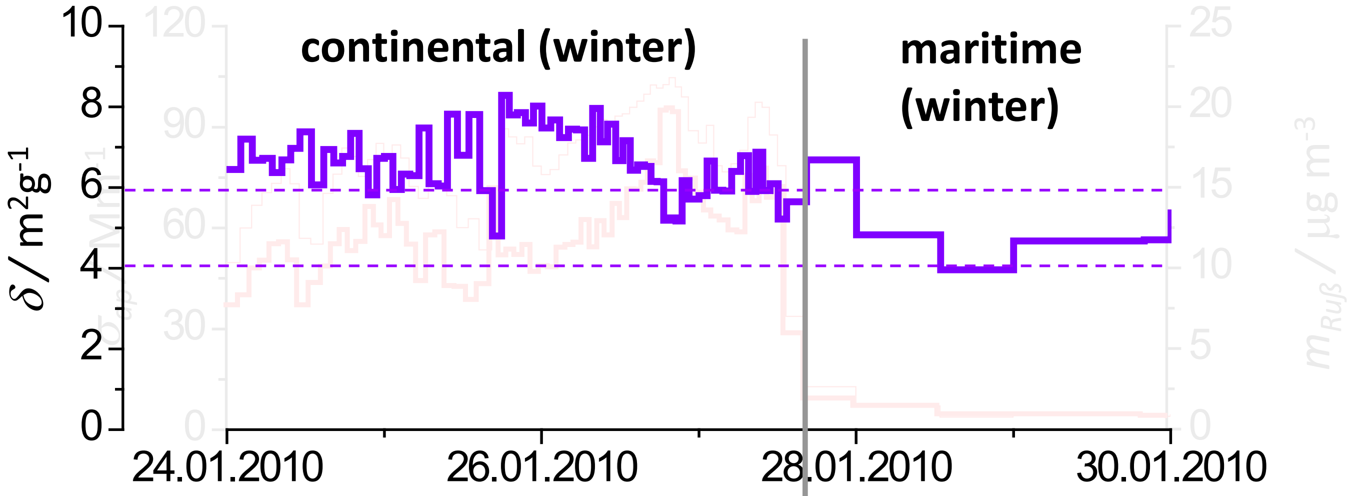
Zugspitze
(mountain)



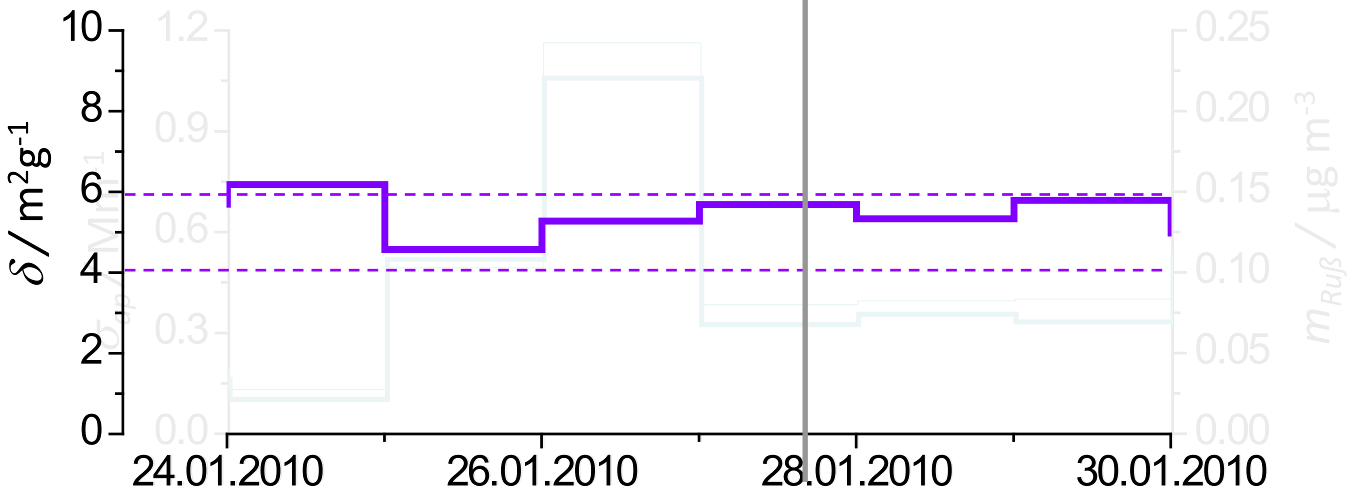
3. Field measurements

Episode II

Leipzig-Tropos
(urban)



Zugspitze
(mountain)



Summary and conclusion

- δ mostly between 4 und 6 m^2g^{-1} , in maritime and continental air mass in summer

- Higher values in a polluted continental air mass in winter.

➡ **Was attributed to the mixing state of soot**

- Considering the default δ value of 6.6 m^2g^{-1} in the MAAP, BC mass concentrations from this measurement device might be too low.

but

- Our results support the assumption of a constant δ for most situations in the Central European troposphere.

Comparison between EC and msoot