

Atmospheric aerosol measurements in the German Ultrafine Aerosol Network (GUAN)

Part 2: Comparison of measurements techniques for graphitic, light-absorbing, and elemental carbon, and non-volatile particle volume under field conditions

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Abstract Since the end of 2008, four experimental methods have been applied in the German Ultrafine Aerosol Network (GUAN) to characterize the light-absorbing and low-volatile components in the atmospheric aerosol known as „soot“. These methods include: a) Multi-Angle Absorption Photometry (MAAP), b) Raman spectroscopy, c) thermographic analysis of samples from Berner impactors, and d) determination of the particle volume of the non-volatile fraction (at 300 °C) from number size distributions. The mass concentration of Graphitic Carbon (GC) measured by Raman spectroscopy correlated well with the light absorption coefficient measured by MAAP, and yielded GC absorption efficiencies in the range of 4.7 to 4.9 m² g⁻¹. The comparison between elemental carbon (EC) mass concentrations from the thermographic method applied on Berner impactor samples and the light absorption measurement yielded a median EC absorption efficiency of 7.5 m² g⁻¹, but showed a considerable scattering within the data set. The particle volume of the non-volatile fraction compared relatively well with the light absorption measurement when assuming an effective particle density in the range of 0.8 to 1.1 g cm⁻³. The results suggested that the non-volatile particle residues in the sub-µm range are closely associated with light-absorbing carbon (LAC) and GC.

Atmosphärische Aerosolmessungen im Deutschen Beobachtungsnetz für Ultrafeine Aerosolpartikel (GUAN) – Teil 2: Vergleich verschiedener Messverfahren für grafitischen, lichtabsorbierenden und elementaren Kohlenstoff sowie das nichtflüchtige Partikelvolumen unter Feldbedingungen

Zusammenfassung Seit Ende 2008 werden im Deutschen Beobachtungsnetz für Ultrafeine Aerosolpartikel (GUAN – German Ultrafine Aerosol Network) kontinuierlich mehrere Messverfahren eingesetzt, die die Konzentration von Ruß in der Außenluft bestimmen. Diese sind im Einzelnen a) die Mehrwinkel-Absorptionsphotometrie (MAAP) als Lichtabsorptionsmessung, b) die Ramanspektroskopie, c) die thermographische Analyse von Partikelproben aus Berner-Impaktoren und d) die Bestimmung des Volumens aus Partikelanzahlgrößenverteilungen nach Verdampfung der bei 300 °C flüchtigen Verbindungen. Die ramanspektroskopisch gemessene Massenkonzentration von grafitischem Kohlenstoff (GC) korrelierte sehr gut mit dem MAAP-Absorptionskoeffizienten, woraus sich Absorptionseffizienzen zwischen 4,7 und 4,9 m² g⁻¹ ergaben. Der Vergleich zwischen thermographisch bestimmten Massenkonzentrationen von elementarem Kohlenstoff (EC) für Berner-Impaktor-Proben und den MAAP-Absorptionskoeffizienten lieferte, bei beträchtlicher Streuung im Gesamtdatensatz, einen Medianwert der Absorptionseffizienz von 7,5 m² g⁻¹. Der Vergleich zwischen der Lichtabsorptionsmessung und dem Volumen der nichtflüchtigen Fraktion zeigte wieder eine relativ gute Korrelation, was zum vorläufigen Schluss führt, dass nicht flüchtige Bestandteile in Partikeln < 1 µm im engen Zusammenhang mit lichtabsorbierendem Kohlenstoff (LAC) und GC stehen.

1 Introduction

Soot is a key component of the atmospheric aerosol because of its strong ability to absorb solar radiation and thus contribute to global warming. Moreover, soot particles are among the fraction of the environmental aerosol that is associated with adverse health effects. Soot particles are emitted in high concentrations during incomplete combustion processes of fossil fuel and biomass. Depending on the particular conditions during their generation soot particles contain also varying fractions of hydrocarbons.

Numerous physical and physico-chemical methods have been developed to quantify the concentration of airborne soot particles [1]. Depending on the measurement principle, different particle properties are detected. Atmospheric soot particles are usually aggregates of small spherical elementary particles that, in turn, consist of stacked layers of carbon atoms in a hexagonal arrangement, i.e. a graphitic lattice. Chain-like aggregates of soot are commonly called black carbon (BC).

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A main optical method is based on the measurement of the attenuation of light that transmits a particle-laden filter medium. Considering the multiple interactions between the light beam, the particles, and the filter medium, a light absorption coefficient can be derived. Using a so-called absorption efficiency, the mass concentration of light absorbing carbon (LAC) can be derived. LAC can contain absorbing carbonaceous species other than BC such as HULIS (humic-like substances, i.e. tarry materials from combustion), which are summarized as “brown carbon” [1]. Applying a BC-based absorption efficiency on LAC data can therefore cause a misestimation of the soot concentration particularly when using measurement devices that operate at a wavelength smaller than 600 nm. A further method that gives unequivocal information on the presence of graphitic structures is Raman spectroscopy [2]. It can serve to quantify the amount of graphitic carbon (GC). Thermographic methods, last but not least, determine total carbon (TC) and separate between organic carbon (OC) and elemental carbon (EC) in bulk samples.

Since the end of 2008, the soot mass concentration and particle number size distribution have been measured continuously at nine observation sites of the German Ultrafine Aerosol Network (GUAN) [3]. GUAN is a joint project of several research and environmental monitoring institutions, with the aim of better describing the sources, concentrations and processes related to ultrafine aerosol particles [3]. Four different experimental methods were implemented for the characterisation of soot: a) Multi-Angle Absorption Photometry (MAAP), b) Raman spectroscopy, c) thermographic analysis of particle samples from Berner impactors, and d) a number size distribution measurement after removing volatile substances at 300 °C in a thermodenuder. This article presents a first quantitative comparison of the results achieved with the four methods, employing data collected at eight observation sites.

2 Instrumental

2.1 Multi-Angle Absorption Photometry

The Multi-Angle Absorption Photometer (MAAP; type 5012, Thermo Scientific Inc.) measures the amount of light (wavelength 637 nm) that is transmitted through and scattered back from a particle laden glass fibre filter [4]. With a two-stream-approximation radiative transfer model the absorption coefficients of the deposited particles can be derived with high accuracy [4]. Alternatively, the MAAP yields a mass concentration of light absorbing carbon (LAC) which requires the knowledge of the absorption efficiency. During instrumental comparisons against a thermal reference method, the originators of the MAAP derived an absorption efficiency of $6.6 \text{ m}^2 \text{ g}^{-1}$ for rural and urban aerosol [5] which is generally used for the conversion of the light absorption into a “soot” mass concentration. The wavelength of the MAAP (637 nm) corresponds to the region of the solar spectrum where black carbon (BC) is the prime absorber, thus minimizing interferences with “brown carbon” and mineral dust.

Tapes of GF10 filter (Whatman) are employed for particle collection, with all filter spots being stored on the tape for eventual Raman analysis. We programmed the progression of the filter tape so that it advances at least once every day (00:00). Additional filter advancements take place when a threshold transmission is underpassed, i.e. at high ambient

particle concentrations. The MAAP has a high time resolution (ca. 1 min) which allows to characterize diurnal cycles, and fast changes in ambient concentrations, for example at near-traffic observation sites. A central comparison of the six MAAP instruments deployed within GUAN yielded a reproducibility of the measurement, with a maximum deviation between the readings of 7 %, and R^2 of all cross-correlations being > 0.99 .

MAAPs are used at all GUAN sites except Augsburg where an aethalometer (type 8100, Thermo Scientific) is operated. The aethalometer data have, however, been made comparable to the rest of the data set by applying a calibration curve derived from a one-month comparison measurements with an MAAP.

Due to non-uniform requirements for the aerosol measurements at the GUAN stations, the upper size cut of the MAAP inlet varies between the stations: Schauinsland, Bösel, Leipzig-Eisenbahnstrasse (1 μm); Augsburg (2.5 μm); Hohenpeissenberg, Melpitz, Leipzig-IFT (10 μm). When comparing MAAP data with EC from Berner impactors below in Section 5.1, EC mass concentrations were consequently summed up over the impactor stages covering the size range measured by the corresponding MAAP.

2.2 Raman Spectroscopy

The Raman spectrum of atmospheric particles shows a characteristic signal in the wave number region between 800 and 1,800 cm^{-1} originating from graphitic carbon in atmospheric soot particles [2]. This signal is a composition of up to five bands that depend on the size and the structure of the graphite crystals in the soot particles [6; 7]. **Figure 1** shows exemplary Raman spectra for soot particles on a GF10 quartz fibre filter. The band around 1,570 cm^{-1} is designated as the D-band (disorder band). The band at $\sim 1,575 \text{ cm}^{-1}$ is attributed to an ideal graphitic lattice vibration [8] and is designated as the G-band (graphite band). It tends to be broadened and shifted to higher wave numbers ($\sim 1,600 \text{ cm}^{-1}$) in atmospheric samples because it merges with another band around 1,620 cm^{-1} (cf. Figure 1). This is the case if the graphite crystals are small and have lower 3-dimensional order [9]. The band visible around 1,450 cm^{-1} is caused by the GF10 filter medium, as can be seen from the Raman spectra of blank filters (Figure 1). Between the G- and the D-band,

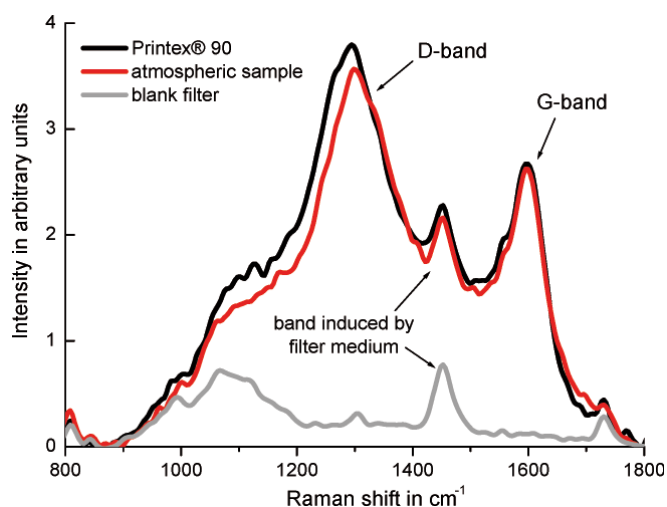


Figure 1. Illustrative Raman spectra of Printex®90 soot, atmospheric sample, and a GF10 blank filter in terms of wave number. The G (graphite), D (disorder), and filter-induced Raman bands are indicated for clarity.

another band exists that has been attributed to the amorphous carbon fraction, i.e. carbon atoms in a non-crystalline structure [7]. The amorphous carbon band is not explicitly visible but appears in the shape of an elevated background between the D- and the G-band. The G-band intensity depends on the amount of graphitic carbon in atmospheric soot particles and has been employed for a quantification of the mass of graphitic carbon [10; 11]. The calibration of the Raman method against gravimetrically determined soot using GF10 filters is presented in Section 3.

For this work a FTIR-Spectrometer (IFS 55, Bruker Daltonik, Bremen, Germany) with a Raman module (FRA 106, Bruker Daltonik) was used. All spectra were recorded at a laser power of 530 mW and a wavelength of 1,064 nm. The spectral resolution in terms of wave number was 8 cm^{-1} .

2.3 Thermographic EC/OC analysis of Berner impactor samples

Particulate carbon was characterized by a thermographic method similar to guideline VDI 2465 Part 2 [12] using a carbon analyzer (Ströhlein, C-mat 5500). In a first step an aliquot from the Berner impactor aluminium foils was heated for 8 min to $650 \text{ }^\circ\text{C}$ in a nitrogen atmosphere. Carbon compounds that evaporate under these conditions are referred to as organic carbon (OC). Evaporated OC is oxidized quantitatively on a CuO-catalyst at $850 \text{ }^\circ\text{C}$ to CO_2 and measured using a NDIR detector. In a second step the remaining elemental carbon (EC) was determined by heating the sample under an oxygen atmosphere at $650 \text{ }^\circ\text{C}$ for 8 min, oxidizing all carbon to CO_2 , the latter being detected by IR absorption. Foil blank values were subtracted from the results. As aluminium melts at $659 \text{ }^\circ\text{C}$, the operational temperature cannot be further elevated. Carbonates, notably, do not decompose at this temperature [15].

Calibration of the instrument was performed with potassium hydrogen phthalate as an external standard. Measurement uncertainties of 5.5% for OC and 8.9% for EC were determined for mass concentration typical for atmospheric conditions [14].

Numerous experimental procedures to distinguish OC and EC have been described [15]. Comparisons between various methods including the one used in this study during INTERCOMP2000 showed reasonable comparability for total carbon (TC), but considerable deviations for OC and EC between the participants [16]. It was concluded that the VDI method [12] and its variations without optical charring correction – a scheme to account for the pyrolysis of OC to EC in the nitrogen atmosphere [17] – may underestimate OC and, in turn, overestimate EC [18].

2.4 Measurement of particle volume after thermodesorption at $300 \text{ }^\circ\text{C}$

In GUAN, particle number size distributions are measured with mobility size spectrometers (SMPS – Scanning Mobility Particle Sizer, or TDMP – Twin Differential Mobility Particle Sizer) [5]. At eight observation sites a thermodenuder [19] is deployed upstream of the mobility size spectrometer. Inside the thermodenuder particles are heated to $300 \text{ }^\circ\text{C}$ in the airborne state. Volatile particulate species evaporate and are adsorbed to the thermodenuder walls during the subsequent cooling step. The particle number size distribution of solid particle cores is measured downstream of the thermodenuder. The particle volume is calculated from the number size distribution assuming spherical particles. It is the non-volatile particle volume, and not number, which is thought to

be associated with the soot mass concentrations derived by the other methods. The species removed at $300 \text{ }^\circ\text{C}$ include, amongst others, ammonium nitrate, sulphuric acid, ammonium sulphate, and the majority of organic compounds [20]. The species not removed by the thermodenuder include elemental carbon, sodium chloride, crustal material, and some multiple functionalized organic compounds like oxalic acid.

3 Calibration of the Raman spectroscopic method using Printex® soot

The Raman spectroscopic method was calibrated in the laboratory using Printex®90 soot particles (Evonik Industries AG, Essen, Germany) with the aim of establishing a relationship between the peak areas of bands in the measured Raman spectra and the mass concentration of GC. Such a relationship had, in particular, not been established for the GF10 filters used inside the MAAP instruments. Calibration particles were atomized from a hydrosol of Printex®90 powder and distilled water, subsequently dried and neutralized, and led into a mixing chamber (volume 1 m^3). The particle number size distribution of the particles had a wide mono-modal shape around 100 nm which coincides with the size range of atmospheric soot particles. A comparison between the Raman spectra recorded for Printex®90 and atmospheric particles showed that the position and shape of the G-band – characteristic for graphitic carbon – was very similar (cf. Figure 1). The position of the D-band was, however, slightly different. Our conclusion is that the graphitic carbon in the atmospheric and Printex®90 particles is similar in structure.

Two filter holders, one with a Nuclepore and one with a GF10 (MAAP medium) filter, were connected simultaneously to the mixing chamber, with the sampling flow through the Nuclepore filters being higher in order to achieve higher mass loadings suitable for gravimetric analysis. The mass of Printex®90 particles on the Nuclepore filters was determined with a microbalance UMT-2 (Mettler Toledo) and converted into the mass on the MAAP media using the flow ratio as conversion factor. Afterwards, the Raman spectra of the Printex®90 loaded MAAP filters were recorded.

The Raman raw spectra were normalized using a vector normalization method implemented in the commercial software OPUS (Bruker Daltonik). The spectra were normalized to the wave band in the region $1,455$ to $1,530 \text{ cm}^{-1}$ (see Figure 1) that stems entirely from the GF10 filter. After normalization, a spectrum representative of all blank filters was subtracted from all spectra of loaded filters, leaving only the signal of the calibration aerosol. Additionally, a baseline correction was performed in the spectral region of the GC signal to remove effects of heating and fluorescence on the Raman spectrum.

The relation between the integrated intensity in the G-band region between $1,510$ and $1,736 \text{ cm}^{-1}$ and the mass loading of Printex®90 on the MAAP filters is depicted in Figure 2. The R^2 value of 0.95 indicates good correlation. The conversion function from Raman integral to mass loading was determined using error weighted orthogonal regression. Figure 2 reveals a y-axis intercept significantly greater than zero. We suspect that uncertainties in the gravimetric mass determination (conditioning, weighing, sampling, after-conditioning, weighing) led to an overestimation of the gravimetric mass. Further uncertainties in the method result from inhomogeneous filter loading, uncertainties in sampling flow, the weighing procedure, and measurement of the spot diameter.

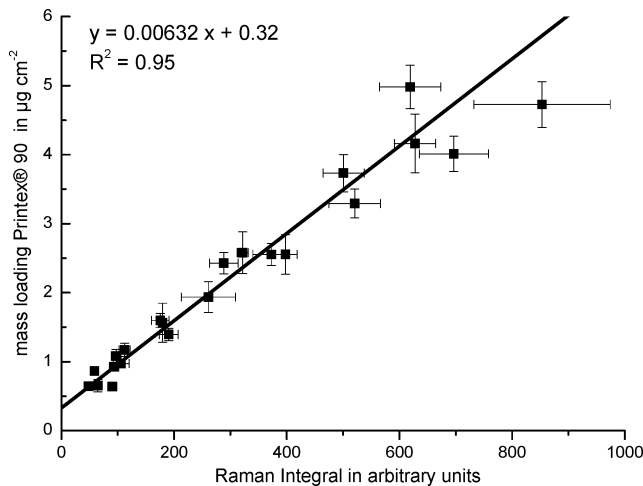


Figure 2. Relation between integrated G-band intensity (Raman integral) and the gravimetrically determined mass loading of Printex®90.

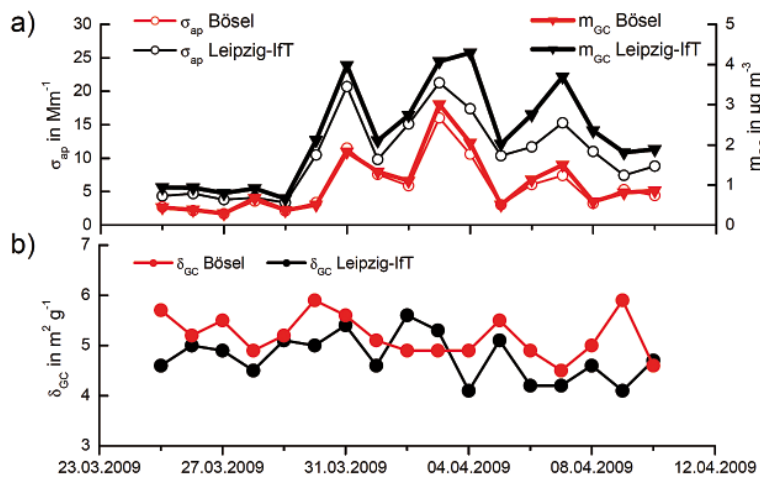


Figure 3. Comparison of MAAP and Raman spectroscopic data for daily samples at Bösel (rural) and Leipzig-I/T (urban background): a) absorption coefficient σ_{ap} (MAAP) and GC mass concentration m_{GC} (Raman spectroscopy), b) the calculated absorption efficiency δ_{GC} .

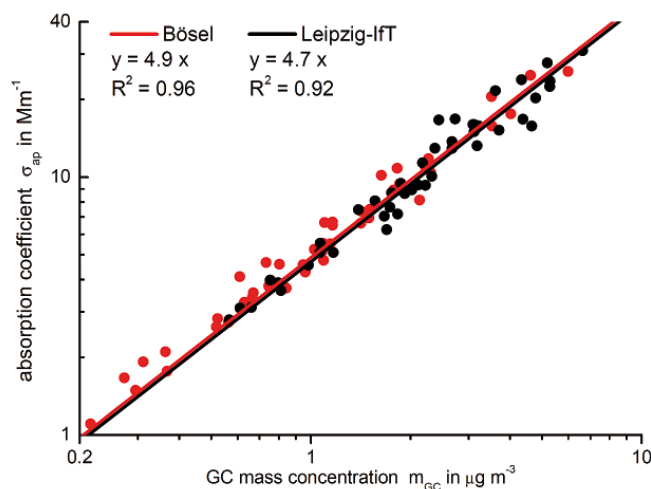


Figure 4. Comparison of GC mass concentrations from Raman spectroscopy and absorption coefficients from the MAAP for the sites Bösel and Leipzig-I/T between March 24 and April 10, 2009. Linear fit lines are added.

They amount to an absolute measurement uncertainty of about 10 %. Using the sampling volume drawn through the filter, GC-mass concentrations can be calculated.

4 Comparison between Raman spectroscopy and MAAP

Spots of particles deposited on the MAAP's glass fibre filter were examined with Raman spectroscopy. GC mass concentrations were determined from the integrated G-band intensity as described above. As the Raman analysis of one single filter spot requires substantial time (~ 1 h), our initial work concentrated on filter spots from two exemplary GUAN sites, Bösel (rural [3]), and Leipzig-I/T (urban background [3]). The number of examined filter spots was 45 for Bösel, and 49 for Leipzig-I/T.

Figure 3a shows daily averages of the absorption coefficient σ_{ap} and the GC mass concentration m_{GC} between March 25 and April 10, 2009. The beginning of the measurement period was characterized by clean Atlantic air and westerly wind directions. The values of m_{GC} were between 0.29 and 0.67 $\mu\text{g m}^{-3}$ at Bösel, and between 0.66 and 0.94 $\mu\text{g m}^{-3}$ at Leipzig-I/T. After March 29, the wind direction switched to easterly winds that were associated with continental air and thus higher soot concentrations. m_{GC} reached values up to 3.0 $\mu\text{g m}^{-3}$ at Bösel and 4.3 $\mu\text{g m}^{-3}$ at Leipzig-I/T. A close time correlation can be seen between m_{GC} and σ_{ap} .

Figure 3b shows the absorption efficiency δ_{GC} , defined as the quotient σ_{ap}/m_{GC} . δ_{GC} indicates the ability of an aerosol sample to absorb light in relation to its GC mass concentration, and is highly relevant for a correct estimation of the radiative effects of soot in atmospheric climate modelling. In practice, δ_{GC} may vary from site to site, and even from sample to sample depending on the state of mixture of GC, and the size distribution of the absorbing particles. The change in air masses around March 30 has no obvious effect on δ_{GC} .

The correlation between σ_{ap} and m_{GC} was scrutinized by linear correlation analysis shown in Figure 4 which employed all individual filters analysed rather than the daily averages. Coefficients of determination (R^2) of 0.96 and 0.92 were achieved for Bösel, and Leipzig-I/T, respectively. The substantial correlation suggests that GC is either the dominant light absorber in the analysed samples, or correlates very well with all other light-absorbing materials present in the samples. The slope of the regression lines, 4.9 $\text{m}^2 \text{g}^{-1}$ for Bösel and 4.7 $\text{m}^2 \text{g}^{-1}$ for Leipzig-I/T, indicate the average absorption efficiencies δ_{GC} for the measurement period. At this early stage of the data evaluation we are unable to conclude whether this rural/urban difference is significant. The absorption efficiencies are in the lower range of data reported in the literature for various types of soot [21]. During the ongoing research project, it is planned to analyse more MAAP glass fibre filters from all GUAN sites with Raman analysis, and extend the comparison to samples from all seasons.

5 Comparison between MAAP and other methods

5.1 MAAP vs. thermographic EC analysis

In GUAN, the chemical composition of size-fractionated aerosol particles is determined at seven observation sites in Germany [3]. Berner impactor samples are taken over 24 h on preselected days, and at all stations simultaneously. Between December 12, 2008, and August 6, 2009, we conducted 16 sampling events on the basis of weather forecasts with the aim of meeting the following criteria: Stable synoptic weather situation over several consecutive days, homogeneous wind direction over Germany, absence of rain (which would infringe on the quality of the five-stage impactor sampling). The mass concentration of elemental carbon m_{EC}

determined by thermographic analysis from the impactor foils is compared against the light absorption coefficient σ_{ap} measured by the MAAP.

Figure 5 shows the EC mass concentration obtained from thermographic analysis and the light absorption coefficient for a total of 94 atmospheric samples. In contrast to the comparison in Section 4, the correlation between both methods is less pronounced. Site-specific linear regression analyses yield a span of R^2 between 0.60 and 0.88, and an R^2 value of 0.65 for the total data set. Linear fits for $\sigma_{ap}(m_{EC})$ yield slopes between 2.3 and 7.4 and considerable axis offsets. Trend lines are indicated in Figure 5 for a rough orientation in the data set. The ratio σ_{ap}/m_{EC} is, like σ_{ap}/m_{GC} , an absorption efficiency. Although its median value of $7.5 \text{ m}^2 \text{ g}^{-1}$ is again in the range of previously published values [21], it shows considerable variation across the data set (quartile range: 4.2 to $14 \text{ m}^2 \text{ g}^{-1}$). At the current stage of the data analysis the reasons for the scattering of the data are not evident. A very basic interpretation is that MAAP and thermographic analysis measure two apparently different aspects of the carbonaceous aerosol content. While the MAAP measures the particles optical absorption properties the thermographic analysis examines the temperature-dependent properties of bulk particle samples deposited on aluminium foils. A limitation of the thermographic method used here is that it cannot be operated with optical charring correction due to the collection of particles on impactor foils rather than on homogeneously loaded quartz fibre filters.

5.2 Comparison MAAP vs. non-volatile particle volume

Elemental carbon is a major non-volatile constituent in the atmospheric sub- μm aerosol. We checked the correspondence between the non-volatile particle volume derived from mobility spectrometers/thermodenuders (Section 2.4) and light absorbing aerosol constituents (LAC; Section 2.1). Figure 6 shows a scatter plot for the non-volatile particle volume ($< 1 \mu\text{m}$ aerodynamic size) and the aerosol absorption measured by the MAAP for four GUAN sites (Leipzig-IFT and Augsburg: urban background; Bösel: rural; Zugspitze: high alpine background) for the period March 24 to April 10, 2009 – corresponding to the period of the measurements described in Section 4. Due to the combination of maritime, continental, and free tropospheric air, the data set spans more than three orders of magnitude in concentration. As can be seen in Figure 6 the data collective follows a similar trend. Linear regression of a straight line with no axis intercept yielded linear slopes of 3.95 (Zugspitze), 4.22 (Bösel), 3.99 (Leipzig-IFT), 5.13 (Augsburg), and 4.48 (all data) with corresponding R^2 values of 0.96, 0.92, 0.95, 0.87, and 0.90.

The results indicate a close correlation between LAC and the non-volatile particulate volume in the sub- μm range. Since LAC could be attributed largely to GC during the same measurement period (Section 4), we conclude that the non-volatile particle volume is associated mostly with GC. Under the assumption of an absorption efficiency of $4.8 \text{ m}^2 \text{ g}^{-1}$ (cf. Sect. 4), both non-volatile volume and LAC would be consistent using an effective particle density in the range 0.82 to 1.06 g cm^{-3} . Effective particle densities $< 1 \text{ g cm}^{-3}$ are possible for fractal agglomerates. Our data show that a size distribution measurement of non-volatile particle residues can act as a surrogate measurement for soot in the sub- μm range. A more extended data set, however, will be evaluated to substantiate the conclusions.

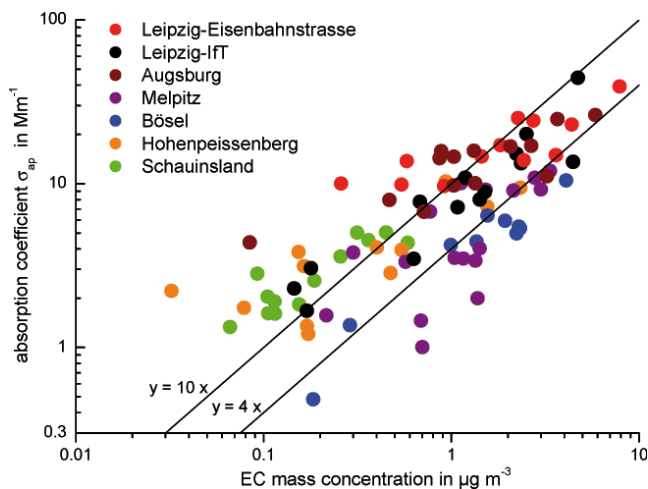


Figure 5. Comparison between elemental carbon (EC) mass concentrations from thermographic analysis and the absorption coefficients for 7 observation sites. Trend lines are indicated for orientation.

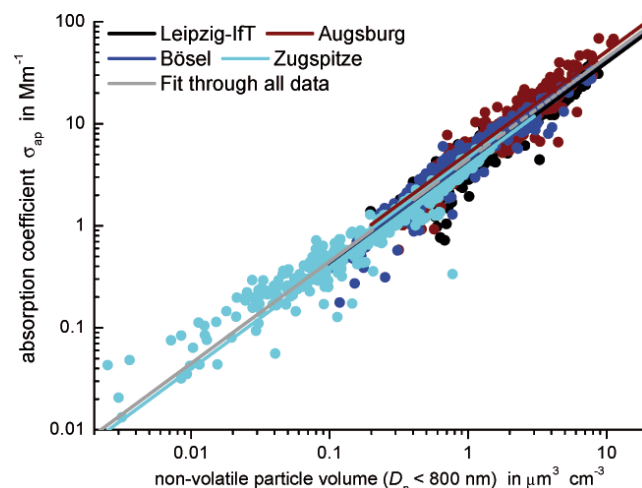


Figure 6. Comparison between the non-volatile particle volume and the aerosol absorption coefficient for hourly data at four GUAN sites between March 24 and April 10, 2009. Linear trend lines are added.

6 Conclusions and outlook

In the German Ultrafine Aerosol Network (GUAN [5]) four different experimental methods have been applied for the characterization of atmospheric soot particles. A Raman spectroscopic method was calibrated with standardized Printex® 90 soot particles, and applied to field samples collected on GF10 filters that are routinely operated in MAAP instruments. Raman analysis showed that atmospheric particles in rural and urban air are similar to the test soot particles with respect to size and structure. Because Raman spectroscopy is specifically sensitive to graphitic structures, a mass concentration of graphitic carbon (GC) could be derived for atmospheric samples. For rural and urban background aerosols, strong correlations (R^2 of 0.92 and 0.96) were found between the GC mass concentration and the aerosol absorption coefficient measured by the MAAP. The absorption efficiency, a parameter that is essential for regional and global climate modelling, could be derived for GC in the range 4.7 to $4.9 \text{ m}^2 \text{ g}^{-1}$.

For seven GUAN sites the mass concentrations of elemental carbon (EC) obtained by a thermographic method from Berner impactor samples were compared with the light absorp-

tion measurements of the MAAP. Although a median EC absorption efficiency of $7.5 \text{ m}^2 \text{ g}^{-1}$ could be determined, there was considerable scattering across the data set. A basic assumption is that the thermographic analysis and the MAAP measure two apparently rather different aspects of the carbonaceous aerosol. The non-volatile (after heating to $300 \text{ }^\circ\text{C}$) particle mass concentration compared relatively well with the integral MAAP measurement if calculated on the basis of an effective particle density of the light absorbing carbon in the range 0.8 to 1.1 g cm^{-3} . R^2 between 0.87 and 0.96 suggest that the non-volatile particle volume in the sub- μm range is closely associated with LAC and, through the comparison with the Raman analysis, ultimately, with GC.

During the ongoing research project more MAAP filters from all GUAN sites will be examined with Raman analysis. All continuous measurements are expected to carry on until at least until the end of 2010. This broader data base will

provide a more comprehensive picture of the abundance and processing of soot in the Central European troposphere. A more extended comparison of the four experimental methods presented here will allow more detailed recommendations for the monitoring of soot in air quality measurement networks.

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