OC and EC analyzed in PM_{10}, $PM_{2.5}$ and PM_1 using thermo graphic and thermo-optical method at Melpitz site in Germany – a two year comparison

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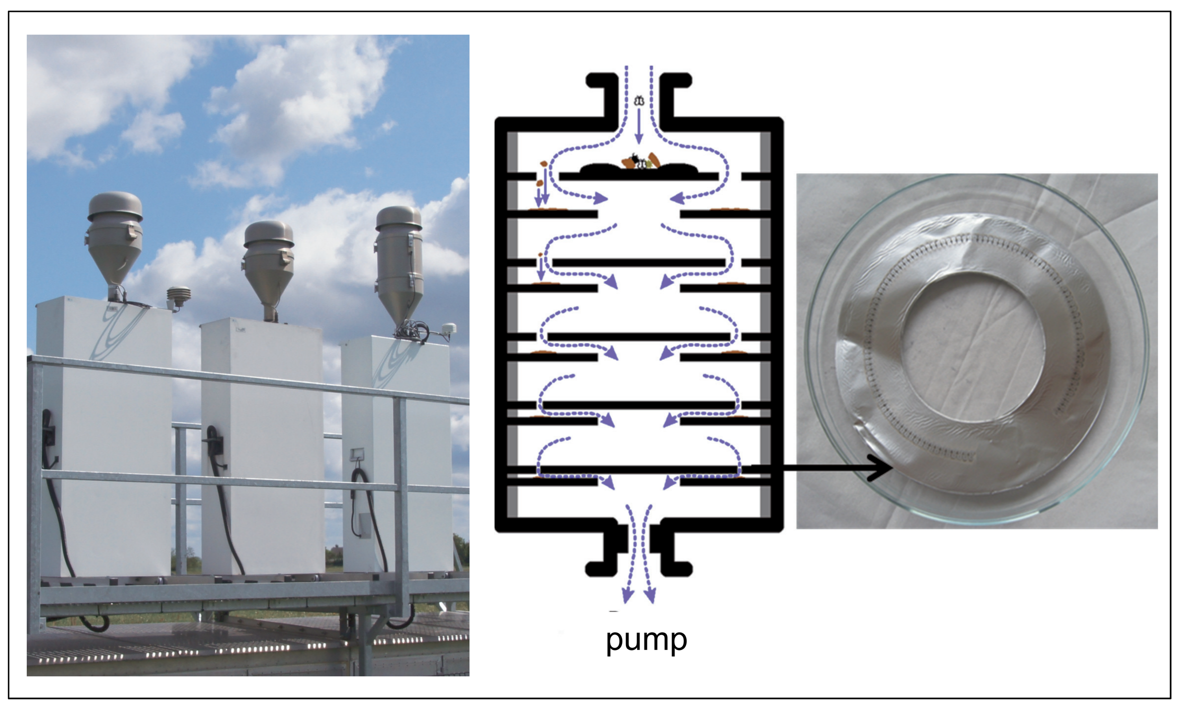

Figure 1: The HV-filter-samplers for PM_{10}, $PM_{2.5}$ and PM_1 at Melpitz site for daily samples on quartz fibre filters and the five stage BERNER-impactor for sampling on Al-foils for several days. The Al-foil for stage 5 is shown (particles with 0.05 to 0.14 µm aerodynamic diameter.

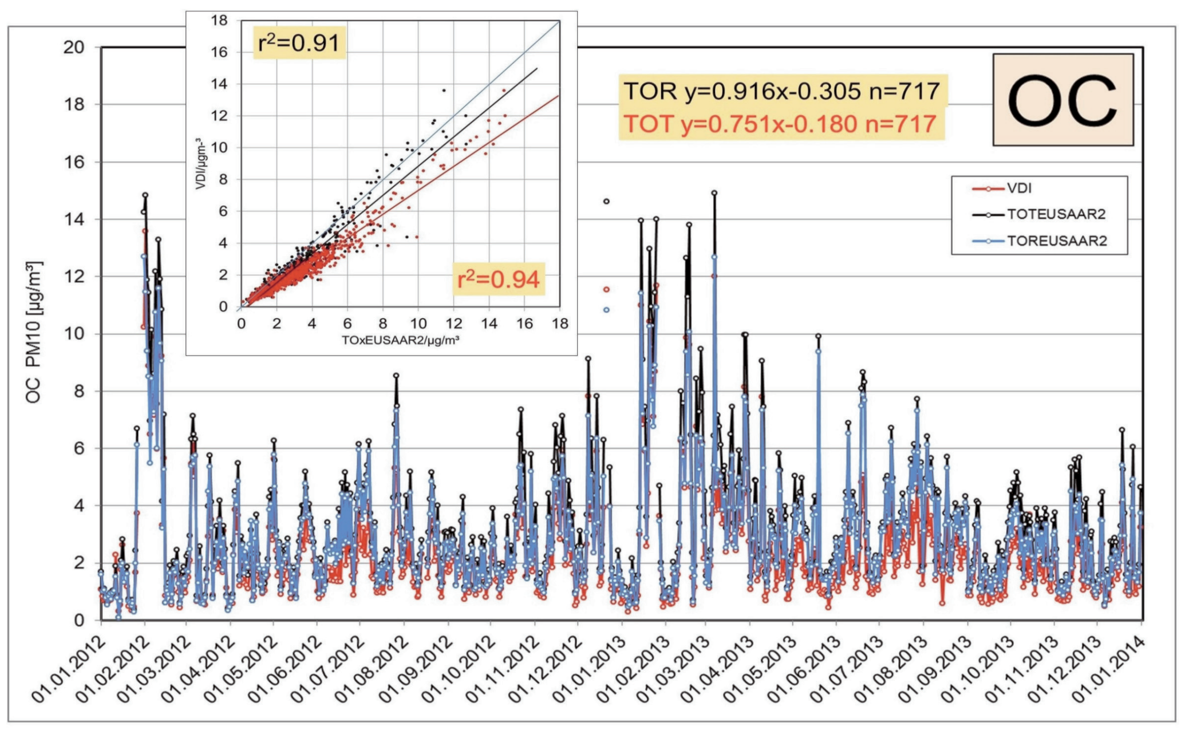

Figure 2: Example for the calculation of the empirical conversion equations for OC in PM_{10} over the whole time (2012 and 2013).

$$[OC;\,EC;\,TC]_{TGVDI} = m_x \times [OC;\,EC;\,TC]_{TOx\,EUSAAR2} + n_x$$

x ≙ Reflectance or Transmittance

		m_R	n_R	r^2		m_T	n_T	r^2	n_x
all days	OC	0.925	-0.279	0.92		0.751	-0.179	0.95	1653
	EC	0.500	0.378	0.66		1.088	0.343	0.58	1653
	TC	**0.840**	**0.008**	**0.98**	≙	**0.840**	**0.008**	**0.98**	**1653**
SUMMER days	OC	0.666	0.125	0.84		0.605	0.098	0.87	854
	EC	0.728	0.305	0.55		1.570	0.307	0.44	854
	TC	**0.786**	**0.123**	**0.93**	≙	**0.786**	**0.123**	**0.93**	**854**
WINTER days	OC	0.987	-0.257	0.97		0.776	-0.163	0.97	801
	EC	0.504	0.308	0.73		1.014	0.299	0.77	801
	TC	**0.848**	**-0.021**	**0.99**	≙	**0.848**	**-0.021**	**0.99**	**801**

The conversion equations depends from season – in approximation convertion equations can be derived monthly.

Figure 3: Calculation of conversion factor m, intercept n and r for all days and selected for Winter: November until April and Summer: May until October over the whole time (2012 and 2013).

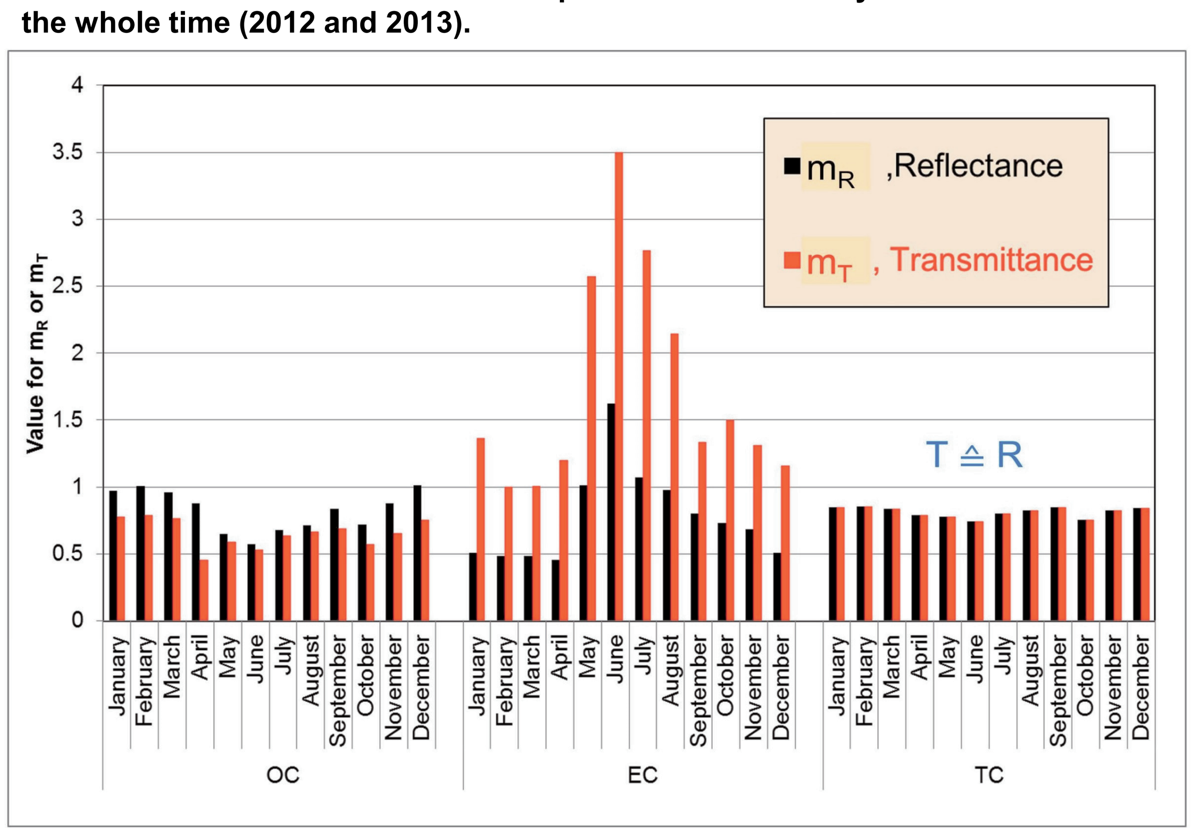

Figure 4: Calculation of monthly conversion factors for reflectance (m_R) and transmittance (m_T) for OC, EC and TC for all sizes over the two years with parallel carbon analysis for Melpitz site. (2012 and 2013).

Method and Motivation

Since 2003 organic (OC) and elemental carbon (EC), in sum total carbon (TC), were quantified at quartz-fibre filters (HV) with an analyzer, C/S-Max, Seifert Instruments, Germany using a variation of the Guideline VDI2465 (Part 2). This thermographic method (TGVDI) can be used for quartz filters from high-volume-samplers and also for samples on aluminum foils (melting point≈660° C) using in BERNER-impactors (IP), because the maximum temperature doesn't exceed 650° C (**Figure 1**). Charring processes cannot be accounted here (Spindler et al 2012). A thermo-optical method (TO) using the Lab OC-EC Aerosol Analyzer by Sunset Laboratory Inc. U.S.A. was introduced at TROPOS in 2012 together with temperature protocol EUSAAR2 (final temperature 850° C, *Cavalli et. al 2009*). The correction value for „pyrolytic carbon" is achieved from measurement of transmission (TOT) or reflectance (TOR)(*Chow, et al. 2004, Bautista VII et al. 2015*) of the sample using a laser (wavelength 678 nm). In European networks, e.g. EMEP[1]) and ACTRIS[2]), TOTEUSAAR2 is the preferred technique for quartz fibre filters. We derive conversion equations from two years parallel analysis of daily samples following TGVDI and TOTEUSAAR2 or TOREUSAAR2 to convert long-time measurements of HV samples of Melpitz site from yesteryears (TG to TO). Furthermore mean mass absorption cross sections were calculated from measured particle light absorption coefficients and EC quantification by the different TG and TO methods.

Experimental and Results

The Melpitz site operated by TROPOS is located in the lowlands of Eastern Germany (12°56'E, 51°32'N, 86 m a.s.l.). The place represents the regional background in Central Europe (*Spindler et al. 2012 and 2013*).

The daily HV samples on quartz fibre filters (every day for PM_{10} and $PM_{2.5}$ and every six days for PM_1) were taken at Melpitz site using three HV samplers DIGITEL DHA-80 (Walter Riemer Messtechnik, Germany).

From the two year data set 10 days with more than 5 µ/m³ EC (TGVDI) in PM_{10} were eliminated because the transmission for TOTEUSAAR2 is here very low. The calculation of conversions equations was done following as y=mx+n, equation 1 (compare the example for OC in **Figure 2**):

$$[OC;EC;TC]_{TGVDI} = m \times [OC;EC;TC]_{TOTEUSAAR2} + n \qquad (1)$$

The conversion factor m and the intercept n were calculated for OC, EC and TC and for the size classes PM_{10}, $PM_{2.5}$ and PM_1 for all days. The correlations r^2 for TOT (PM_{10}) are for OC, EC and TC 0.94, 0.58 and 0.98, respectively. Alternatively EC can by calculated as EC=TC-EC. The results for TOR and TOT show that the conversion equations depends not essential on particle size and can be calculated for all sizes in one step. The conversion variable m depends on the season (Winter: November until April, Summer: May until October), compare **Figure 3**. As a compromise the conversion equations for OC, EC and TC were derived for the twelve month in a year using the 2012 and 2013 monthly data for all sizes. The conversion factors for EC (TOTEUSAAR2) show a strong variation over the year for the rural site Melpitz. The high values in summer are caused by a relative high amount of "pyrolytic carbon" (PC) that is formed by charring of OC (TGVDI) (**Figure 4**). **Figure 5 and 6** shows the variability of the EC/OC ratio over the year for the TGVDI and TOREUSAAR2 and TGVDI and TOTEUSAAR2, respectively. The lower EC/OC-ratios where found in the summer. The spreading for the TGVDI is much higher as for the thermo-optical method and the detection of PC by reflectance provides a much higher EC/OC ratio as for transmission, especially in winter it reaches the values for TGVDI. For an independent estimation which off-line method gives more realistic OC concentrations the OC measurement of PM_1 filter-samples where compared with online AMS measurements (**Figure 7**). Because AMS provides OM the ratio OM/OC was calculated based on the elemental analysis of the high resolution mass spectra (Canagaratna et al. 2015). For samples from different regions and seasons it can be found that the thermo-optical method with transmission (TOTEUSAAR2) gives the most realistic OC concentrations in comparison to TGVDI or TOREUSAAR2. This method provides the highest OC concentrations and a lower EC/OC ratio compared to TOREUSAAR2 and TGVDI (Figure 5 and 6).

Figure 8 shows an example for the estimation of quasi TOTEUSAAR2 values for OC and EC from long-term HV-filter measurements of OC and EC using TGVDI. The recalculation was done using monthly conversion equations derived from 2012 and 2013. So historical data for OC and EC measurements by TGVDI can be compared with the new introduced method and continued in future for Melpitz site as TOTEUSAAR2 OC-EC-measurements.

The particle light absorption coefficient in PM_{10} σ_{ap} measured with a Multiangle Absorption Photometer (MAAP 637 nm) shows an annual variation in therange 0.2 and about 30 Mm^{-1}. It is common to calculate Black Carbon (BC) from σ_{ap} using a constant mass absorption cross section of 6.6 m^2g^{-1}. A comparison between σ_{ap} and results of the used different EC measurements here for 2012 and 2013 allows to calculate mass absorption cross sections for the different month (equation 2, **Figure 9**). The mass absorption cross section (αC) mostly depends on

$$\sigma_{ap} = \alpha_{C[TGVDI,\,TOxEUSAAR2]} \times [BC], [EC]_{[TGVDI,\,TOxEUSAAR2]}\,; \; x \triangleq T \text{ or } R \qquad (2)$$

EC measurement method, but also on season. The monthly derived α_C shows lower values for summer as for winter. The annual variation is mostly distinct for TGVDI.

Summary

- We can derive mean conversion equations for OC, EC and TC. They do not depend on particle size (range PM10 to PM1) but from season.
- As a compromise conversion equations were derived monthly.
- The thermo-optical method can give a more stable split for OC and EC. A comparison with AMS measurements for OC in PM1 give hints for more realistic OC quantifications using transmittance.
- EUROPE has unified the OC-EC-Determination for the future to the TOTEUSAAR2 method in March 2015.

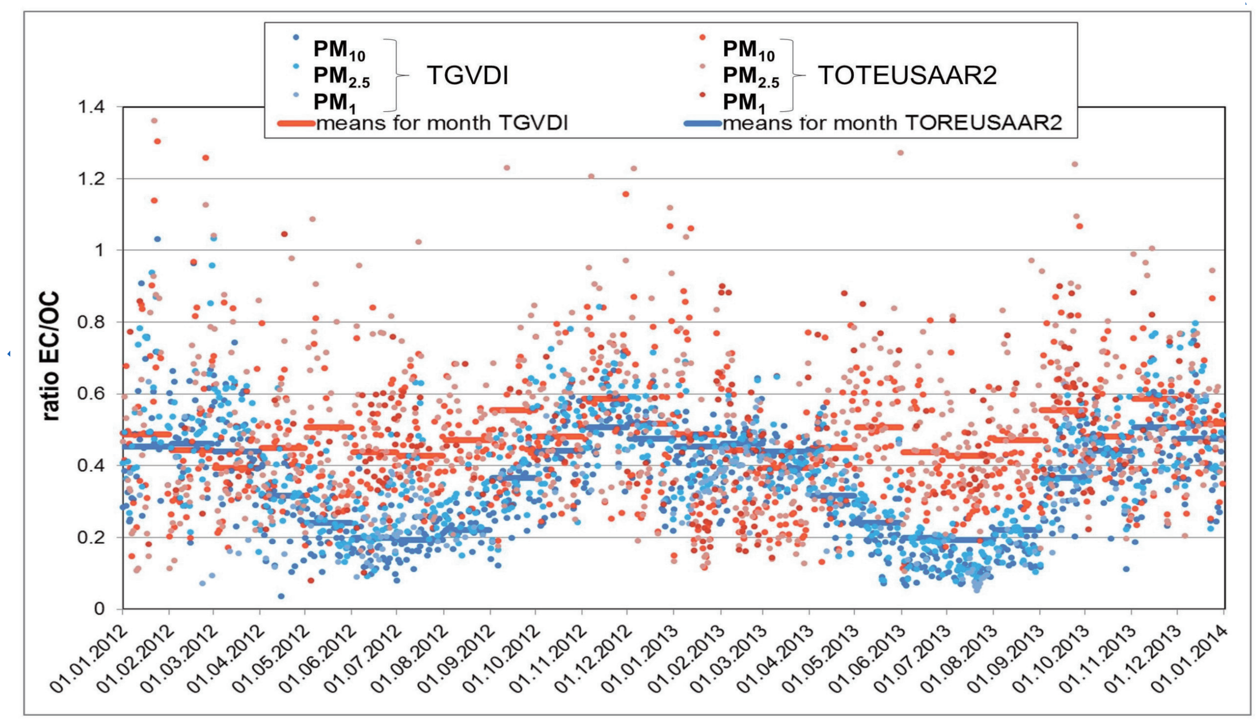

Figure 5: Daily ratios of EC/OC in 2012 and 2013 for PM_{10}, $PM_{2.5}$ and PM_1. Method TGVDI in comparison to TOREUSAAR2.

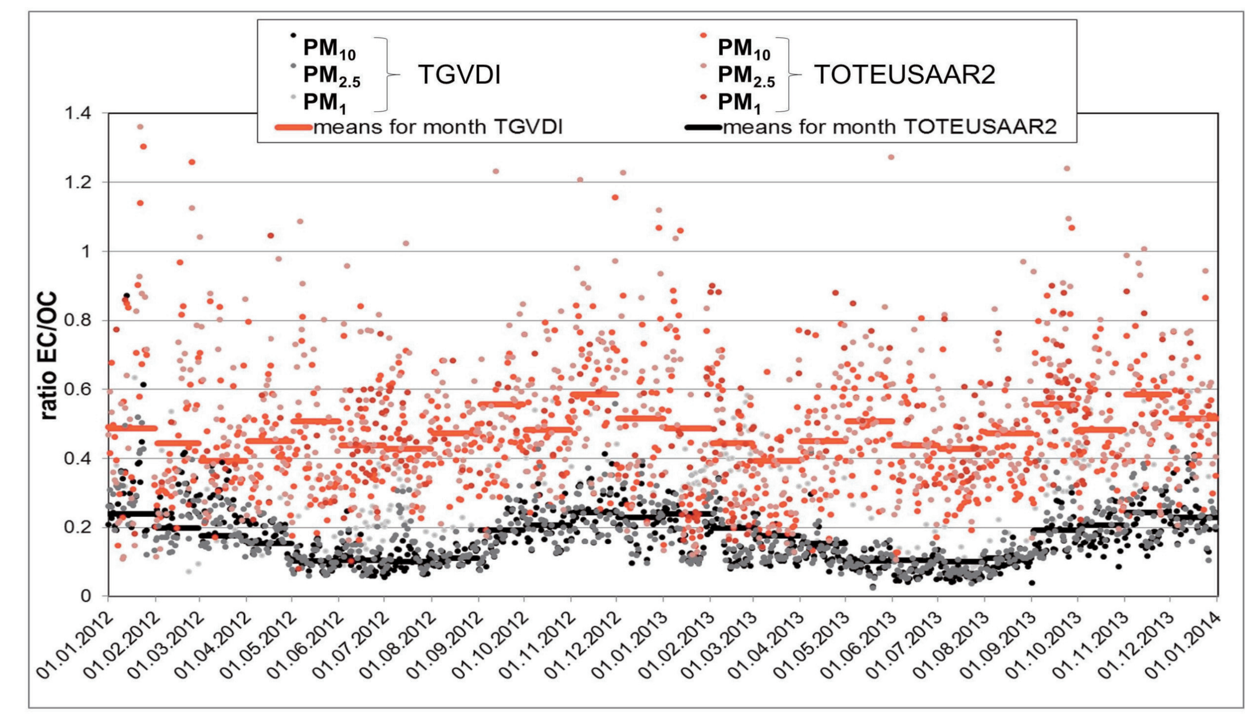

Figure 6: Daily ratios of EC/OC in 2012 and 2013 for PM_{10}, $PM_{2.5}$ and PM_1. Method TGVDI in comparison to TOTEUSAAR2.

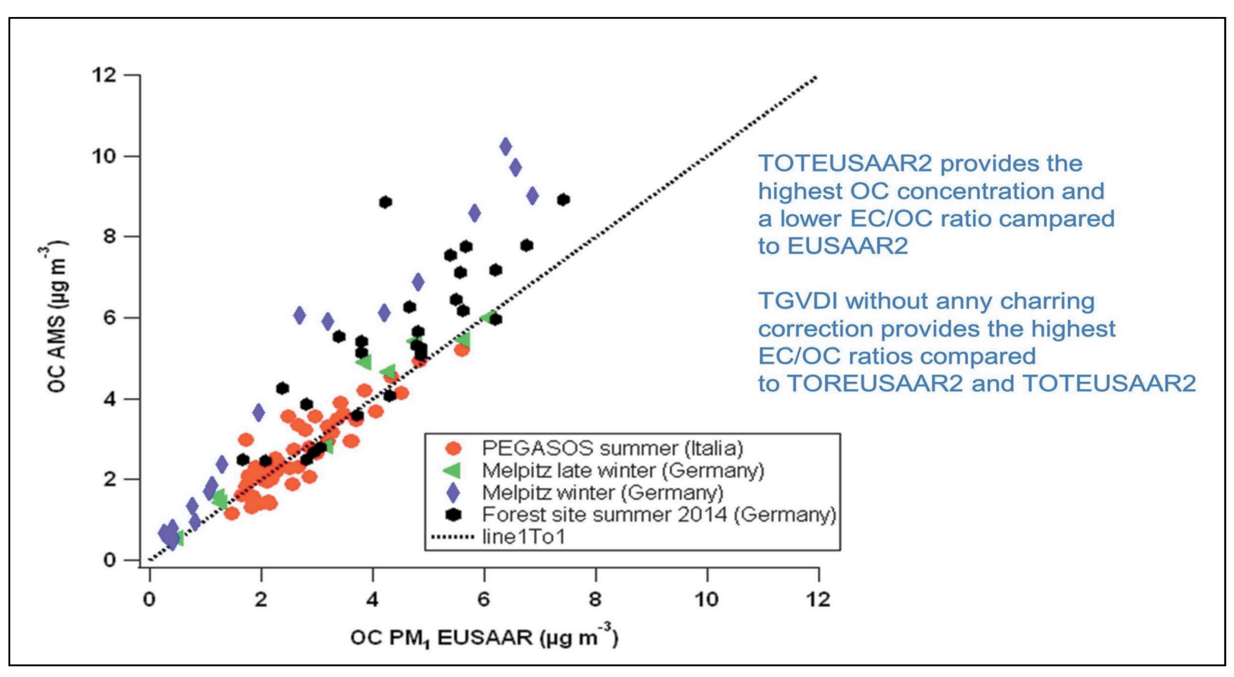

Figure 7: OC PM1 off-line samples analyzed with TOTEUSAAR2 vs. AMS on-line measurements.

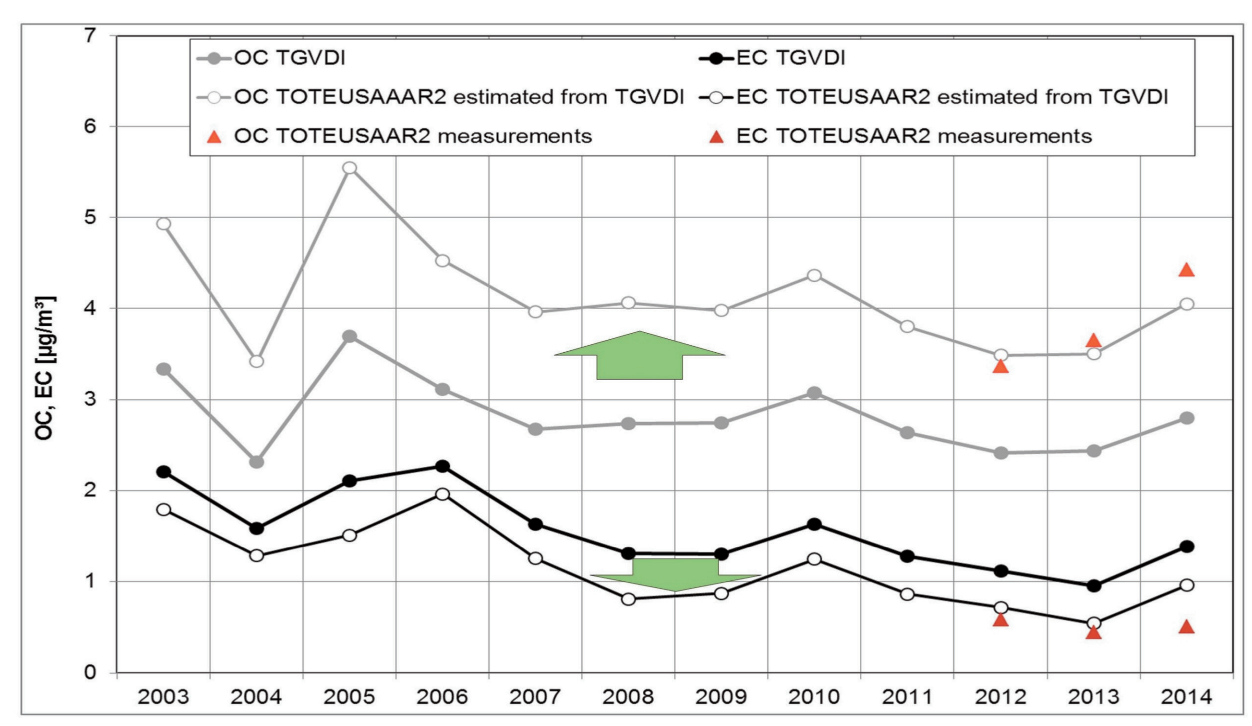

Figure 8: Long-term HV-filter measurements for OC and TC for Melpitz site using TGVDI (open circles) and estimation as results from TOTEUSAAR2 (full circles). The recalcultion was done using monthly conversion equations derived from 2012 and 2013 (EC was calculated via TC-OC). For 2012-2014 the yearly means for direct TOTEUSAAR2 measurements are shown (triangels). All data are yearly means.

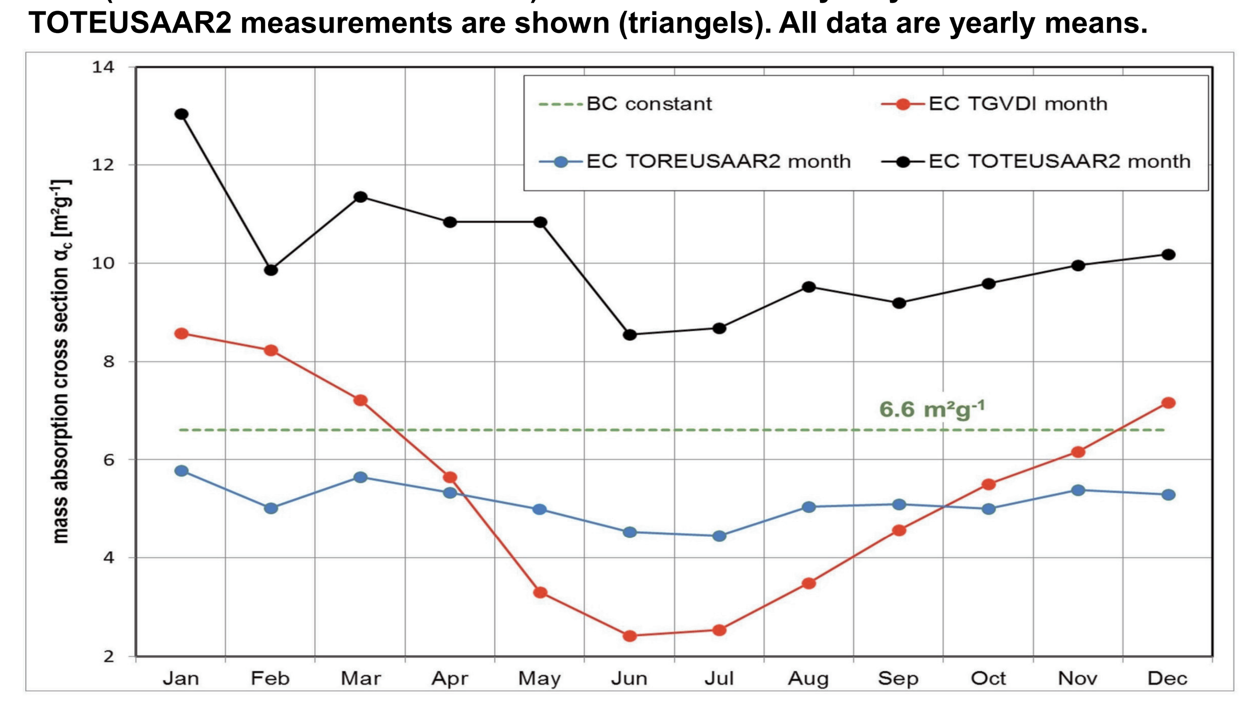

Figure 9: Monthly Mass Absorption Cross Section (σ_{ap}) derived from the particle light absorption coefficient measured with a MAAP for PM_{10} using the EC quantification by TGVDI, TOREUSAAR2 and TOTEUSAAR2. The common used constant σ_{ap} of 6.6 m^2g^{-1} is shown.

References

Bautista VII, A.T., Pabroa, P.C.B., Santos, F.L., Quirit, L.L., Asis, J.L., Dy, M.A.K., Martinez, J.P.G.: Intercomparison between NIOSH, IMPROVE_A, and EUSAAR_2 protocolls: Finding an thermal-optical protocol for Philippines OC/EC samples. Atmospheric Pollution Research 6, 334-342, 2015

Cavalli, F.; Viana, M.; Yttri, K.E.; Genberg, J.; Putaud, J.-P.: Toward astandardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmos.Meas.Tech. 3, 79-89, 2010

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E.,Williams, L. R.,Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., Worsnop, D. R.: Elemental ration measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys. 15, 253–272, 2015

Chow, J.C., Watson, J.G., Chen, L.-W. A., Arnott, W.P., Moosmüller, H.: Equivalence of Elemental Carbon by Thermal/Optical Reflectance andTransmittance with different Temperature Protocols. Environ. Sci. Technol. 38, 4414-4422, 2004

Spindler, G., Gnauk, T., Grüner, A., Iinuma, Y., Müller, K., Scheinhardt, S., Herrmann, H.: Size-segregated characterization of PM_{10} at the EMEP site Melpitz (Germany) using a five-stage impactor: a six year study. J. Atmos. Chem., 69, 127-157, 2012

Spindler, G., Grüner, A., Müller, K., Schlimper, S., Herrmann, H.: Long-term size-segregated particle (PM_{10}, $PM_{2.5}$, PM_1) characterization study at Melpitz – influence of air massinflow, weather conditions andseason. J. Atmos. Chem., 70, 165-195, 2013

1) **E**uropean **M**onitoring and **E**valuation **P**rogramme
2) **A**erosol, **C**louds, and **T**race gases **R**esearch **I**nfra**S**tructure Network